
Provenance of late Quaternary loess along the Middle and Lower Danube River, Europe

Kaja Fenn

Supervisors: Professor D.S.G Thomas, Dr J.A. Durcan, and Dr
Ian Millar

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Abstract

Loess-palaeosol sequences along the Danube River are often the only Quaternary environmental and climatic archive spanning the whole last glacial-interglacial (and beyond) in Eastern and Central Europe. Despite long standing loess research their origins and formation processes are still debated. This thesis aims to fill this gap by investigating timing of deposition and provenance of loess deposits along the Danube River. The analysis pivots around geochemistry and geochronology.

Application of the latest luminescence dating protocols provides a basis for answering questions regarding the timing and rate of sediment accumulation, while detrital zircon U-Pb dating and Hf isotopes were utilised to better understand the source(s) of loess deposits along the Danube River. The timing of deposition and sediment origins provides insights into depositional history and sediment transport pathways.

The luminescence dating supports previous suggestions that loess deposits are not continuous and likely contain hiatuses. The hiatuses may not be spatially extensive, therefore high-resolution sampling approaches are critical to better understand these deposits. Further spatial analysis of mass accumulation rates shows deposition is not constant over time but varies greatly. Importantly comparison of multiple sites indicates that activity periods are not uniform spatially but rather site specific.

Provenance results show the Danube's alluvium is the immediate geomorphological source of sediment for the loess profiles, indicating that sediment is predominantly transported over short distances. Rivers remain a crucial component of the source-to-sink loess model, though this research goes a step further showing that they are responsible for homogenising sediment, e.g. Danube sits on a mixing line between the Alp draining Sava and the Carpathian draining Tisza. Moreover, the results suggest that the Alps, Bohemian Massif and Carpathians are the main sediment proto-sources. However, for the first-time the importance of smaller not extensively glaciated mountain belts e.g. Dinaric and Balkan Mountains is shown which questions glacial action as a crucial sediment producing mechanism. Finally, the results suggest that sites along the Danube share sources and that sediment source remained unchanged over the Quaternary timescale.

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Units

Å ångström

°C Degrees Centigrade

Ga Billion years

g cm⁻³ Gram per cubic centimeter

g m⁻²a⁻¹ Grams per square meter per year

Gy Gray (1 Gy = 1 J kg⁻¹)

Gy ka⁻¹ Gray per thousand years

Hz Hertz

J cm⁻² joules per square centimetre

ka Thousands of years before
present

kg kilogram

Ma Millions of years

mg milligram

ms millisecond

nm nanometer

s Second

µm Micrometers

Abbreviations

ADL	Average Danubian Loess	LA-ICP-MS	Laser Ablation
CAD	Cumulative Age Distributions		Inductively Coupled Plasma Mass Spectrometry
CAM	Central Age Model	LGM	Last Glacial Maximum
CHUR	Chondritic Uniform Reservoir	LREE	Light Rare Earth Elements
CL	Cathodoluminescence	LILE	Large-Ion Lithophile Elements
De	Equivalent Dose	Lx	Natural or regenerative dose
DRAC	Dose Rate and Age Calculator	MAR	Mass Accumulation Rates
DRC	Dose Response Curve	MAAD	Multiple Aliquot Additive Dose
DM	Depleted Mantle	MDS	Multidimensional Scaling
HFSE	High-Field-Strength Elements	MIS	Marine oxygen-isotope stage
HREE	Heavy Rare Earth Elements	OSL	Optically Stimulated Luminescence
ICP-MS	Inductively Coupled Plasma Mass Spectrometry	PCA	Principle Component Analysis
IR	Infra-red	pIRIR	Post-infrared Stimulated Luminescence
IRSL	Infrared Stimulated Luminescence	PH	Pre-heat
KDE	Kernel Density Estimation	REE	Rare Earth Elements
KS	Kolmogorov-Smirnov Statistic	SAR	Single Aliquot Regenerative

T_x Test dose

UCC Upper Continental Crust

X_{FD} Frequency dependent magnetic
susceptibility

X_{hf} High frequency magnetic
susceptibility

X_{lf} Low frequency magnetic
susceptibility

Chapter 1: Introduction

1.1. Rationale

While the exact loess definition is still elusive (Sprafke and Obreht, 2016; Wright, 2001), the term represents silt-size, mineral aeolian dust deposit that preserves records of past environmental and climate change. Loess deposits are found on every continent (Figure 1.1) covering around 10% of the Earth's land surface (Pye, 1995), and can provide information about the dust cycle, such as past dust fluxes, interactions with other Earth cycles, sediment transport pathways, and deposition periods (Shao *et al.*, 2011). This thesis makes a contribution to loess and palaeoenvironmental studies by investigating the complexity of origins and chronologies of loess deposits in an import part of the central European system: the Danube valley.

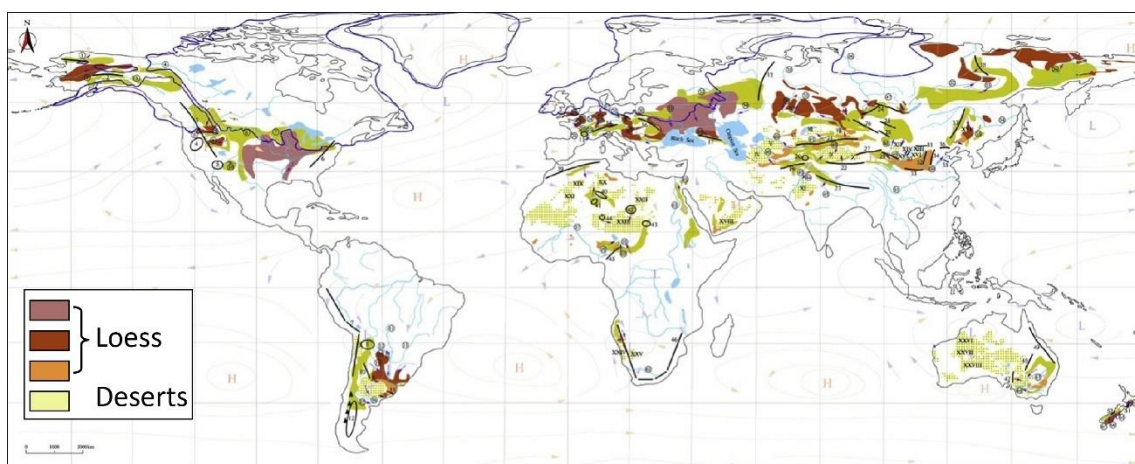


Figure 1.1 Global distribution of loess and loess like deposits (modified after Li *et al.*, 2020)

In terms of structure, loess and palaeosols commonly occur in alternating layers, developed in a cyclical manner reflecting large, often global or regional changes in climate (e.g. glacial and interglacial) and environment (e.g. landscape stability) (Derbyshire *et al.*, 1998; Kukla, 1977; Liu and Chang, 1964). The loess units represent periods of accelerated dust accumulation as a result of cold, arid climatic conditions often combined with an

environmental instability (i.e. glacial and stadials). Conversely palaeosols are associated with stable environmental and climatic conditions during which the rate of pedogenesis exceeds the rate of dust accumulation (i.e. interglacials and interstadials). These sequences can span multiple glacial-interglacial cycles (Ding *et al.*, 2002; Guo *et al.*, 2002; Marković *et al.*, 2011), providing a unique long-term insight into terrestrial climatic and environmental drivers that is only matched in terrestrial contexts by a few lacustrine and speleothem records in terms of record preservation. Therefore, due to their extensive spatial and temporal resolution, loess deposits are often considered one of the most important Quaternary terrestrial archives. Additionally, they offer an opportunity to compare and correlate terrestrial signals with ice- and marine- core records (Antoine *et al.*, 2009a; Kukla, 1977; Stevens *et al.*, 2018) and therefore to investigate leads and lags between terrestrial records and global climatic signals.

Loess-palaeosol sequences represent not only dust sinks, but are also dust emitters, and therefore understanding their activation periods, and the drivers behind them is important for dust and climate change modelling (Aoki *et al.*, 2006; Perlwitz and Miller, 2010; Shaffer and Lambert, 2018). Further, as many of the loess regions are located near human populations emissions of dust from these sources may have impacts on human health (Griffin and Kellogg, 2004; Kan *et al.*, 2012), and can cause large scale economic damage (Baddock *et al.*, 2013). Therefore, there is a need to understand the causes of activation of loess deposits from the human aspect. Identifying the sources of these deposits, and the relationship between the activation and any potential climatic and environmental factors, is essential in utilising loess as an archive.

Despite their potential as palaeoarchives, loess-palaeosol sequences can suffer from a lack of robust, high-resolution chronologies. Geochronological controls on loess deposition are essential to place and contextualise the proxy data into global and regional climatic

records, and to provide a basis for correlation between loess sites and other palaeoarchives. In the absence of an independent chronology, loess researchers have relied on the use of stratigraphy and magnetic susceptibility to correlate loess records across regions (An, 2000; Marković *et al.*, 2009, 2012; Porter, 2001), and wiggle-match these records to other palaeoclimatic archives, e.g. marine records (Marković *et al.*, 2008, 2015; Thompson and Goldstein, 2006). While palaeomagnetism provides independent chronological tie-points for the older parts of loess profiles (typically Brunhes-Matuyama 0.78 Ma and older; Kukla and An, 1989), correlations based on magnetic susceptibility curves assume continuous loess deposition at a given site, no erosion, and ubiquitous sediment accumulation rates. These assumptions have been shown to be erroneous (Constantin *et al.*, 2019; Kohfeld and Harrison, 2003; Stevens *et al.*, 2008, 2011, 2018), and can lead not only to proxy record misinterpretation, but also misconstruction of the regional and global picture. Radiocarbon (^{14}C) dating, widely used in paleoenvironmental research, is in most cases unsuitable for providing chronological data for loess-palaeosol sequences, as it requires suitable organic material, e.g. charcoal, wood, bones, gastropods, earthworm granules (Haesaerts *et al.*, 2010; Moine *et al.*, 2017; Újvári *et al.*, 2014a) which, except for gastropods and earthworm granules, does not preserve well in calcareous sediments. In addition, dating of the bulk sediment has long been shown to be problematic, being prone to contamination (Blockley *et al.*, 2004; Walker *et al.*, 2003). Moreover, due to the shape of the calibration curve, ^{14}C determinations are commonly limited to the last 40-50 ka (Reimer *et al.*, 2013), and therefore does not fully capture the glacial-interglacial cycle. This demonstrates a great need for absolute, independent chronological approaches to support any proxy investigations of loess sequences.

Optically stimulated luminescence (OSL) dating of quartz, and infrared stimulated luminescence (IRSL) dating of feldspar, offer an absolute chronological approach, which is particularly applicable to loess deposits (c.f. Buylaert *et al.*, 2012; Wintle and Adamiec,

2017), as these techniques only require the presence of the aforementioned minerals. Luminescence dating offers a direct measure of time passed since the sediment has been deposited. This in turn can provide an estimation of sediment accumulation rates (Constantin *et al.*, 2014; Perić *et al.*, 2019; Stevens *et al.*, 2011) and in some cases an additional sedimentological proxy.

Loess production is a result of complex interactions between endogenic and exogenic factors (Leeder *et al.*, 1998; von Blanckenburg, 2006). Therefore, understanding sediment provenance can be a powerful tool in establishing sediment system dynamics, and through them, climate and environmental change (Hales and Roering, 2005; Herman *et al.*, 2013). Long term loess records preserve evidence of source regions, and therefore can be used to investigate and quantify the production, transport and deposition of loess during the past (Hao *et al.*, 2010; Licht *et al.*, 2016; Maher *et al.*, 2009; Muhs *et al.*, 2008, 2013; Nie *et al.*, 2014b). These investigations also offer insights into sedimentary dynamics on a range of scales, from local to continental (Asahara *et al.*, 1999; Gaiero, 2007; Nie *et al.*, 2015; Pullen *et al.*, 2011; Smith *et al.*, 2003; Újvári *et al.*, 2015). By supporting the sedimentary processes and provenance information with robust independent chronologies, rates of process over long term can be quantified. These insights not only improve our understanding of the Earth's past, but they can also provide powerful means for understanding the future by refining climate model outputs (Albani *et al.*, 2015; Lambert *et al.*, 2015; Shaffer and Lambert, 2018; Sima *et al.*, 2009). While extensive research has been carried to better understand the sources of loess deposits on the Chinese Loess Plateau (e.g. Che and Li, 2013; Licht *et al.*, 2016; Nie *et al.*, 2015, 2013; Pullen *et al.*, 2011; Stevens *et al.*, 2013, 2010; Xiao *et al.*, 2012), by comparison only limited research has been focused on identifying loess sources in Europe. The application of inconsistent methods, and theoretical approaches, has led to conflicting ideas, and therefore the source of these deposits remains controversial. Spatial and temporal variability of loess deposits in the Danube valley have

not received much attention in the past. In most cases geographical differences have been investigated using different methods, therefore comparisons between studies are difficult. Bulk sample geochemistry approaches are commonly applied, however they only provide averaged geochemical signal between an unknown number of sources, therefore precluding fingerprinting of the sources of material. Finally to date mostly single samples from loess units, relating to different glacial periods, have been compared making it impossible to test for provenance changes. As a result, previous research has failed to reach conclusive arguments as to whether any spatial or temporal source changes occur in loess deposits in the Middle and Lower reaches of the Danube.

1.2. Research aims and objectives

The overall aim of this research project is to ***understand the depositional history of the late Quaternary loess-palaeosol sequences along the Lower and Middle reaches of the Danube River***. This aim is addressed by field and laboratory approaches that examine the following research questions and objectives:

Question 1: What does loess in the Danube valley record in terms of timing of accumulation? To address the parts of this question, a detailed review of previous work is carried out with the aim of identifying key sites for detailed analysis.

Objective 1: To produce a relatively high-resolution chronology for the sites identified through the analysis of previous studies, and therefore determine the

Question 2: What is the source of the loess-palaeosol deposits along the Danube River? Detailed laboratory analyses of sediments from the sites identified in Question 1 will facilitate the following objectives:

Objective 2: To investigate any potential source changes over time at each site.

Objective 3: To compare loess source(s) across all investigated sites, and investigate any variability

Objective 4: To identify and discriminate between source areas for the loess-palaeosol deposits along the Danube and determine the most dominant sediment contributors.

Question 3: What are the main sediment transport pathways in the context of the sedimentary basin dynamics during the late Quaternary?

Objective 5: To explore the drivers of sediment production, transport, and deposition on a basin scale by combining the results of chronological and provenance investigations.

The fieldwork and laboratory analysis undertaken in this project provides empirical luminescence, provenance and sedimentological datasets. While a number of sites in the region had chronologies constructed in the past, often the protocols used are now considered outdated as they are known to produce age underestimations. In all cases, the most up to date luminescence dating protocols for quartz, feldspar and polymineral samples are used in this thesis to produce chronologies and calculate sediment accumulation rates.

Luminescence dating is carried out on sediment samples from three study sites, in Croatia, Serbia and Bulgaria. To explore the relationships between timing and any potential source changes for each luminescence sample, a corresponding provenance sample is also analysed. Laboratory techniques selected for provenance investigation are focused on single-grain zircon geochronology and hafnium isotope analysis, supported by bulk sediment geochemistry. The application of multiple provenance proxies aids a more

robust source investigation. Additionally, for Bulgaria, a full-scale sedimentological investigation is undertaken to provide an environmental background for the sites.

1.3. Thesis structure

The format and structure of this thesis follows the paper route guidelines of the School of Geography and the Environment, University of Oxford. The chronological and sedimentological results are presented in three papers submitted to the respective journals. The majority of provenance results are presented in chapter form, with some data presented in two of the papers. A more in-depth structure of the thesis is presented below. Co-author contributions are noted in Appendix A.

Chapter 1 provides an overview of this thesis, including a brief background overview, project rationale, research aims and objectives. An in-depth background on loess research in Central Europe, the current understanding of loess provenance is presented in **Chapter 2**. Background information on regional geology and the modern climate of the region are also explored.

Chapter 3 focuses on methodology. It provides details of fieldwork design, site selection and sampling strategies. In the context of luminescence dating, it provides details of experiments conducted for appropriate dating protocol selection. For provenance techniques a brief method overview is provided as well as analytical details, such as measurement conditions and standards.

Luminescence dating results are presented in **Chapters 4, 5 and 6**. **Chapter 4 (Paper 1)** provides a new chronology for Erdut (Croatia) based on new feldspar luminescence dating protocols. It revises previous work using old protocols and shows that this site is older than previously suggested. In light of the new chronology, proxy records from Erdut are re-examined. **Paper 2 (Chapter 5)** provides chronological, provenance and

sedimentological results for Slivata (Bulgaria). This paper provides a palaeoenvironmental and palaeoclimatological interpretation of the results and reviews current loess interpretation practices in the context of local and global palaeoenvironmental signals.

Chapter 6 (Paper 3) outlines a new chronology for the third site, Surduk (Serbia). While previous work conducted at the site provided 10 ages, these were calculated based on old protocols shown to often underestimate ages. This paper provides a chronology based on 13 quartz and 10 polymineral luminescence ages, and explores discrepancies between the quartz and polymineral approaches. Finally, it reviews the previously published proxy records in light of the new chronology.

Chapter 7 provides an overview of the bulk sample geochemistry, single grain zircon U-Pb dating and Hf isotopic analysis results for all individual samples. **Chapter 8** interprets the provenance analysis from **Chapter 7** together with the results presented in **Chapters 4-6**. The discussion is first focused around potential sources, followed by a sediment provenance examination in the spatial context of the Danube valley. Secondly, temporal provenance changes are investigated at each site. Finally, the wider implications for sediment transport and deposition during the late Quaternary in the context of the Carpathian Basin and Lower Danube are discussed.

Chapter 9 summarises previously discussed findings of the thesis to present how the original aims and objectives were satisfied. This final chapter reviews findings from each chapter in the context of the wider literature, and outlines scope for future work.

Finally, a series of **Appendices** provide the supporting data for this study, including sedimentological data for Bulgaria (**Appendix C**), tephra geochemical compositional data (**Appendix D**), U-Pb and Hf zircon data (**Appendices E and F**).

Chapter 2: European loess, the surrounding environment, and climate

2.1. Introduction

This chapter provides essential background information for the research that has been carried out. It first summarises existing research of loess-palaeosol deposits in Central Europe, in terms of their distribution, stratigraphy, chronology and provenance. This is followed by background on the geology of the region highlighting potential source region history and signatures. Finally, it briefly outlines climatic setting in the region.

2.2. Loess in Central Europe

2.2.1. Distribution

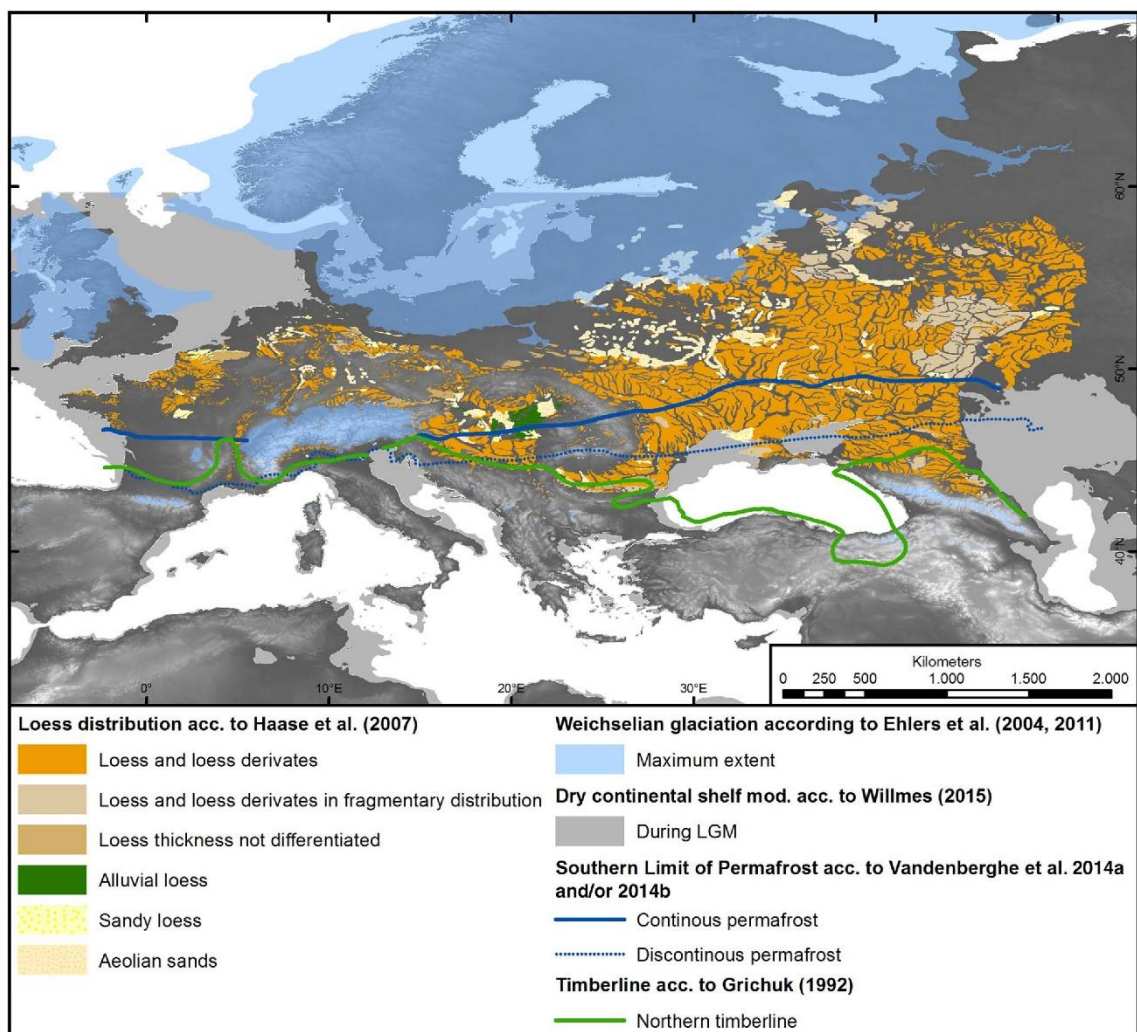


Figure 2.1 Loess deposits distribution in Europe including the extent of the Last Glacial Maximum, sea-levels, permafrost distribution, and northern timberline (from Schaetzl *et al.*, 2018).

Loess-palaeosol sequences in Europe are found stretching from northeast France and southern England across to the Black Sea and the East European Plains (Figure 2.1). Therefore, they can be considered the most extensive terrestrial record of the Quaternary in Europe. The deposits in western Europe usually form discontinuous patches that are relatively thin (Haase *et al.*, 2007; Lehmkuhl *et al.*, 2016, 2018). Additionally their proximity to the North Atlantic and the glacial margins makes them subject to more humid climate and periglacial processes, respectively, which often results in a more complex stratigraphy (Antoine *et al.*, 2009b; Haesaerts *et al.*, 2016; Lehmkuhl *et al.*, 2016).

In contrast, the thickest loess cover developed in proximity to major river systems (Figure 2.1), e.g. the Danube, Dnieper, Rhine, Volga (Antoine *et al.*, 2009b; Frechen *et al.*, 2003; Komar *et al.*, 2009; Smalley *et al.*, 2009; Tudryn *et al.*, 2013). In Central Europe the most extensive deposits can be seen along the Danube River and its tributaries (Stevens *et al.*, 2011; Zeeden *et al.*, 2018c), the second largest river system in Europe. The Danube's drainage basin covers an area of over 800,000 km² (ICPDR, 2004) and represents the largest European loess region, the Russia Plains excluded. Due to its position outside of the continuous permafrost zone, these loess deposits are often providing a uniform spatial cover (Marković *et al.*, 2012; Rousseau *et al.*, 2018), and thought to provide a continuous or semi-continuous record of the last glacial-interglacial cycle (Marković *et al.*, 2015; Thiel *et al.*, 2014). The palaeomagnetism analysis and luminescence dating have shown that numerous sites preserve longer records spanning multiple glacial cycles, e.g. Bulgaria (Jordanova *et al.*, 2008; Lomax *et al.*, 2018), Croatia (Wacha *et al.*, 2018; Wacha and Frechen, 2011), Hungary (Thiel *et al.*, 2014; Újvári *et al.*, 2014a), Serbia (Bösken *et al.*, 2017;

Murray *et al.*, 2014), Romania (Balescu *et al.*, 2010; Vasiliniuc *et al.*, 2012) and Russia (Panin *et al.*, 2018). With some sites in e.g. Serbia (Marković *et al.*, 2011), and Bulgaria (Jordanova *et al.*, 2008; Jordanova and Petersen, 1999) shown preserve the late Matuyama and early Brunhes geomagnetic reversal associated with the MIS 20/19. However, in the case of Stari Slankamen (Serbia) it is thought that the Kamikatsura and Santa Rossa polarity excursions are also preserved, which occurred at 0.92 Ma (Yang *et al.*, 2004).

In addition to providing an exceptional Quaternary terrestrial record, the Danube's corridor has been shown to serve as a ecological refuge, to both fauna and flora, during the cold, glacial stages (Gavriločić *et al.*, 2019; Marković *et al.*, 2007; Molnár *et al.*, 2019; Sümegi *et al.*, 2016). The relatively milder climatic conditions and/or biological refuge are reasons why this region has likely played a key role in the dispersal of hominins into Europe (Hauck *et al.*, 2018; Hoffecker, 2009; Nigst *et al.*, 2014; Staubwasser *et al.*, 2018).

2.2.2. Stratigraphy

Due to the comparatively dry climate, constant sediment supply, and absence of permafrost, loess sequences along the Danube river preserve a relatively “straight forward” stratigraphy and broadly similar stratigraphic units, in comparison to the loess deposits in the Eastern parts of Europe. However, there is a lack of a unified stratigraphic model across the Danube Basin. Though attempts at departing from local and regional nomenclature and stratigraphic schemes, by creating a uniform system using Vojvodina region (Serbia) loess as a type section, have been made (Buggle *et al.*, 2009; Marković *et al.*, 2012, 2015). This approach, based on the one used on the Chinese Loess Plateau (Kukla, 1987; Kukla and An, 1989), allocates “L” and “S” letters, to loess and palaeosol respectively, and numbers the units from top down, with Holocene soil being “S0”, the last glacial loess being “L1”, and the last interglacial soil “S1”, and so on (Figure 2.2). The application of this scheme has a number of benefits, including better transparency and preventing confusion

stemming from numerous national systems (Marković *et al.*, 2012). However, Figure 2.2 highlights the diversity of loess deposits over distances of less than 100 km, from the sediment thickness and therefore accumulation rates, to the number of palaeosols. Therefore, while beneficial in principle if labels are assigned prior to verifying a unit's “true” age, making an assumption of uniform and continuous accumulation at a given site this approach will not resolve correlation errors.

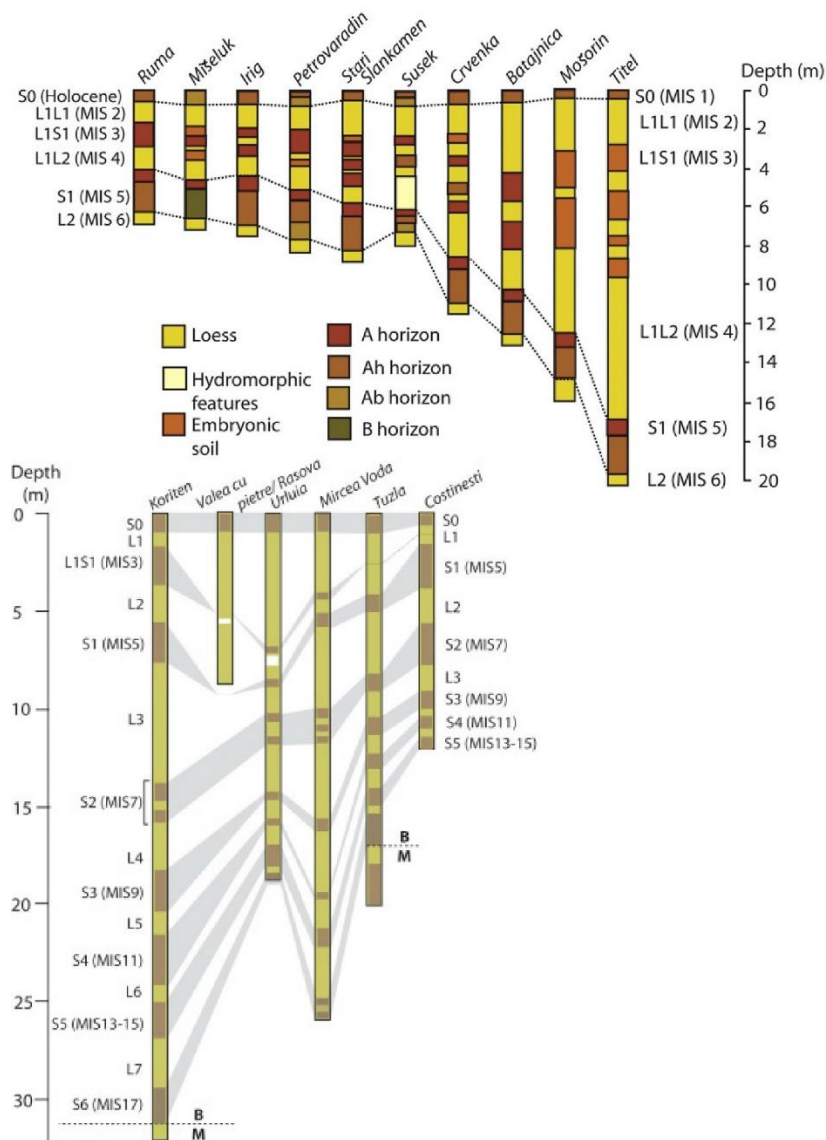


Figure 2.2 Lithostratigraphy and stratigraphic scheme for sites in Serbia and Dobrogea (adopted from Fitzsimmons *et al.* (2012) and Fitzsimmons (2017)).

2.2.3. Chronological controls

Until recently, researchers in Central Europe have typically relied on utilising geomagnetic properties of sediments, such as polarity reversals, to provide chronological tie points (Marković *et al.*, 2011, 2012; Sümegei *et al.*, 2018). Alternatively, broad stratigraphy, including the position and number of palaeosols (Marković *et al.*, 2015), and magnetic susceptibility (Marković *et al.*, 2008, 2012), are used to provide a broad chronological overview and to ‘wobble-match’ between sites, which relies on the continuity assumptions highlighted above. While using polarity reversals provides an absolute age, it requires sediment sequences to be long enough to preserve them and in best case scenarios, it offers a few tie-points over more than several hundred thousand years. Attempts have also been made to utilise ^{14}C ages for correlation purposes, however these are often restricted to preserved organic material such as charcoal or snail shells (Sümegei *et al.*, 2007, 2019; Újvári *et al.*, 2014a). The use of gastropods for the ^{14}C dating presents an additional set of challenges, such as the applicability to only certain species and the carbon reservoir effect (Bokhorst *et al.*, 2009; Pigati *et al.*, 2013; Újvári *et al.*, 2014a). Finally, while able to provide relatively precise ages (in comparison to luminescence dating, the technique has only a 50 ka age range). Recently promising chronological results, based on dating earthworm calcite granules, have been presented. However these have been predominantly conducted on loess deposits in western Europe (Moine *et al.*, 2017).

In the last ten years, luminescence dating of quartz and feldspars has become the chronological approach of choice within the loess community, and as a result have been widely applied across the Danubian region, including in Bulgaria (Balescu *et al.*, 2018), Croatia (Wacha and Frechen, 2011), Hungary (Novothny *et al.*, 2002, 2011; Újvári *et al.*, 2014a), Serbia (Perić *et al.*, 2019; Stevens *et al.*, 2011), and Romania (Constantin *et al.*, 2014; Fitzsimmons and Hambach, 2014; Vasiliniuc *et al.*, 2011). The development of the post

infra-red (pIRIR) dating of feldspar has overcome the problems of ‘anomalous fading’, which causes signal loss in room temperature and results in age underestimation. This provided the opportunity to date material as old as 300-500 ka in some contexts (Thomsen *et al.*, 2011). Therefore a number of studies have constructed chronologies for loess-palaeosol sequences that extend beyond the last-glacial cycle in Bulgaria (Lomax *et al.*, 2018), Croatia (Wacha *et al.*, 2013, 2018; Wacha and Frechen, 2011), Hungary (Schatz *et al.*, 2012; Thiel *et al.*, 2014; Újvári *et al.*, 2014a), Serbia (Bösken *et al.*, 2017; Murray *et al.*, 2014), and Romania (Fitzsimmons and Hambach, 2014; Vasiliniuc *et al.*, 2012). While an increasing number of sites benefited from luminescence chronologies, they often utilise low sampling resolution, apply old dating protocols (e.g. multi-aliquot additive dose (MAAD), or un corrected IRSL), lack synthesis and comparison with other luminescence studies, and as a result of a low sampling resolution do not attempt calculating mass accumulation rates.

Increasingly, chronologies derived from luminescence and radiocarbon dating are supported by the analysis of tephrochronological markers. These volcanic marker horizons have very small uncertainties associated with their ages, if dated directly (Lowe, 2011), their deposition can be assumed to be synchronous on geological timescales (Lowe and Alloway, 2015; Stevenson *et al.*, 2012). Moreover, tephra deposits have very good preservation potential in loess (Marković *et al.*, 2015). Therefore, where present, they provide another absolute chronological marker in loess deposits and stratigraphic control in the absence of other absolute dating methods. The Campanian Ignimbrite (Fitzsimmons *et al.*, 2013; Veres *et al.*, 2013), and the Bag tephra (Bradák, 2009; Horváth, 2001) are the two most commonly investigated tephra horizons in the Middle and Lower Danube contexts, due to their relatively proximal Italian source (Barberi *et al.*, 1978; Pouclet *et al.*, 1999). However only a handful of studies have conducted full tephra geochemical investigations and correlations to identify the tephra horizon (Fitzsimmons *et al.*, 2013;

Obreht *et al.*, 2016; Veres *et al.*, 2013). These studies have been restricted to the visible tephra horizons, however as numerous distal tephras have been reported in lacustrine and peat deposits in the region (Kearney *et al.*, 2018; Ramsey *et al.*, 2015a, 2015b), there is a scope for identifying more cryptotephras in loess and therefore providing additional chronological markers.

EUROPEAN LOESS SUMMARY

Loess deposits can be found across Europe. However the sequences found in the Danube's extensive drainage basin (817,000 km²) are particularly widespread (~101,500 km² in Carpathian Basin (Lehmkuhl *et al.* 2018)), thick, and well preserved.

There is a notable lack of high-resolution geochronological approaches, which results in the use of stratigraphy and sedimental proxies to correlate sites across the region, and with other archives of global environmental change. This relies on the assumptions that loess deposition is continuous and did not undergo post depositional alterations. These approaches additionally assume a synchronous response by the loess deposits, both the proxies as well as stratigraphic boundaries, to the global climatic changes. However, recent developments in luminescence dating and tephrochronology are beginning to challenge these assumptions.

While attempts are made to develop a unified stratigraphic scheme, and depart from local nomenclature, these need to be supported by absolute chronological research.

2.3. The source of loess deposits in Central Europe

The source(s) of loess-palaeosol deposits all over the world has been the subject of debate since the beginning of loess research, both in the context of their geomorphic source, e.g. river terraces, floodplains, periglacial processes, glacially derived deposits (Badura *et al.*, 2013; Mahaney and Andres, 1991; Obruchev, 1945; Pye, 1995; Sindowski, 1949; Smalley, 1966; Smalley *et al.*, 2009; Smalley and Krinsley, 1978), and their source rocks signatures (Taylor *et al.*, 1983; Teruggi, 1957).

In the context of the loess-palaeosol deposits along the Danube River, a number of contesting source hypotheses have been proposed based on theoretical discussion, geomorphological interpretation, laboratory experiments, proxy data, and geochemical approaches. Despite these varied approaches, the current understanding of the source of loess deposits can be explored through two hypotheses; ‘dominant’ and ‘multiple’ source. Both have ramifications for the interpretation of the commonly used physical proxies, as they imply either homogenous or heterogeneous sediment sources across a vast sedimentary basin.

2.3.1. Dominant Source

A single dominant source would see a single region or mountain belt, not only generating, but also delivering sediment to the wider “Carpathian Basin”. Typically, ice-sheets and glaciers are envisaged as agents able to produce large quantities of sediment (Mahaney and Andres, 1991; Wright, 2001). During the LGM the Fennoscandian Ice-Sheet extended south to Northern and Central Poland (Figure 2.1). It had the mass and the power to erode sediment from Scandinavia as well as regions between its origin and termination, and transport and deposit it. This sediment would be further transported and re-distributed via glaciofluvial action (Smalley and Leach, 1978). Additionally, during the LGM an ice-

cap and smaller glaciers developed over the Alps and Carpathians, respectively. In both cases the glaciofluvial and fluvial processes would aid the sediment delivery to the Carpathian Basin. The size, extent, and thickness of the Alpine ice-cap could erode more sediments than smaller and unconnected glaciers that developed in the Carpathian Mountains (Hughes *et al.*, 2007, 2011; Hughes and Woodward, 2008). Therefore, from the perspective of an eroding agent, the Fennoscandian ice-sheet and the Alpine ice-cap would be the proto-source(s) of the sediment under the dominant source hypothesis. The transport and delivery of sediment from the Fennoscandian ice-sheet would pose potential problems as the Carpathian Basin is not in the outwash of the ice-sheet, or directly connected, as the Carpathian Mountains form a natural barrier. As the Danube has its headwaters in the Alps, this source more likely provides the sediment for the Carpathian Basin, which is transported and re-distributed by the Danube across the region.

The outer Eastern and Western Carpathians are most commonly formed by flysch, ophiolites and siliciclastic rocks thrust in Neogene and Palaeogene as nappes (Schmid *et al.*, 2008; van Hinsbergen *et al.*, 2020). The Central and Inner parts of the Carpathians are commonly formed by limestones and ophiolites. Basement and volcanic rocks are exposed at the surface only in some parts around the mountain chain, mostly in the Southern (e.g. Apuseni Mountains) and Western (e.g. Tatra Mountains) Carpathians. While in the Eastern and Western Alps calcareous rocks, such as limestone and *grauwacke*, are still exposed at the surface, metamorphic nappes (e.g. blueschist, eclogite) are more wide spread (van Hinsbergen *et al.*, 2020), in areas such as the Tauern or Engadine Window (Schmid *et al.*, 2008). In both mountain belts there are proto-rocks that are very prone to weathering e.g. limestone (chemical weathering), or siliciclastic sedimentary rocks (physical and chemical weathering). However, in the case of metamorphic and igneous rocks in the Alps and Carpathians, the potential for erosion is dependent on the rock type, and its exhumation and weathering history.

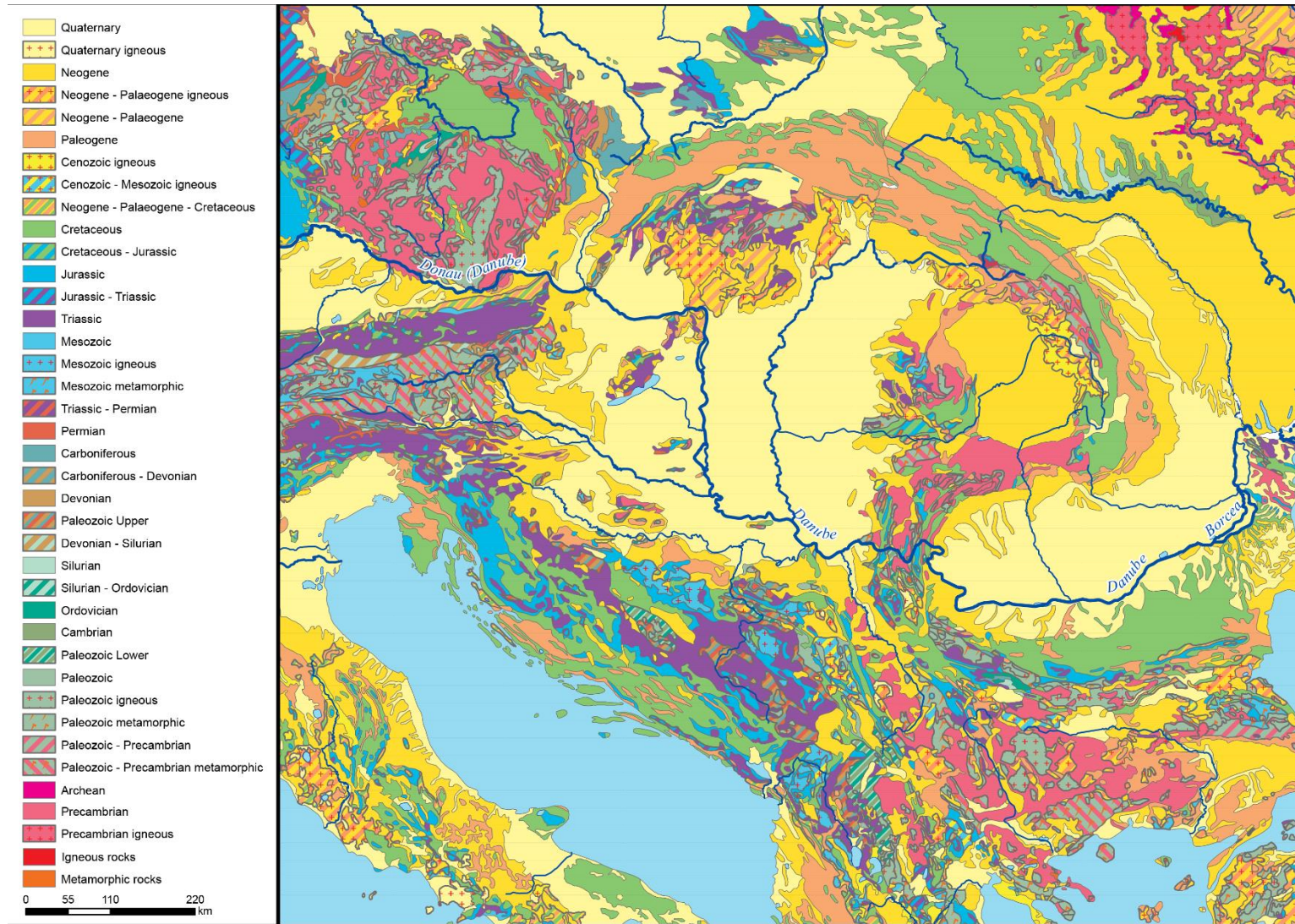


Figure 2.3
Generalised
geological map of
Central Europe
(Data source:
USGS).

While it is not impossible to envisage a single production mechanism, some sections in Serbia and Romania contain over 50 m thick loess deposits (Jipa, 2014; Marković *et al.*, 2015), which would require a combination of heavy erosion and/or rapid tectonic uplift in the source region. This hypothesis would have huge implications for our understanding of sediment generation mechanisms, erosion rates, and uplift. It would also require a further investigation into why regions of similar nature are active sediment producers and others are not.

One of the main, geomorphological sediment generators proposed for the dominant source category are glaciers (Mahaney and Andres, 1991; Smalley, 1966). Consequently, the Alps or Carpathian Mountains (Figure 2.4) have been suggested as the main sediment producing regions, and the ice-cap and glaciers identified as a sediment generating mechanism (Smalley and Leach, 1978). In this case sediment would have been delivered directly to the Danube River, which originates in the Alps, and distributed across the course of the river, and finally to the loess sites. While the Alpine glaciers and ice-caps had a definitive ability to generate large quantities of sediment, there is still a debate in the literature as to whether the Carpathian Mountains supported features larger than individual, unconnected glaciers during the glacial periods (Ehlers and Gibbard, 2007; Hughes and Woodward, 2017; Urdea, 2004; Urdea *et al.*, 2011). The implication that the role of glaciers in loess production was previously exaggerated was stressed by the bulk sample geochemical results from Serbia (Buggle *et al.*, 2008) and supported by theoretical analysis (Smalley *et al.*, 2008, 2009).

Alternatively, the Fennoscandian Ice-Sheet has been suggested as source in the past, as capable of generating large quantities of sediment for the loess in the Carpathian Basin. The growing Fennoscandinavian Ice-Sheet was thought to erode sediment from a range of terrains, including the Scandinavian mountains, continental shields, regional exposed

bedrock outcrops, and Quaternary sedimentary covers (Smalley and Leach, 1978). This theoretical work suggested large quantities of glacial meltwater entering the into the Danube River channel via the Moravian depression (Figure 2.4). In the last stages of the sediment transport, fluvial sediment would have been deposited within the river valley and over alluvial plains, and finally deposited via aeolian processes as loess.

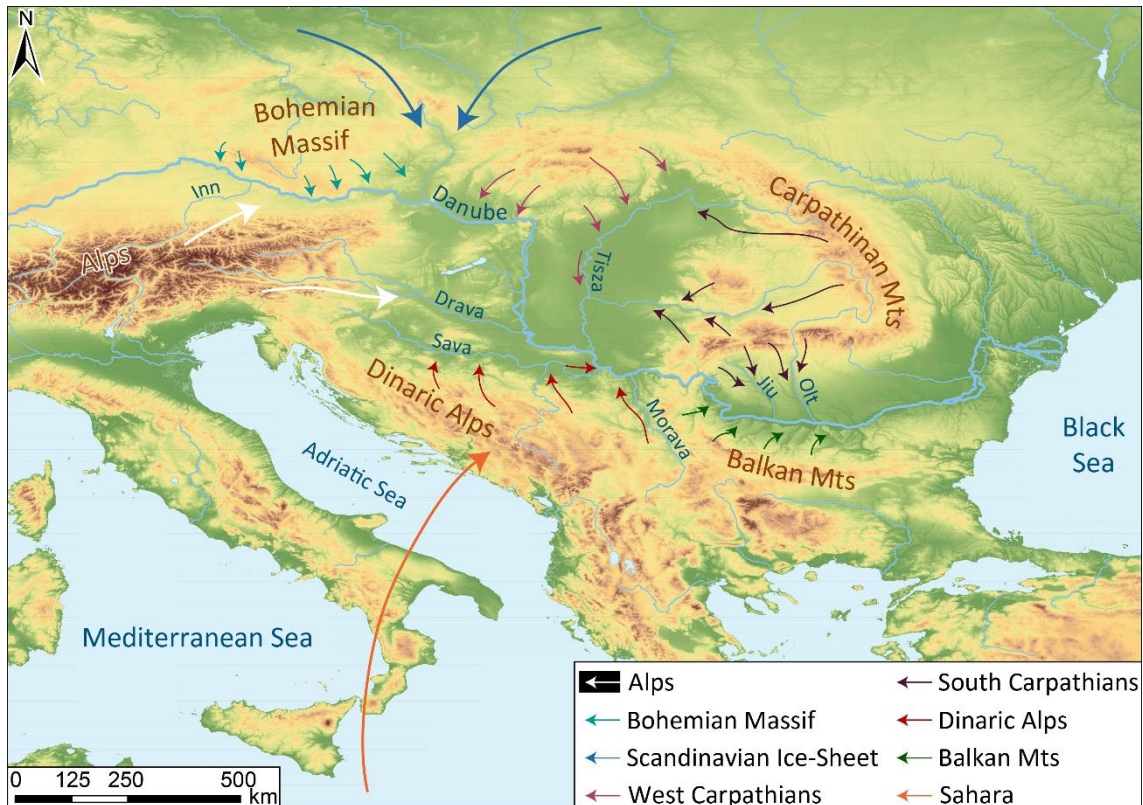


Figure 2.4. Generalised source regions and the direction of transports for the loess deposits along the Danube River (DEM Source: ©JAXA).

The theoretical paper by Smalley et al. (2009) analysed loess deposits worldwide and propose the source to sink transport model, which strongly argued for the necessity of a fluvial component in sediment delivery. This work further indicated the Alps, Carpathians or Sudeten as the proto-source for the Danubian loess deposits. The Alps or Carpathian were also suggested as the main source for loess in Serbia (Buggle *et al.*, 2008) and Hungary (Újvári *et al.*, 2008) based on the analysis of bulk sample major and trace

elements. While the study of Buggle *et al.* (2008) excluded contributions from the northern Alpine nappes and argued for no Fennoscandinavian Ice Sheet inputs in Serbia.

Lastly, laboratory simulation of silt-size sediment production and abrasion power suggested that Miocene–Pliocene sands, underlaying the Quaternary deposits in the Pannonian Basin (Carpathian Basin), could be the dominant source of Hungarian loess (Smith *et al.*, 1991; Wright and Smith, 1993).

2.3.2. Multiple Sources

The second category of source hypotheses envisages multiple sources generating and contributing sediment to the Danubian loess sequences. It is likely that there are a few sources which are contributing more than others. However, this also implies that there could be a countless number of end members for each given site, that either contribute equally or are found on a mixing line. If this was the case, it could provide invaluable information about smaller system activation, e.g. geomorphological conditions in the system, absence or presence of glaciers, or fluvial modes of delivery. Finally, this hypothesis would have implications for the interpretation of proxy data, such as grain size, as changes in particle sizes could be linked to changes in dominance of source, rather than changes in wind strength or wind direction.

In most cases the Danube's alluvium is seen as the immediate, geomorphological source of the loess deposits (Banak *et al.*, 2013; Frechen *et al.*, 1997; Galović, 2016; Jipa, 2014; Obreht *et al.*, 2016; Újvári *et al.*, 2012, 2014b) with the Alps or Carpathians seen as the primary sediment suppliers. Additionally, the role of the Danube's tributaries, such as Tisza, Drava, Sava, Olt or Jiu, is often highlighted as a mechanism for delivering material from smaller source regions (Bösken *et al.*, 2019; Jipa, 2014; Schatz *et al.*, 2015). The Danubian floodplains and alluvium have also been indicated as a main sediment supplier to Hungarian loess through comparison of heavy mineral assemblages from 216 samples

(Thamó-Bozsó *et al.*, 2014), though the primary sources of the sediment were shown to be the Alps, Western Carpathians, Bohemian Massif and the Transdanubian Central Range. This work also highlighted the contribution of local smaller mountain ranges, such as the North Hungarian Range, Transdanubian Central Range, and Transdanubian Hilly Region, and the role tributaries play in delivering material to the Danube River system.

Heavy mineral from loess profiles in Croatia also supports importance of the additional proximal source rocks, such as the Slavonian Mountains (Banak *et al.*, 2012; Galović, 2016). While single grain rutile and zircon analysis of three loess profiles in Austria indicated that sediment has strong proximal (Alpine and Bohemian) affinities (Újvári *et al.*, 2013; Újvári and Klötzli, 2015). However, one of the sites is located by the Alp-draining the Traun River, rather than the Danube, which could explain the strong Alpine signature. Jipa's (2014) re-analysis of the published geological maps, geomorphological, and sedimentological data, suggested that material for the Lower Danube loess was sourced from several locations, including the Carpathian Mountains, Balkan Mountains and Black Sea (Figure 2.3).

A study by Schatz *et al.* (2015) investigated bulk sample major and trace element, and isotopic composition at Tokaj (Hungary) and Grub (Austria). The results also pointed to dominant contributions from source rocks in the East Carpathians, the Bohemian Massif and Alps. However, this work also highlighted the difficulty in source identification when the single provenance method is used, as well as the source mixing effect precluding definitive source identification based on bulk sample analysis. While they were unable to exclude contributions from the Miocene local sands and fluvial sediments from the Western Carpathians, the Bohemian Massif, the Danube and the Tisza Rivers, they considered contributions of local/proximal sediments as negligible. Research by Újvári *et al.* (2012) utilised single grain provenance methods in the European loess context alongside Sr–Nd isotopes, and bulk and clay mineralogy for the first time. They have been

able to show similarities between the Tortonian and Pleistocene fluvial samples and discount Messinian sand sources.

The results of high-resolution major and trace element analysis of loess at Paks (Hungary), suggested that sediment most likely originated from felsic rocks, likely sourced from local outcrops (Újvári *et al.*, 2014b). Similarly at Süttő (Hungary), felsic rocks have been proposed as the primary source of sediment (Profe *et al.*, 2018). Instead dolomite rocks have been suggested as one of the primary sources for Hungarian loess, based on the dolomite to calcite ratio in the bulk sediment (Hum and Fenyés, 1995; Nemecz *et al.*, 2000; Újvári *et al.*, 2010a), which could point to the Eastern Alp as the source.

Mass accumulation rates and re-evaluation of mineralogical data from 33 sites across the Carpathian Basin highlighted again the significance of glaciogenic and mountain sources for loess deposits (Újvári *et al.*, 2010a).

Finally, contributions have also been suggested from some distal sources, such as the Sahara Desert, based on an analysis of particle size and modern dust sources (Stuut *et al.*, 2009), modern observations (Varga *et al.*, 2013), past contributions into palaeosol (Varga *et al.*, 2016) and dust flux and elemental composition in peat bogs (Longman *et al.*, 2017). This has been supported by the suggestion that glacial periods were characterised by increased frequency and magnitude of dust storms coming over from Africa (Goudie and Middleton, 2001). However, strong Saharan inputs have not been confirmed so far in loess deposits as bulk sample geochemistry, and the absence of indicator minerals, thus far only support minor contributions (Újvári *et al.*, 2012).

2.4. Spatial variability of provenance signals in Danubian loess deposits

Spatial source variability has only been briefly tested on the broad European scale, despite the importance of understanding dust/sediment transport pathways. Source changes

occurring across the Carpathian Basin would firstly imply that there is no one dominant source of sediment. Alternatively, this could suggest multiple dominant sources, the importance of which shift through the Basin. On the broader scale this could imply diverse drivers behind activation of source regions, varied mechanisms of transport, and mixing prior to final deposition. However, to date insufficient data have been published to robustly evaluate source shift across the Danube valley, which has mostly been investigated indirectly.

A bulk sediment geochemical and isotopic study (Schatz *et al.*, 2015) argued for sediment homogeneity in the Carpathian Basin, suggesting that sites in Hungary and Austria share a source, despite the distance between the sites. This result would indicate predominantly long distance aeolian transport, due to the sites' distance and locations. However, as Grub is located in the Moravian Gap at the foothills of the Western Carpathians and Bohemian Massif, while Tokaj is located at the foothills of the Eastern Carpathians. The two sites are separated by the Western Carpathians, therefore it most likely that these sites do not share sources and that the bulk sample approach used is not able to distinguish between the source rocks with similar timing of deposition and composition.

The theoretical work on the provenance of loess deposits in the Carpathian basin argued that the main source shifts were due to new tributaries entering the Danube's system, e.g. the Moravian gate or Tisza (Smalley and Leach, 1978). Újvári *et al.* (2008) supported this suggestion, showing bulk sample geochemical homogeneity between numerous loess-palaeosol profiles across southwestern Hungary. The study of Buggle *et al.* (2008) reached a similar conclusion, showing source uniformity between sites in Serbia and Romania. However, some variability has been noted between different regions. The Romanian site reported Buggle *et al.* (2008) might be experiencing additional sediment inputs from other large glaciofluvial sources in Ukraine. Subsequently supported by the conceptual

model of sediment transport in the Lower reaches of the Danube demonstrated that despite many similarities there is variation between sites in Bulgaria and Romania, attributed to inputs from tributaries and therefore changing geologies (Jipa, 2014).

At least four times higher calcite to dolomite ratio has been reported for the sites in Hungary (Hum and Fenyés, 1995; Nemecz *et al.*, 2000; Újvári *et al.*, 2010a) compared with the sites in Serbia (Kostić and Protić, 2000), indicating that Hungary may experience fresh inputs of dolomite or that one of the tributaries, e.g. the Drava or Tisza, is diluting the ratio with calcite. Slight shifts in mineral assemblages were also shown between Croatian sites, where it is thought the differences can be tracked to the proximity to the Sava's alluvium and regionally exposed bedrock (Banak *et al.*, 2013; Galović, 2016).

2.5. Provenance changes over time in Danubian loess deposits

Questions of the temporal changes in sediment source are important to our understanding of palaeoclimate and sediment production. Any source changes occurring during the main sediment accumulation periods would have implications for our understanding of sediment transport, e.g. regional activation, or wind/fluvial regimes. This also has consequences for the interpretation of proxies, such as grain size, as at present the changes in the particle size are often interpreted as an indicator of wind strength or direction changes. However, if shifts in sediment source(s) were occurring, this could be the driver behind particle size changes.

Lack of changes over time, both long term and abrupt ones, would suggest that the sediment sources are unaffected by large climatic reorganisations, nor local or regional factors, thus requiring additional work to understand the drivers behind sediment production beyond climate and tectonics. Thus far only a handful of studies investigated temporal provenance shifts within individual sites and they mostly argued for stable

sediment sources over time. The research of Schatz *et al.* (2015), using elemental composition of bulk samples and Sr-Nd isotopes, indicated an homogeneous source of loess in Tokaj over the last 60 ka. No change in provenance over 800 ka has also been argued for in the Paks loess profile, based on major and trace element analysis (Újvári *et al.*, 2014b). Lastly a lack of source changes between loess units have been argued for based on the Nd-Sr isotopic composition at multiple sites along the Danube (Újvári *et al.*, 2012).

On the orbital timescale, provenance variation between loess and palaeosol units could imply changes to either transport or production modes. For example, changes to wind patterns between glacial and interglacial periods, as the high pressure centres migrate, as a result of growing ice sheets (Bokhorst *et al.*, 2011; Obreht *et al.*, 2016). At the same time growing ice-sheets and glaciers are likely to become the main sediment producers, eroding both sediment and rocks alike, and injecting a large sediment volume into the Danube's system. During glacial period, rocks that otherwise would take a long time to erode due to their position or exposure, and to make their way as a sediment into the system (Wright, 2001). Conversely, during interglacial periods, it is fluvial action and colluvial processes are likely the main sediment producing forces. Identifying shifts in sediment sources on the orbital timescales can therefore point to a system re-organisation, and/or changes in fluvial and aeolian transport. Major and some trace element analysis of loess-palaeosol units at Süttő (Hungary), suggested that there have been changes in sediment source between interglacial/interstadial and glacial stages over the last 100 ka (Profe *et al.*, 2018), a similar trend has also been reported in Serbia (Orlovat) (Obreht *et al.*, 2015). Minor shifts in mineral assemblages, and therefore the source area, have also been reported for Croatian loess (Banak *et al.*, 2013). This indicates that there is a potential for provenance occurring around the Carpathian Basin between the main sedimentary units that requires more systematic investigation.

EUROPEAN LOESS PROVENANCE SUMMARY

The proposed source areas for the Danube loess are crystalline basement rocks outside of the Carpathian Basin delivered by melt water from the Fennoscandinavian Ice Sheet, recycled sediments infilling the Carpathian Basin, Miocene flysch and molasse, and felsic rocks in the NW Carpathians, the Alps, and Sudeten. These can be broken down into two hypotheses; (1) Sediment has predominantly the same source throughout the basin and is produced via major ice-sheets and glaciers; and (2) source changes along the river, with dominant inputs from local areas and geologies.

Following on from that, there are questions regarding spatial variability in source across the loess deposits in the Carpathian Basin, which has only been considered by a handful of studies and still lacks a consensus.

While some studies have investigated temporal changes within loess, samples were mainly collected to reflect the LGM. Therefore, very little is known about source changes through a full glacial-interglacial cycle, or in fact over longer time scales.

2.6. Geology of Central Europe

Central Europe preserves a complex geological record (Figure 2.3), shaped by numerous orogenic and metamorphic events. This figure highlights the potential problems that might be encountered when investigating primary loess sources along the Danube River as the catchment is surrounded by a mosaic of rock types and ages. The current structure was largely formed during the Alpine Orogeny, when Africa collided with Eurasia, closing off the Tethys Ocean and creating the Carpathian, Alps, Dinaric Alps and Balkan Mountains that now surround the Pannonian Basin/Carpathian Basin (Schmid *et al.*, 2008). While the primary Alpine Orogeny events occurred between 65 Ma and 2.5 Ma, elements of this region have previously been part of several supercontinents, and reshaped by a number of continental breaking and building events (e.g. Meert, 2012; Meinhold *et al.*, 2013; Spencer *et al.*, 2013; Stampfli and Borel, 2002). The palaeocontinent reconstructions and orogenic events central to understanding the evolution of the modern Europe are outlined below, together with signatures expected to be seen in some of the source terranes. Therefore section 2.6.1 summarises the current understanding of Europe's evolution, starting from outlining the proto-Baltica block (one of Europe's early building blocks) and moving through time and various supercontinent stages. The continent building and break-up events are crucial to understanding zircon U-Pb signatures as they are likely to be preserved in the potential source rocks outlined in section 2.3 (e.g. Scandinavia, Alps, Bohemia, and Carpathians). Further as one of the principal goals of this research is identifying the primary source rocks for the loess deposits along the Danube, it is integral to this research to understand the distribution of rocks and age signatures across modern Europe.

2.6.1. Continental evolution and potential source signatures in Central Europe

2.6.1.1. Precambrian rocks

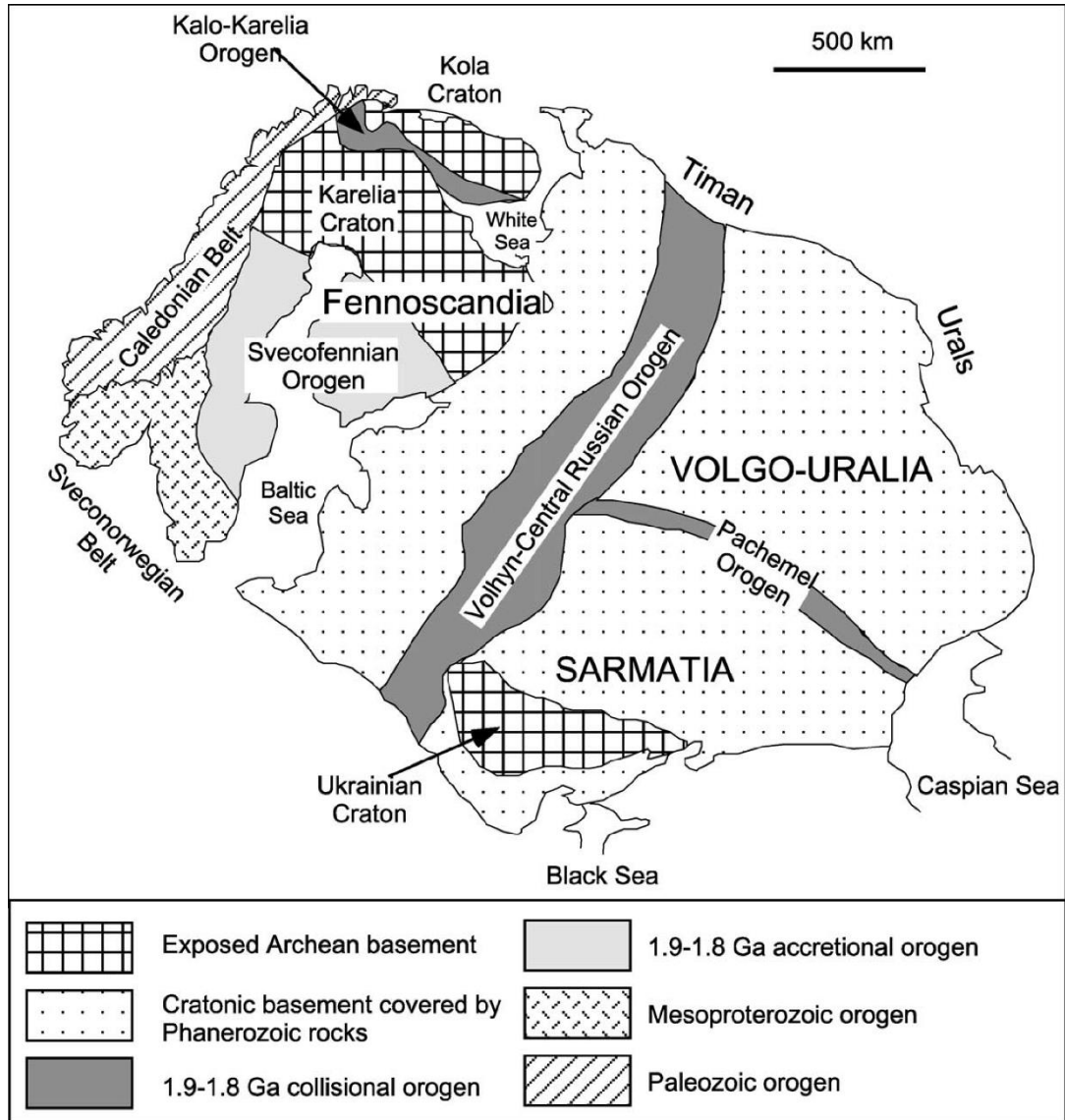


Figure 2.5 Generalised outline of the East European Craton in the context of the present day Eurasian continent (Zhao *et al.*, 2002).

The East European Craton is the core constituent of the Baltica proto-plate and is made of three blocks; Fennoscandian, Volgo-Uralian, and Sarmatian (Figure 2.5). The blocks began to collide c. 2.05-2 Ga and concluded their consolidation into Baltica around 1.8-1.7 Ga (Bogdanova, 2005). As a result this region comprises some of the oldest rocks in Europe

(Slabunov *et al.*, 2006). In the north of Baltica the Fennoscandian terranes range in ages from Archaean accretional relicts (3.5-2.7 Ga) to Proterozoic crust (2.5-1.7 Ga) (Bogdanova *et al.*, 2001; Gorbatshev and Bogdanova, 1993). In the south, the Sarmatia (or Scythian Plateau), comprises older Archaean crust, with rocks dating to 3.8-3.2 Ga in the Voronezh Massif (Claesson *et al.*, 2006; Shchipansky and Bogdanova, 1996), and Palaeoproterozoic orogenic belts (Terentiev *et al.*, 2017). These terranes were further influenced by several events during the Neoproterozoic and early Palaeozoic, e.g. Sveconorwegian-Grenvillian Orogeny (1.2-0.9 Ga), break up of Rodinia (c. 800 Ma), and Caledonian Orogeny (c. 500-400 Ma) (Balling, 2000; Cocks and Torsvik, 2005; Gorbatshev and Bogdanova, 1993; Meert and Torsvik, 2003).

From the potential source regions point of view, the Sarmatia signatures can be excluded due to their geographical location. The only transport pathways for these sediments is via the Siret and the Prut rivers, which follow the outer parts of the Carpathian Mountains and have their confluences less than 150 km from the mouth of the Danube. Therefore, Sarmatia is an unlikely source of sediment to the Carpathian Basin, though these signatures should be seen in alluvium and any loess profiles found along the final reaches of the Danube.

The Fennoscandian signatures would, however, reflect Fennoscandinavian Ice-Sheet inputs into the Carpathian Basin and transport via the Moravian Gap evoked by Smalley and Leach, (1978). The age distributions of zircons would display predominantly Archaean and Proterozoic age populations (Figure 2.6A and B), while ϵ_{Hf} would show predominantly positive to slightly negative values (Figure 2.6C and D). Therefore, large contributions of sediment from Scandinavia would produce zircon distributions with dominant age peaks in the 1000-3000 Ma age ranges.

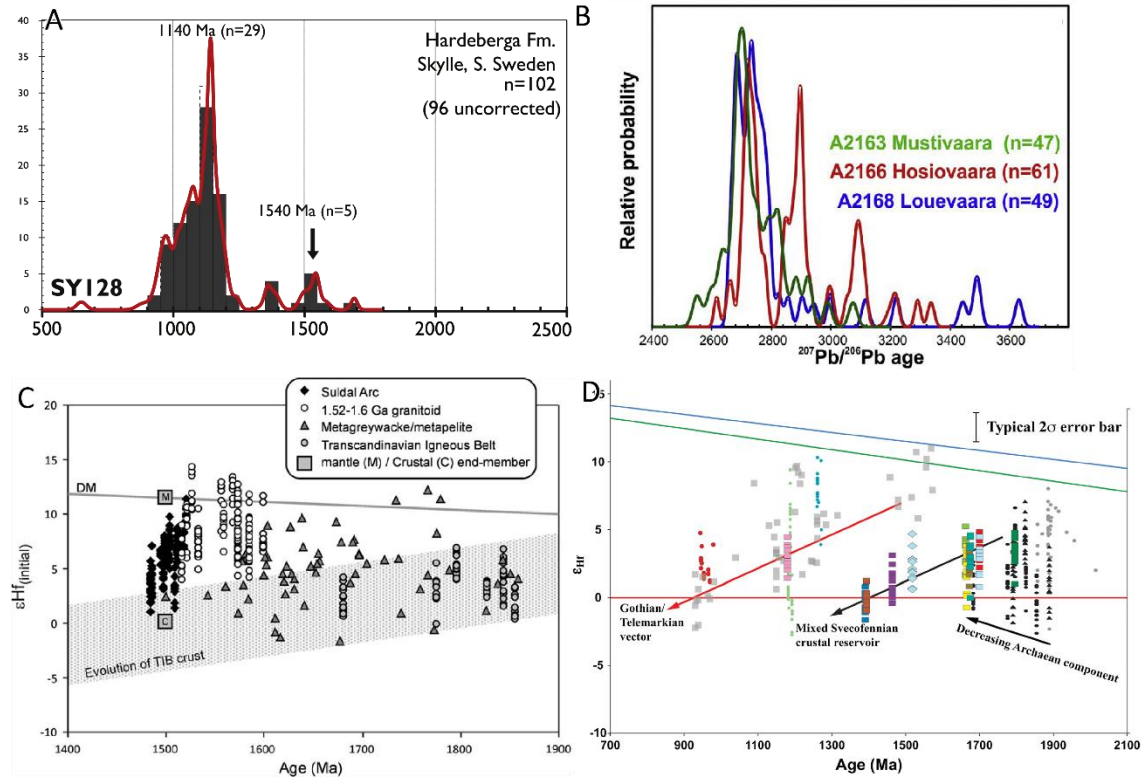


Figure 2.6 A typical zircon U-Pb age distributions (A. South Sweden (Lorentzen *et al.*, 2018); B. Finland (Ranta *et al.*, 2015);) and εHf (C. Proterozoic crustal blocks Southwest Norway (Roberts *et al.*, 2013); D. South Sweden's Proterozoic rocks (Petersson *et al.*, 2015)) from the Fennoscandian igneous rocks.

2.6.1.2. Gondwana and peri-Gondwana terranes

The assembly of Gondwana commenced “shortly” after the break up of Rodinia, and began with the East African Orogen during the Neoproterozoic, c. 750 Ma (Meert and Van Der Voo, 1997). The internal building events are thought to have started c. 650 Ma (Cawood and Buchan, 2007; Squire *et al.*, 2006) and concluded between c. 570 and 510 Ma, by an amalgamation of East and West Gondwana (Cawood and Buchan, 2007), creating the Gondwana supercontinent (Figure 2.7). During its existence, and as a part of its continental assembly process, a number of Neoproterozoic orogenic events took place that

are broadly termed “Pan-African Orogeny” (Hefferan *et al.*, 2014; Meert, 2003; Veevers, 2003).

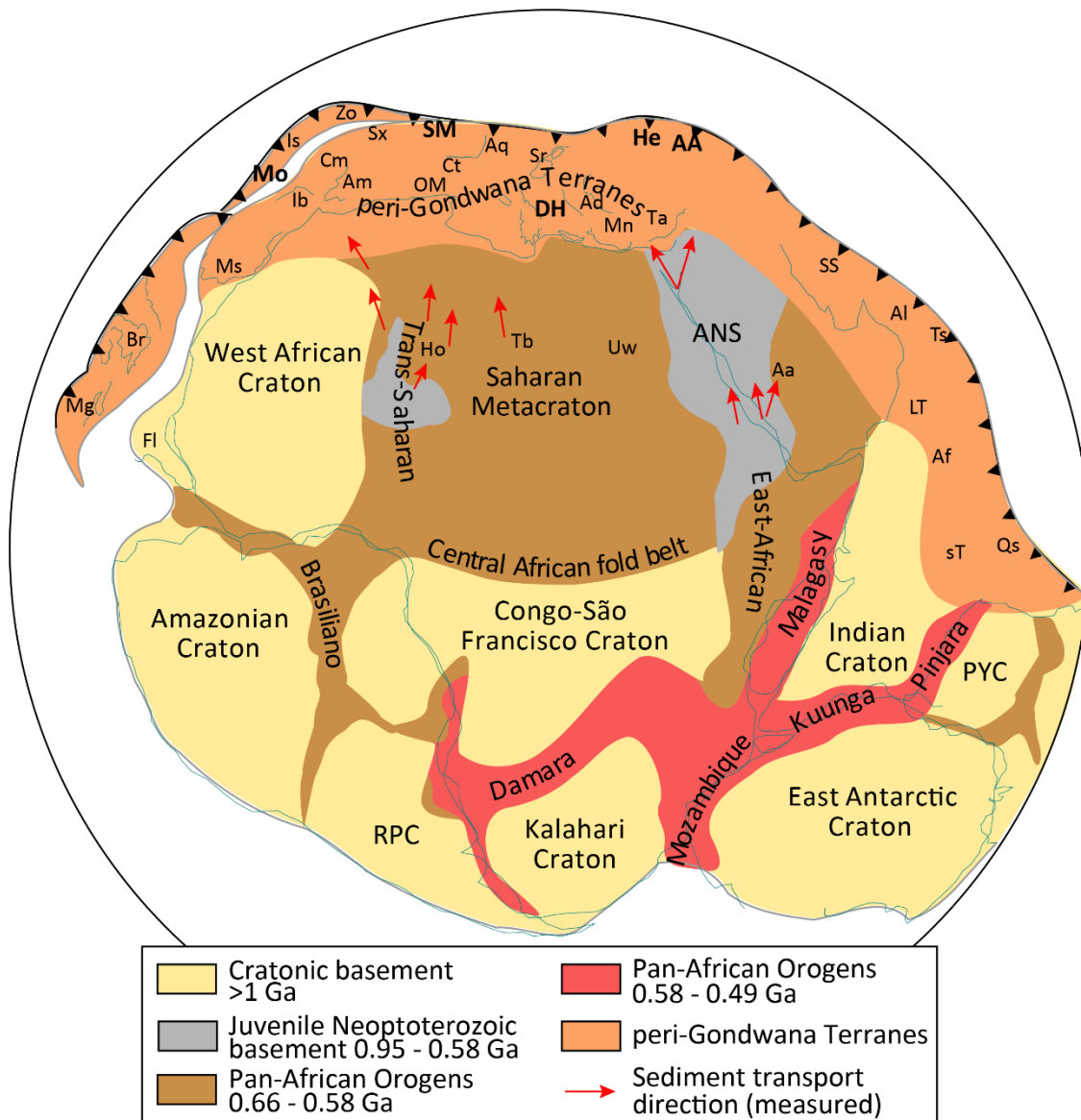


Figure 2.7 A model of Gondwana for the Cambrian period, incorporating locations of older Proterozoic rocks and highlighting the Pan-African Orogens across the palaeocontinent. Terranes of interest to this study are presented in bold AA – Austro-Alpine, Ad – Adria, DH – Dinarides-Helenides, He – Helvetic, Mo – Moldanubian, SM – Serbo-Macedonian (adopted from Abbo *et al.* (2018) and Avigad *et al.* (2017). See references for the remaining abbreviations).

Figure 2.7 shows that continental margins of Gondwana were dominated by Palaeoproterozoic and older crusts (Spencer *et al.*, 2013). Additionally, a series of detached basement rocks, peri-Gondwanian terranes (Figure 2.7), were developing in-between Gondwana, Baltica and Laurasia (Zeh and Gerdes, 2010). These terranes represent proto-blocks of modern day Europe (Abbo *et al.*, 2018; Avigad *et al.*, 2017; Meinhold *et al.*, 2013), and were separated by the ocean-arc development that followed the mid-ocean ridge subduction (Stampfli and Borel, 2002). The active arc margins have over time evolved into more mature passive margins (Hefferan *et al.*, 2014; Stampfli and Borel, 2002), with pelagic sedimentation at the northern continental margins (Abbo *et al.*, 2018). The sediment deposited at the margins was sourced from the erosion of extensive Neoproterozoic Pan-African terranes, with some of the sedimentary transport direction reconstructed (Avigad *et al.*, 2017).

These peri-Gondwana terranes and sedimentary deposition at the continental margins are particularly important as these sediments will, in part, form the modern Carpathian Basin and surrounding mountain belts. It is therefore expected that the majority of source rocks for the Danubian loess deposits will contain the “Gondwanian” zircon signatures, clustered around the 600 Ma. Figure 2.8A shows a comparison of summary zircon age distributions from Avalonia, East and West Africa, while 2.8B shows a compilation of the Nile catchment, the detrital African sediments and modern African river datasets. All figures show dominant c. 600 Ma age populations that represent the Pan-African orogenic events, with additional large populations at 1000 Ma. A distribution of the ϵ_{Hf} isotopic values from the Gondwanian terranes (Figure 2.8B), also shows that while the majority of the ϵ_{Hf} values are clustered between +5 and +10, and represent juvenile magma, there are smaller populations of strongly negative grains that suggest recycling of older, cratonic crust.

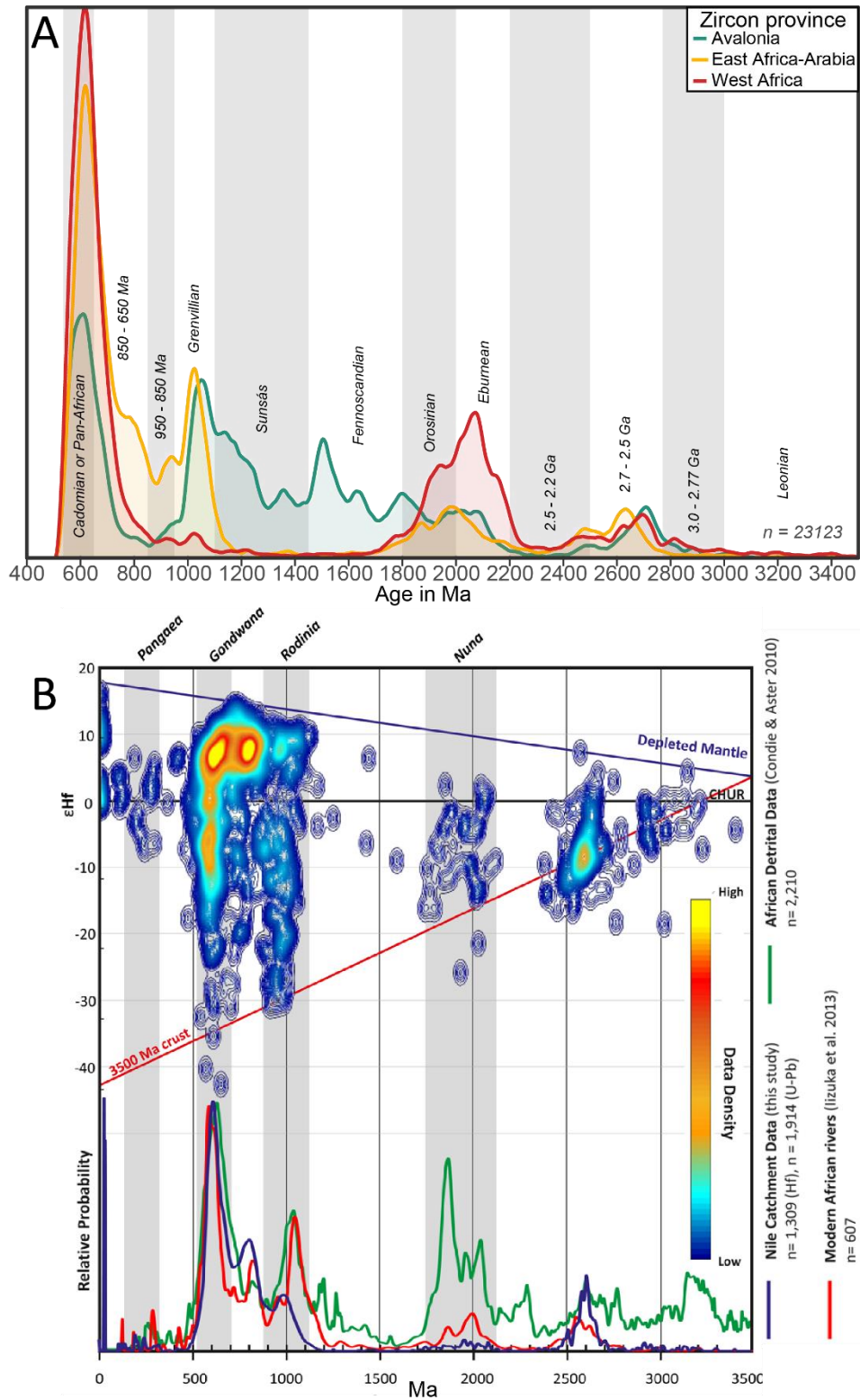


Figure 2.8 A) Kernel density estimation of the zircon U-Pb age spectra for the northern Gondwana provinces (Stephan *et al.*, 2019). B) ϵ_{Hf} isotope evolution for the Nile source regions (Fielding *et al.*, 2017).

2.6.1.3. From Gondwana to Pangea

A sequence of pre-Variscan rifting events occurred during the Cambrian-Ordovician at the northern margins of Gondwana (Figure 2.9). These events resulted in the separation of Avalonia and Cadomia (Kroner and Romer, 2013; Stampfli *et al.*, 2002; von Raumer *et al.*, 2003) and opening of the Rheic Ocean (Nance *et al.*, 2010). The Avalonia and Cadomia terranes collided with the East European and North American Cratons forming Laurasia and the rocks representing these events can be found within Central Europe (Balintoni *et al.*, 2014). However, many of these rocks have inherited Gondwanian signatures.

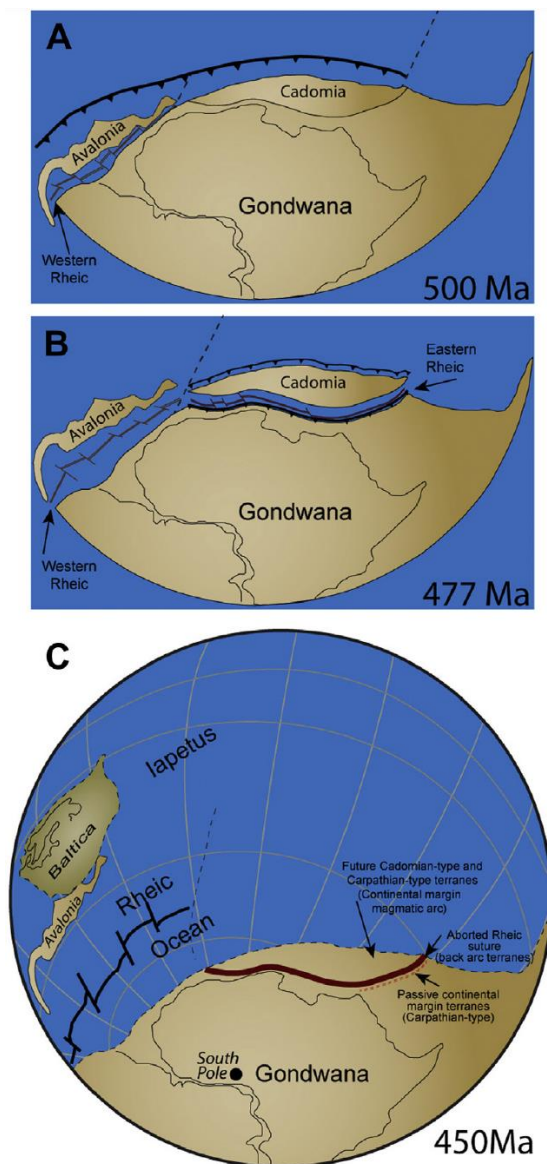


Figure 2.9 Modelled paleogeography evolution and the distribution of the North African and the European terrains during the late Cambrian and Ordovician (450-500 Ma). Note the Carpathian and Cadomian terrains emergence towards the Upper Ordovician (adopted from Balintoni *et al.*, 2014).

The rifting events concluded with the Variscan Orogeny (c. 370-290 Ma), during which Laurasia and Gondwana collided, causing the assembly of the supercontinent Pangea (Figure 2.10). The blocks derived from Avalonia (eastern and western North Gondwana shelf), formed the Rheno-Hercynian–Moravo-Silesian arc at c. 390 Ma (Stephan *et al.*, 2019), which stretches across the whole of Central Europe. The three zones created in the process (Renohercynian, Saxothuringian, and Moldanubian) (Eckelmann *et al.*, 2014) have strongly overprinted Variscan signatures on relict terranes in Central Europe (von Raumer *et al.*, 2003). This orogenic event is preserved as a series of complex metamorphic, magmatic and deformation events (Kroner and Romer, 2013), and of the reasons behind the complex geological record in Central Europe.

The Variscan zircon signatures are likely to be found in most of the rocks surrounding the Carpathian Basin (Figure 2.11), including the Alps, Bohemian Massif, Balkan Mountains, and some bedrock outcrops pockets in the Carpathians and Dinarics. It must be noted however, that zircon signatures of rocks from the zones created during the Variscan orogeny can either produce heterogenous zircon age distributions (preserving a strong Variscan imprint (Figure 2.11B)), while others preserve predominantly peri-Gondwana and earlier terranes source signals (Figure 2.11C).

If a single Variscan source controls the sediment supply for the loess deposits along the Danube River, the resulting zircons age distributions would approximate Figures 2.11A and 2.11B (D540-ZR4), showing a dominant age peak around 340-350 Ma. However, it is likely that there would be a small tail present preserving the 450-500 Ma rifting and arc development episodes, and 600 Ma Gondwana and Pan-African signatures. From the hafnium isotopes perspective, zircons in eastern Bavaria show mildly negative values (ϵ_{Hf} values -5 to 0) for the 299-328 Ma ages, indicating mixing between juvenile crusts with some crustal signatures (Siebel and Chen, 2010). The Moldanubian Zone (Bohemian

Massif) ϵHf signatures for the c. 350 Ma zircons have juvenile close to oceanic-arcs signatures (average 3.6) (Sláma *et al.*, 2007).

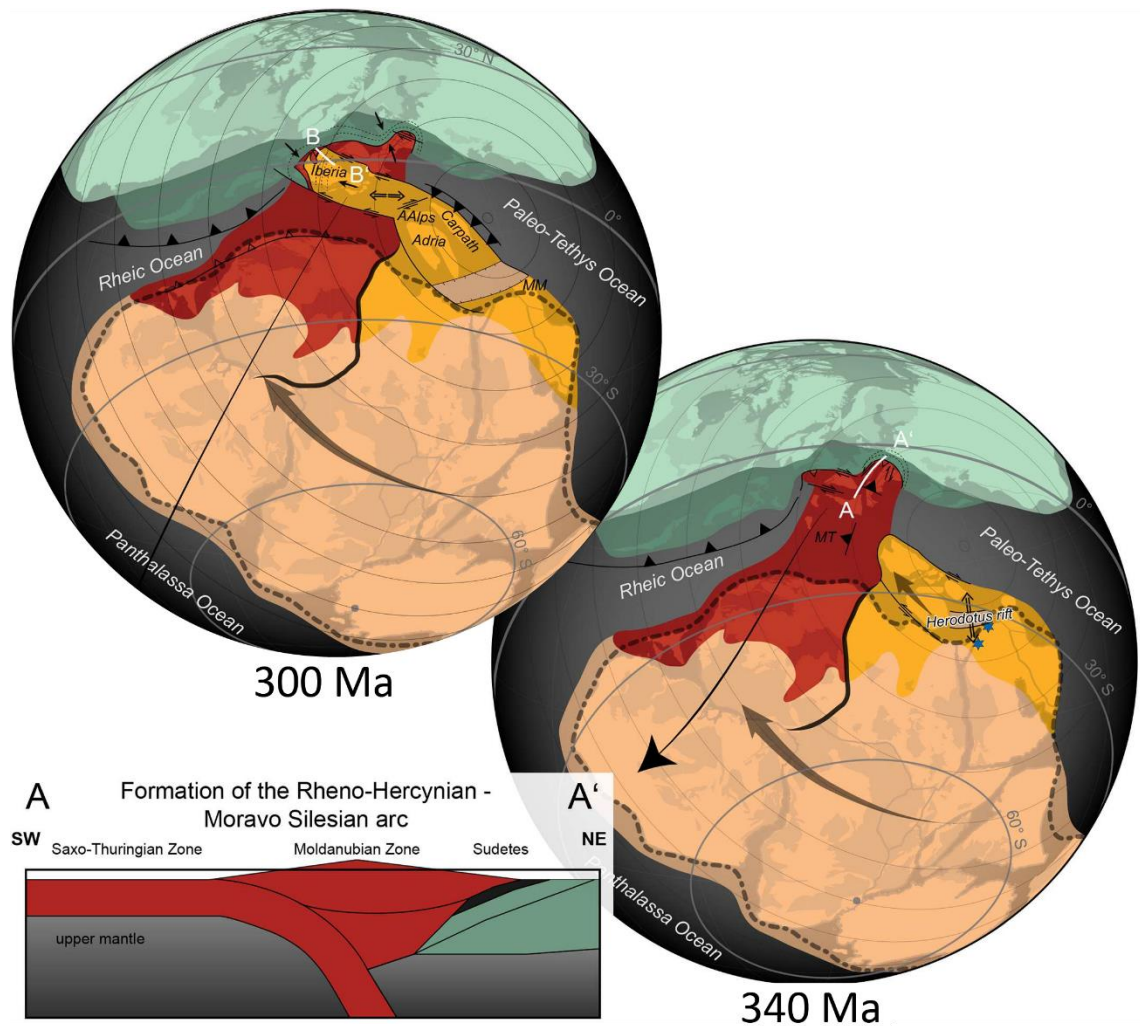


Figure 2.10 Modelled paleogeography evolution of the Peri-Gondwana terrains, especially Austro-Alpine (AAIps) and Proto-Carpathians (Carpath) regions, between 340 Ma and 300 Ma (adapted from Stephan *et al.*, 2019). Red represents West African zircon provinces and yellow East-African ones.

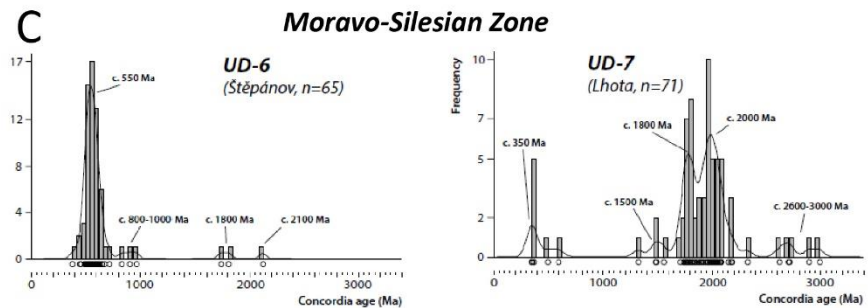
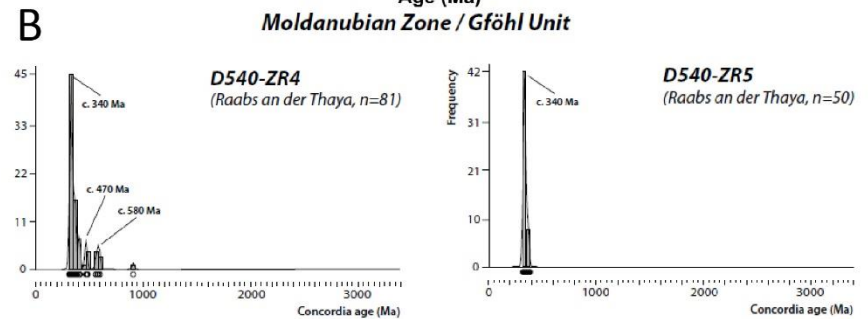
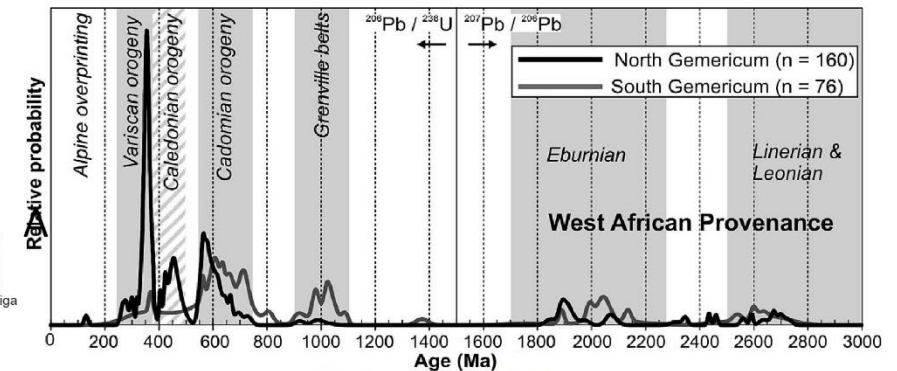


Figure 2.11 Distribution of the European Variscides (Linnemann *et al.*, 2014). Zircon U-Pb age distributions from A) Western Carpathians, Variscan peak at 355 Ma (Vozárová *et al.*, 2013); B) Moldanubian Zone, peaks at 340 Ma; and C) Moravo Silesian Zone, peaks 350 Ma, 550 Ma and 1500-2000 Ma (Košler *et al.*, 2014).

2.6.1.4. Closing of Tethys Ocean and Alpine Orogeny

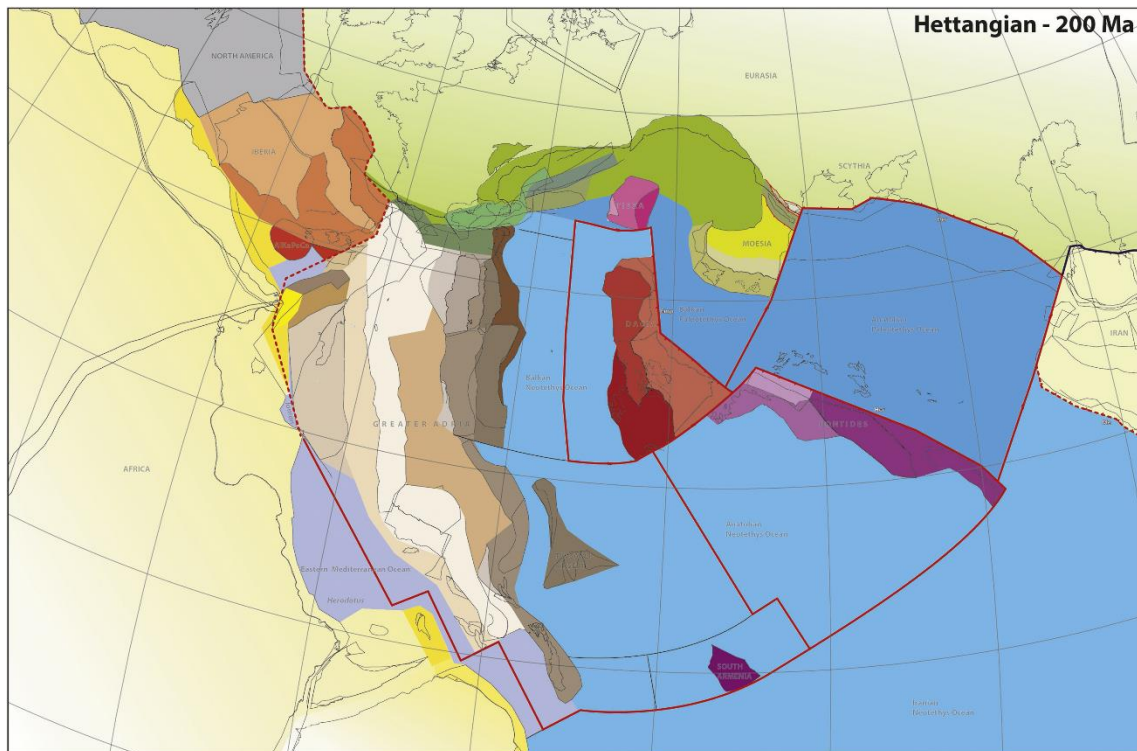


Figure 2.12 Modelled paleogeography of the Mediterranean region during the Bajocian (170 Ma), showing the opening of the Mediterranean Sea and the onset of the Tethys Ocean closure. Note source of terrains that make up the present day Carpathian Basin (after Hinsbergen *et al.*, 2019).

The modern Europe's tectonic structure represents the collision of Africa with Europe, and the closure of the Tethys Ocean (Figure 2.12). While the Alpine Orogeny is only associated with the final colliding stages (the Upper Cretaceous to the Palaeogene), the movement of the final peri-Gondwana terranes had already commenced during the Jurassic, as seen in Figure 2.12 (Chu *et al.*, 2016; Rosenbaum and Lister, 2005; Schmid *et al.*, 2008; van

Hinsbergen *et al.*, 2020). Hence, a sequence of collision signatures can be found across Central Europe, as some smaller terranes were progressively pushed into proto-Europe. Many of these blocks will have pre-existing Pan-African signatures, with the Cambrian-Ordovician rifting imprinted, onto which the final stages are also added, sometimes even within the same zircon grains. For example, parts of the Rhodope Complex in SW Bulgaria show large populations of grains with ~140 Ma cores but 56-30 Ma rims (Jahn-Awe *et al.*, 2010), and therefore periods of zircon re-growth during the Palaeogene. In the Apuseni-Banat-Timok-Srednogorie Mountain belt (South Carpathians and Balkan Mountains), an active continental margin was reconstructed, showing a progressively migrating magmatic arc from 100 Ma until its subduction at 67 Ma (Gallhofer *et al.*, 2015). The Dinaric Mountains in Southern Serbia show two groups of zircons ages, ~31 Ma and 18-21 Ma, with predominantly positive ϵ_{Hf} (0.5-3.5) signatures that link to the Oligocene and Miocene magmatism and closing of Tethys.

EUROPEAN GEOLOGY SUMMARY

Section 2.6.1 highlights the complexity of the Danubian region, tectonically and geologically. Understanding the geological evolution of the continent is essential for interpretation of zircon U-Pb signatures preserved in loess and source rocks. This is especially important as fragments of Europe are Archean in age and have been subject to multiple continental break-up and building processes since then. With each cycle new features and terranes have been developed via orogenies or sedimentary deposition, which resulted in the new set of zircon ages. Crucial for understanding the Central European structure are events resulting from the progressive break up of Gondwana and the development of peri-Gondwanian terranes (~600-450 Ma), the Variscan orogeny (~300 Ma), and the final collision of Africa with Europe since the Jurassic Period.

2.7. Modern climate in Central Europe

Climate does not directly impact loess deposition, per se, however it is thought to be linked to its deposition in several ways (An, 2000; Kukla and Cílek, 1996; Porter, 2001). In its simplest definition loess is a windblown mineral dust. Hence dust transport and loess deposition links with climatic circulation and therefore wind patterns (An, 2000). The windier, drier, and/or colder climates are where dust flux is the highest and when combined with limited vegetation cover and higher sediment production it results in the deposition of the thickest loess units (Frechen *et al.*, 2003; Kohfeld and Harrison, 2003; Porter, 2001; Pye, 1995). Consequently, loess units are associated with glacial and stadial periods when climate deteriorates and sediment is not effectively trapped in the landscape by vegetation (An *et al.*, 1991a; Bokhorst *et al.*, 2011; Kukla and An, 1989). Soil development is a function of a number of drivers, but critically climate (Jenny, 1994). The range of precipitation and temperature in a given area impacts (in combination with other abiotic and biotic factors) the type of soil and vegetation (Catt, 1991; Weil and Brady, 2017) as well as the intensity of the pedogenic processes (An, 2000; Kemp, 2001; Porter, 2001). Critically pedogenesis is an ongoing process and occurs at all times, but only when its rate exceeds the rate of sediment delivery do soil profiles develop. As a result, these features are associated with periods of milder climate (during which the pedogenesis rate and vegetation increases) and environmental stability (when vegetation traps and stabilises sediment) i.e. interglacial and interstadial periods (An *et al.*, 1991a; Catt, 1991; Kukla and An, 1989). Therefore, climatic influences on the wider Central and Eastern European regions should be explored which this section aims to address.

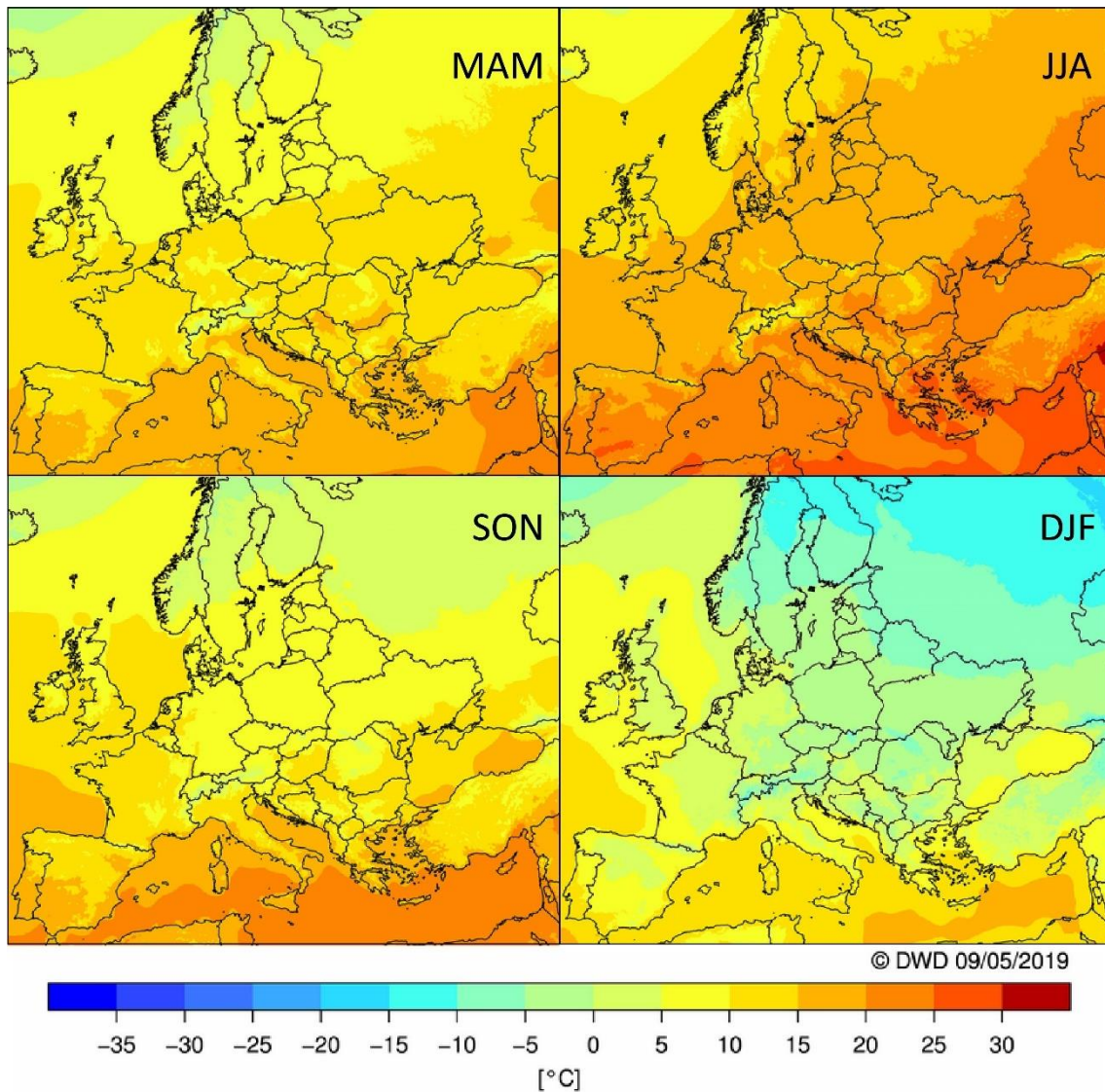


Figure 2.13 Seasonal mean temperatures over Europe averaged over the period 1961-1990 (adapted from DWD, 2018).

Loess deposits in Central Europe are mostly located in the mid-latitude westerlies zone and experience the three competing air masses of the North Atlantic, Mediterranean, and Siberian (Cheval *et al.*, 2017). These are driven by three large scale synoptic circulation centres; the Mediterranean cyclone, Siberian high, and Azores anticyclone (Tošić *et al.*, 2018). On top of these, orographic effects from the surrounding Carpathian, Balkan and Dinaric Mountains are superimposed. This results in a complex, seasonal climatology (Figures 2.13 and 2.14), which on the large continental scale remain fairly stable. However,

it has the potential to create a set of various local “microclimates” which can in turn impact local soil development or sediment deposition. Especially when considered over Quaternary timescales. Nonetheless, the climate is mostly classed as a warm temperate climate zone, fully humid with warm summers (Cfb) and fully humid with hot summers (Cfa), while some mountainous areas fall under snow climate fully humid with warm summer (Dfb) climates (Kottek *et al.*, 2006).

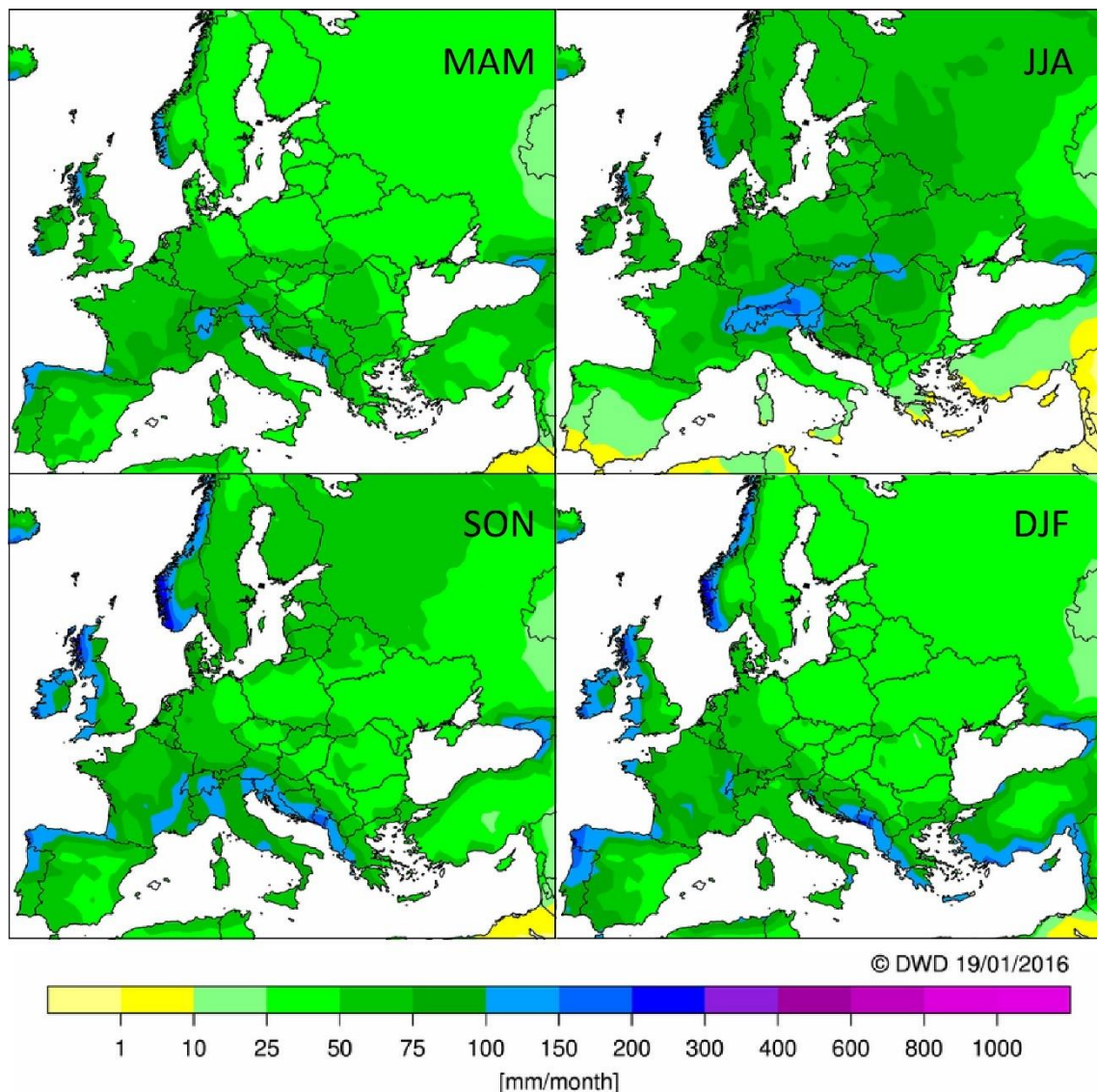


Figure 2.14 Seasonal mean precipitation over Europe averaged over period 1951-2000 (adapted from DWD, 2018).

In the winter the climate over Europe is dominated by the competing influences of the North Atlantic Oscillation (NAO)(Bojariu and Giorgi, 2005; Ionita, 2014) and the East Atlantic Western Russia (EAWR) (Krichak and Alpert, 2005). These two teleconnections drive and modify winter temperatures and precipitation regimes in the region. This is predominantly seen as increased rainfall and/or snowfall over winter months.

In the summer the climate in Central Europe, is lightly influenced by the eastern Mediterranean and Continental climatic patterns. The eastern Mediterranean is determined by interactions between the Asian Monsoon and African branch of the Hadley Cell (Ziv *et al.*, 2004), which drives the subsidence over the region (Staubwasser and Weiss, 2006). While over the eastern Black Sea and southern Caspian an uplift is seen.

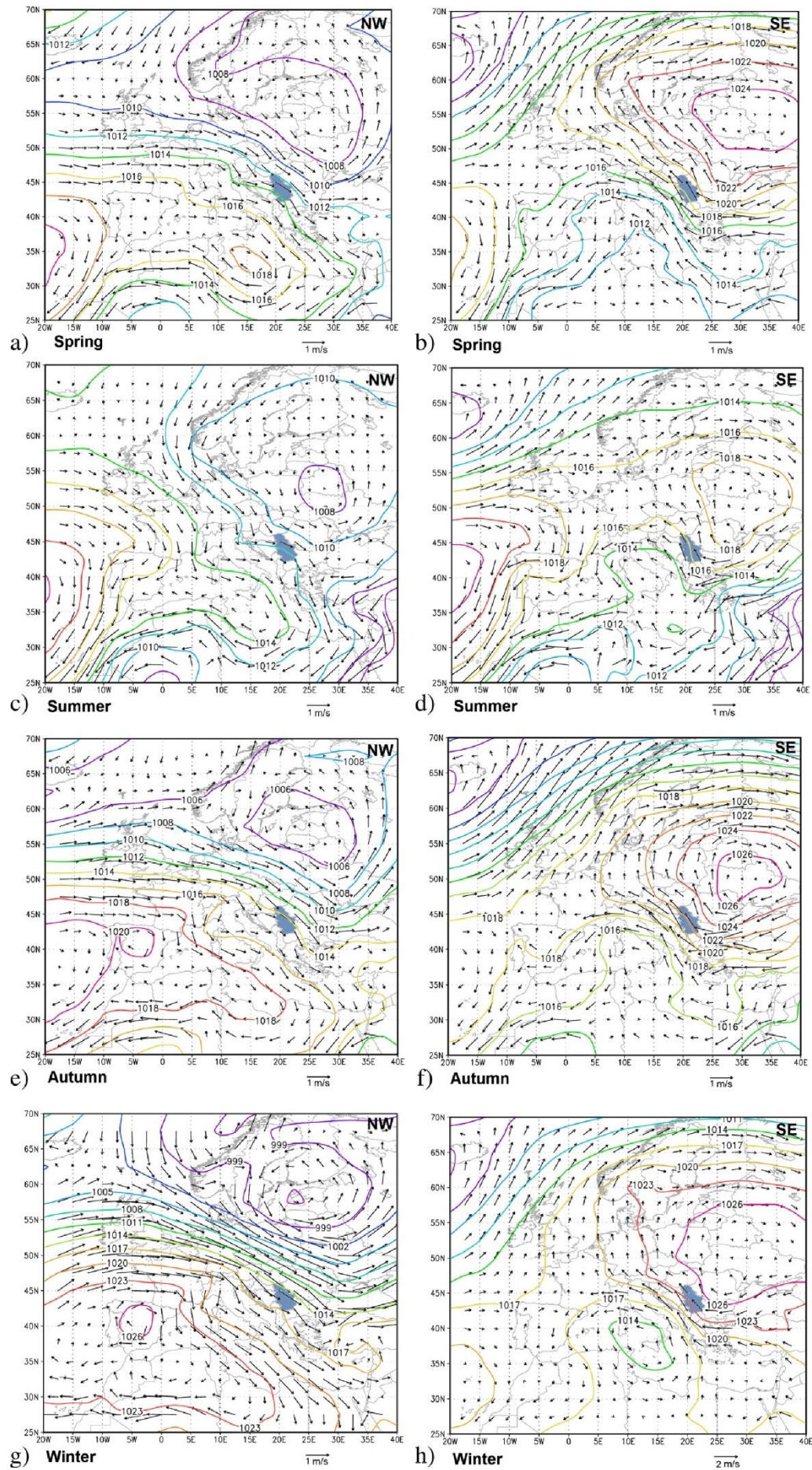
The climate is quite seasonally varied, with relatively hot summers and cold winters (Figure 2.13). Winter temperatures are on average found below 0°C throughout the region, though usually above -10°C, whilst during the summer the average temperature maximums can reach 30°C.

Mean annual precipitation varies mostly between 500-800 mm a⁻¹, with small areas of Serbia and Croatia receiving up to 1000 mm a⁻¹ (Nixon *et al.*, 2003). Additionally potential annual evapotranspiration varies between 400-500 mm with lower values over parts of the Carpathians and Alps (<400 mm) (Cheval *et al.*, 2017). The differences drive soil and vegetation types, and the feed into the aridity indices. Crucially the region experiences large seasonal variations, with the majority of rainfall attributed to the summer months (Figure 2.14), and many areas becoming moderately to even severely wet on the drought index (Cheval *et al.*, 2017; DWD, 2018). This is supported by drought analysis of Serbia which shows that the climate is on average semi-humid to humid, though it can drop down to Mediterranean on the De Martonne aridity scale over the summer months (Hrnjak *et al.*, 2014). During autumn and winter months the inside of the Carpathian Basin

experiences mild drought, driven in part by the orographic effect of the surrounding mountain belts. For example, the Dinaric Alps create a strong precipitation gradient, as the western Adriatic coast receives over 100 mm month⁻¹, whilst the interior of Croatia, Bosnia and Serbia drop to as little as 25 mm month⁻¹ (Figure 2.8). Finally, in the winter most of Central Europe's precipitation comes in the form of snow. Many areas sustain snow for at least 2 months a year, with many supporting snow cover for 3-4 months annually (DWD, 2018).

The synoptic conditions that develop over central Europe drive the wind direction and are predominantly linked to the position of the polar front (Figure 2.15). When the polar front moves over the North Atlantic and penetrates past the Alps and into Central Europe, strong north-westerly winds develop in the Carpathian Basin (Putniković *et al.*, 2016; Radinović, 1965; Tošić *et al.*, 2013). However, when the Alps prevent the polar front from advancing, low pressure centres develop around the Gulf of Genoa (Gavrilov *et al.*, 2018). Other synoptic systems usually drive stable weather conditions over the regions and are driven by either the Siberian or Azores high pressure systems (Putniković *et al.*, 2016). In the case of the Azores anticyclone, a stationary cyclone develops over Northeastern Europe (Figure 2.15 a, c, e, g) while the high pressure system shifts towards Spain in winter and autumn. The interaction of those two systems is primarily responsible for the northern winds. While during the strong Siberian cyclone (spring, autumn and winter) a depression forms over the Western Mediterranean Sea and influences the development of the eastern and southern winds over central Europe (Tošić *et al.*, 2018).

Figure 2.15. Long-term geostrophic winds and surface pressure based on the 1961-2010 period. Differences for each season are presented based on the NW (a, c, e, g) and SE (b, d, f, h) circulation weather types (Tošić *et al.*, 2018).



The geostrophic and pressure centre patterns outlined in Figure 2.15 in combination with the mountainous areas that surround the Carpathian Basin result in the surface wind patterns observed (Figure 2.16). The annual mean surface wind patterns are highly variable across the region. In Austria, Serbia, and Bulgaria the dominant winds come from a NW direction which results from the interplay between the three pressure centres shown in Figure 2.15. While in Hungary this shifts to the N direction and clearer N-S winds can be observed; this is likely a result of the Western Carpathians to the North of the country. In Romania annual average surface winds blow from all directions (with a slight dominance of W and N winds), which is likely due to the averaging effect of a very topographically varied country. While for each location more site specific wind directions need to be explored, this shows the general wind patterns observed.

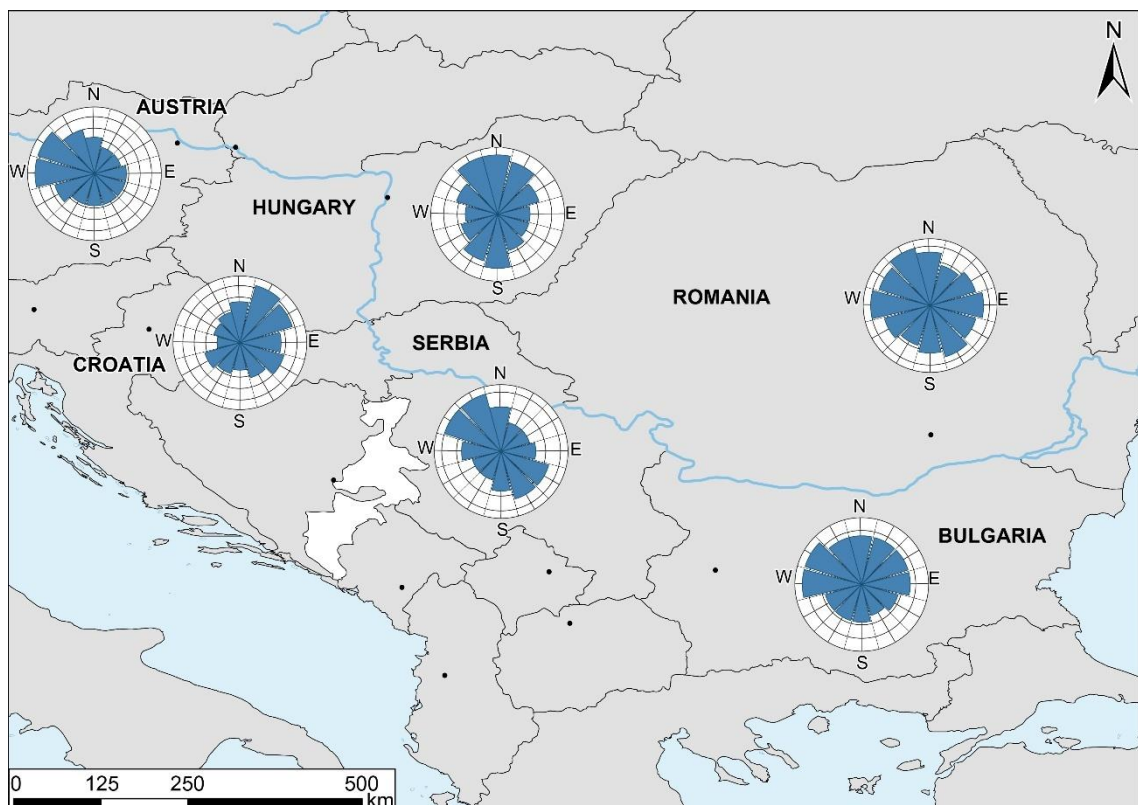


Figure 2.16 Mean annual wind direction at 100 m height in the key countries along the Danube River (data from Global Wind Atlas 3.0).

Chapter 3: Methods

3.1. Introduction

This chapter details the techniques utilised to address the aims and objectives of this research project, including both fieldwork design and laboratory approaches. The former details site selection and sampling. The latter covers chronological approaches, in particular the principles, details of laboratory preparation, and age measurements for luminescence dating; and an overview of the isotope geochemistry methodology, used to determine sediment provenance. The protocols presented here provide a more in-depth account of the methodologies that lie behind the research presented in the three papers (Chapters 4-6).

3.2. Site selection

One of the crucial factors considered in the design of this study was spatial coverage of loess deposits in the Danube catchment. The Danube River extends for 2,850 km and has a drainage network that covers over 817,000 km². While estimates for the whole Danube drainage basin are not available, it is estimated that loess and loess derivatives in the Carpathian Basin cover approximately 101,500 km² (Lehmkuhl *et al.*, 2018). Intensive sampling was accordingly not achievable under the time constraints of this project. Based on the background material provided in Chapter 2 three specific areas of the Danube Basin were targeted, using large tributaries and their drainage areas as a proxy for source areas. Additionally, these tributaries were used as a point of potential change of source influence. To identify Alpine signals, sites downstream of the Drava and Sava Rivers were considered. For Carpathian inputs, sites downstream of the Tisza River confluence were investigated. Lastly, to test for changes between sites within and outside the Carpathian Basin, Middle Danube and Lower Danube respectively, a site beyond the Iron Gates was selected. These three broad regions provide appropriate spatial coverage to test for the potential

provenance shifts in the loess deposits preserved within the Danube River basin, and therefore satisfy Objective 5.

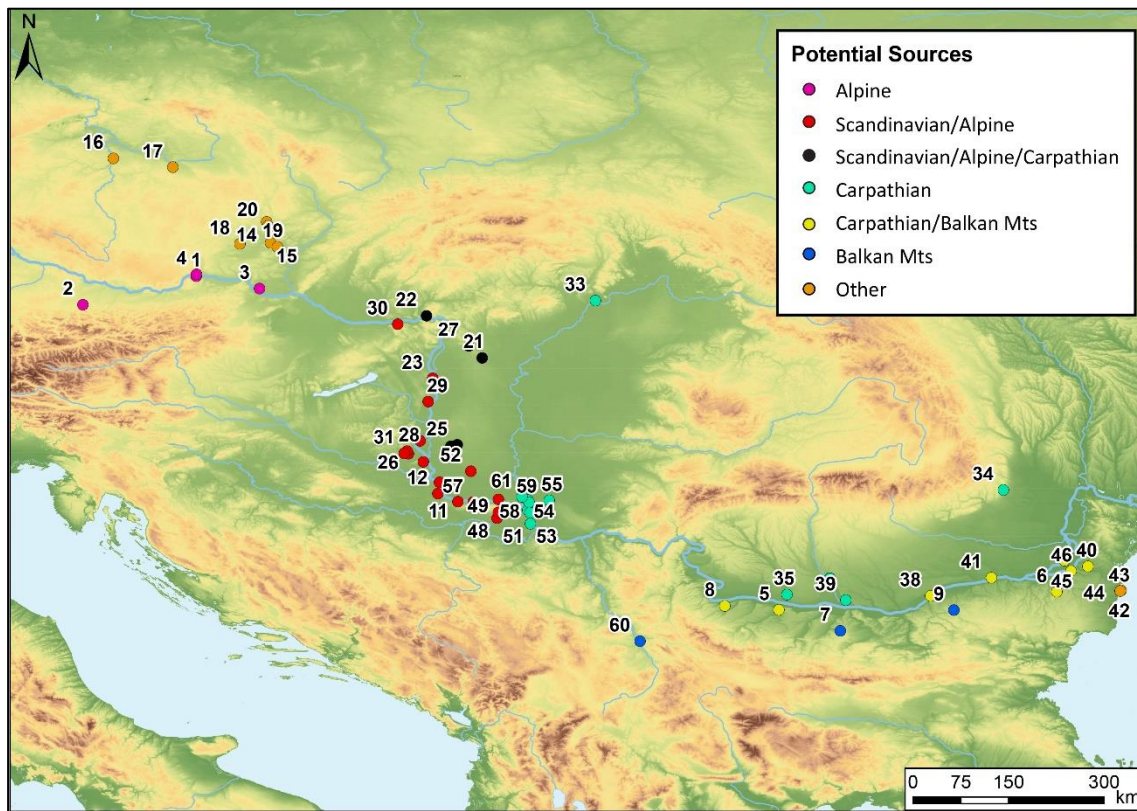


Figure 3.1 Location of sites investigated as potential study sites for this research project. Sites are colour coded to reflect the potential dominant source(s) for the sediment. See Appendix B for the details of site name and screening factors. (DEM Source: ©JAXA).

A number of factors were taken into consideration to select the most appropriate loess sections (Table A.1 and Figure 3.1):

1. *Proximity to the Danube* – to ensure selected sites in the different source regions have sediment delivered predominantly by the Danube, sites in proximity to the Danube’s main channel were preferentially selected.

2. *Preservation of the last glacial-interglacial cycle* – the key focus of this research is the last glacial-interglacial period and therefore sites with a published absolute chronology, for that period were considered.
3. Building on the previous point, *the thickness of a section* is an additional consideration. Thinner deposits inhibit chronometric differentiation especially in OSL where errors are large, while thick deposits may be difficult to sample at high resolution.
4. *Previous palaeoenvironmental studies*, which would help to understand climatic and environmental records observed at the site and provide a background to the provenance work.
5. *Previous provenance work* – sites where single grain work was carried out were avoided in favour of those where bulk sample geochemistry was researched, to provide an updated provenance view.
6. *Access* – although this is not a purely scientific factor it is an important one. This includes, for example, land ownership, car access to pick up samples, access from the top or bottom of the section, vegetation coverage, and land surface stability.

Further, as little was known about sites in the upper parts of the Lower Danube, a reconnaissance trip to Romania and Bulgaria was carried out to help identify the most appropriate site in that region.

The above process, combining scientific and practical considerations, led to the selection of three loess sites in Croatia (Erdut), Serbia (Surduk) and Bulgaria (Slivata) (Table A.1; Figure 3.2). Erdut was selected due to its proximity to the Drava-Danube confluence (15 km downstream) and existing sedimentological and luminescence research (Galović *et al.*, 2009). The high resolution particle size and magnetic susceptibility analysis, IRSL chronology (Antoine *et al.*, 2009a; Fuchs *et al.*, 2008), and proximity to the Tisza-Danube

confluence led to the selection of Surduk. Slivata (Bulgaria) was chosen to examine changes between loess within and outside the Carpathian Basin. Not much is known about loess deposits in the upper reaches in the Lower Danube, therefore the final site was selected during a reconnaissance trip. The selection focused on the area above two large tributaries, the Jiu and Olt rivers, to avoid a strong Carpathian influence on deposits.

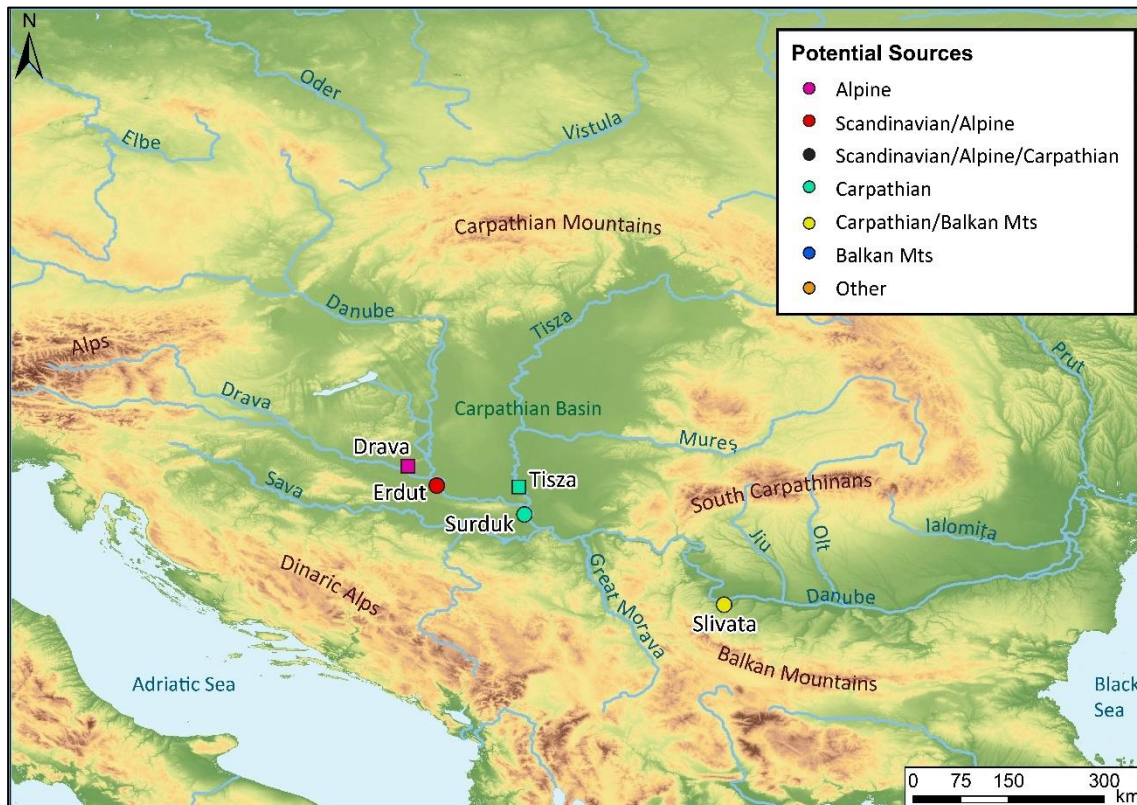


Figure 3.2 Location of sites selected for this research project (see Table 3.1 for more detail). Loess sequences are marked by circle, whereas modern river sample locations are marked by square (DEM Source: ©JAXA).

Additionally, for loess sites located downstream from the Danube's tributaries, modern river sediment from the exposed sandy-silty alluvium, was sampled as a proxy for source areas. For the Drava, samples were collected a few kilometres upstream from the confluence with the Danube, near the city of Osijek. In the case of Tisza, to avoid strong signatures in the fluvial sediment coming from the nearby Titel Loess Plateau, a site 40 km upstream of the confluence was selected.

Table 3.1 Site location and the nature of the sediments sampled for this study.

Location	Country	Sediment Type	Latitude	Longitude	Elevation
Erdut	Croatia	Quaternary loess	45°30'49.78"N	19°4'39.07"E	97 m
Surduk	Serbia	Quaternary loess	45°4'50.24"N	20°18'50.12"E	107 m
Slivata 1	Bulgaria	Quaternary loess	43°46'0.91"N	23°04'48.49"E	154 m
Slivata 2	Bulgaria	Quaternary loess	43°45'45.44"N	23°03'29.55"E	154 m
Drava	Croatia	Modern fluvial sediment	45°33'43.27"N	18°42'51.98"E	92 m
Tisza	Serbia	Modern fluvial sediment	45°23'31.74"N	20°12'24.95"E	53 m

3.3. Sampling strategy

To address Research Question 1, sediments at each site were sampled at a high resolution, appropriate to the characteristics of each vertical section and a method selected (details outlined below). In all cases profiles were cleaned and logged in detail prior to sampling. Samples were collected vertically for age determination and provenance (Figure 3.3). Additionally in Bulgaria, a sample was taken from a tephra horizon for geochemical analysis and 527 samples were taken at a 2 cm resolution throughout both profiles for sedimentological analysis.

All luminescence samples were collected by hammering opaque, light-tight plastic (20-30 cm long and ~7 cm ø) tubes into the profiles. At each luminescence sample depth, a corresponding bulk sediment sample (1-2 kg) was taken for provenance. In Croatia 27 samples for luminescence and provenance were collected, at 50 cm intervals. In Serbia, 25 samples for provenance and 23 for luminescence were collected, at 30-40 cm intervals.

Higher sampling resolution at Surduk was chosen to avoid missing sedimentary features (e.g. Surduk soil) which were previously reported at this site, but could not be seen as a result of conditions in the field. Due to the sediment compaction and cementation only provenance samples were collected from the palaeosol unit at the bottom of the profile in Surduk, as the luminescence tubes were unable to penetrate it. In Bulgaria, 24 samples were collected for both analyses at a 50 cm resolution.

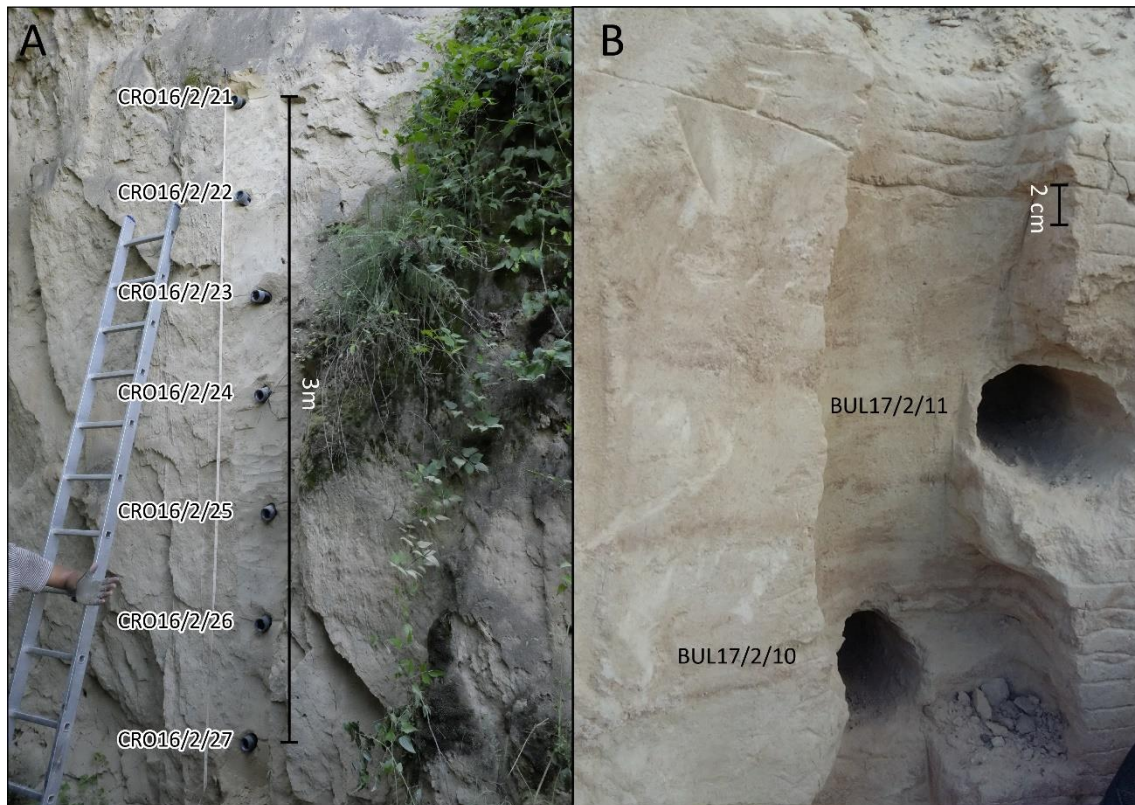


Figure 3.3 A) One of the loess profiles sampled at Erdut, Croatia, sampled at a 50 cm resolution. B) Slivata 2 profile showing the sedimentological sample resolution as well as gaps remaining after provenance sample collection.

3.4. Sedimentology

Samples were analysed in the laboratory for sedimentological properties, to provide a better understanding of the environmental and climatic context of their deposition, and to guide sample preparation for other techniques, such as OSL and provenance analysis.

The number of samples analysed was dependent on the extent of previous research at the site.

3.4.1. Particle size analysis

Particle size measurements are one of the most basic, yet crucial, techniques used in loess-palaeosol research. Grain size distributions and various particle size indices are commonly used to investigate and reconstruct palaeoclimate characteristics, such as wind strength and direction, or pedogenesis intensity, though more broadly they are used to indicate glacial and interglacial periods (Obreht *et al.*, 2019). The typical loess has a mean grain size of ~30 μm (medium silt) though inclusions of coarse silt and very fine sand are not uncommon (Pye, 1995). Palaeosols have a much larger fine grain component due the post depositional mineral breakdown during pedogenesis (Schulte and Lehmkuhl, 2018; Vandenberghe *et al.*, 2018). The broad basis for wind reconstructions is the physics behind aeolian transport mechanisms, such as suspension, saltation and rolling (Vandenberghe, 2013). The samples with larger proportions of coarser grain sizes are interpreted as having been subjected to stronger winds and often colder climatic conditions (Antoine *et al.*, 2001, 2009b; Bokhorst *et al.*, 2011). These shifts are often used to correlate with marine oxygen isotope curves or ice-core data (An, 2000; Antoine *et al.*, 2001; Porter, 2001; Rousseau *et al.*, 2017b). This however can be an oversimplification of the problem as this could also relate to changes in sediment source or proximity to the immediate, geomorphological source (e.g. sand dunes or alluvial planes). The progressive fining or coarsening across sites is also used to identify wind directions and distance from the source (Bokhorst *et al.*, 2011; Porter, 2001). Apart from plotting mean, modal grain size, or a specific category of interest (e.g. >63 μm , <4 μm , >6 μm , <2 μm , >44 μm), several methods for quantifying particle size variability have been utilised including U-ratio (Obreht *et al.*, 2016; Sümegi *et al.*, 2019; Sun *et al.*, 2006; Vandenberghe *et al.*, 1985, 2014;

Zech *et al.*, 2013), grain size index (Antoine *et al.*, 2009a, 2013; Prud'Homme *et al.*, 2015; Rousseau *et al.*, 2011; Varga *et al.*, 2019), and end member analysis (Bokhorst *et al.*, 2011; Vandenberghe, 2013; Varga *et al.*, 2019; Weltje and Prins, 2003, 2007). While various indices are used across the field, not many studies have looked into how comparable these are (Újvári *et al.*, 2016; Varga *et al.*, 2019). As they often represent different elements of the grain size distribution, they may relate to different modes and direction of aeolian transport.

For Croatia and Serbia, analysis was carried on the OSL samples as previous high resolution sedimentary research has been carried out in the past (Antoine *et al.*, 2009a; Galović *et al.*, 2009). In the case of Bulgaria, a detailed analysis was required, as this site has not been investigated in the past.

Prior to analysis, samples were dried overnight and homogenised. To determine the impact of organic material and carbonates on the particle size distributions, a comparison test was carried out. Seven samples from Bulgaria and five from Croatia were selected for the analysis. All samples were first measured untreated and then with carbonates and organic material removed (Post-treatment). The results presented in Figure 3.4 A, B, and C show three examples of measured grain size distributions, which shows minor variability between samples pre- and post- treatment. To investigate the effect of sample homogeneity on the analysis, five subsamples of sample BUL17/1/2 were also analysed (Figure 3.4 D). This suggests that when compared with variability recorded within the same sample treatment has a negligible effect on the results. Similar conclusions were presented by Schulte *et al.* (2016), however they found that the H₂O₂ treatment was still necessary, therefore suggesting that the need for pre-treatment may be sediment and site specific. As the effect of treatment was found to be minor, the removal of carbonates and organic matter prior to measurement was concluded to be unnecessary. Grain size

distributions were measured using a Malvern Mastersizer Hydro 2000MU laser diffraction particle size analyser, and data analysed and plotted in R.

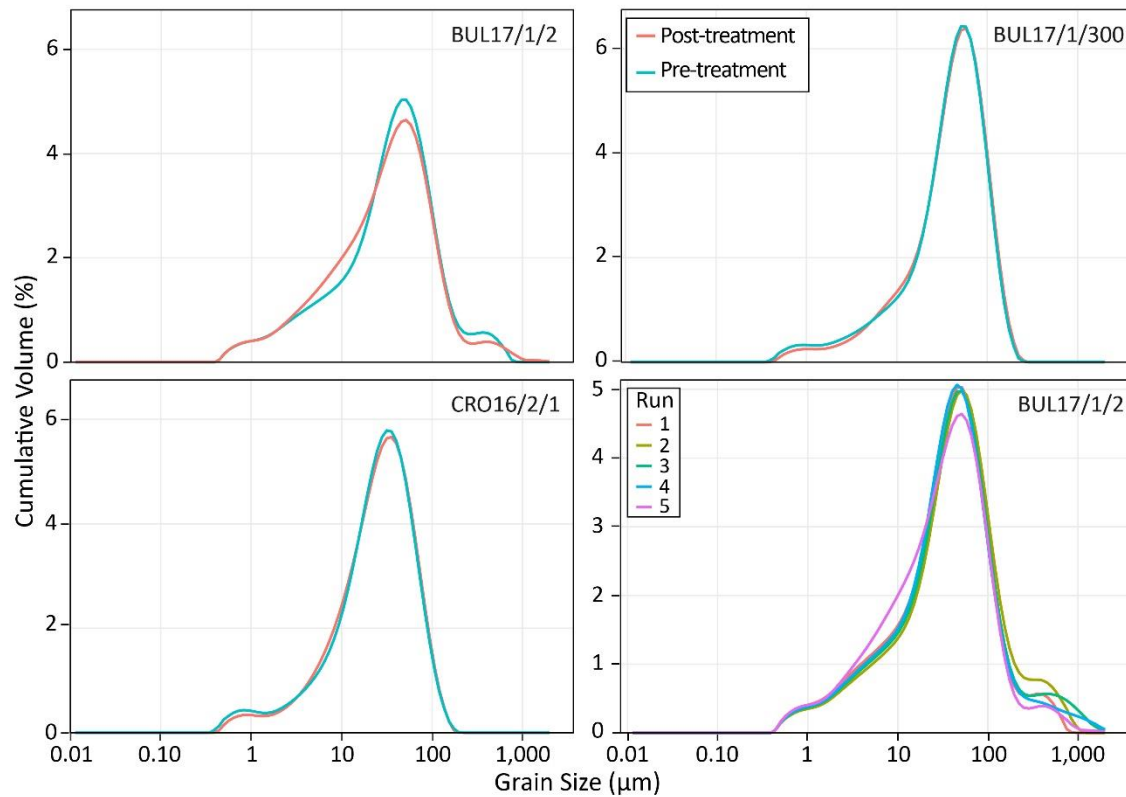


Figure 3.4 Comparison of the grain size distribution post and prior to removal of carbonates and organic matter. A) BUL17/1/2 B) BUL17/1/300 C) CRO16/2/1 D) Comparison of grain distribution in the untreated sample BUL17/1/2.

3.4.2. Magnetic susceptibility (MS)

Magnetic properties of rock are, alongside of particle size analysis, one of the fundamental techniques in loess research (Kukla and An, 1989; Obreht *et al.*, 2019). The method relies on measuring the magnetic signal (the occurrence, abundance and properties) of a sediment bulk sample. This signal is driven by the concentration, type, and grain size of iron-bearing minerals (hematite, magnetite, goethite, maghemite, ferrihydrite, lepidocrocite) (Buggle *et al.*, 2009), which are found in all sediments in relatively minor (<1%) concentrations (Evans and Heller, 2001). The magnetic susceptibility strength is

driven by the presence of fine grained particles at the boundary between single-domain and superparamagnetic grains (Kukla *et al.*, 1988; Maher and Thompson, 1991). The chemical alteration of silicates during the post-depositional diagenesis, dissolution, and pedogenesis, transforms and enhances the proportion of superparamagnetic grains (Maher, 1986; Schaetzl *et al.*, 2018; Zeeden *et al.*, 2018c). As a result, soils typically have enhanced magnetic properties in comparison to loess, which is deposited during arid cold climates (Heller *et al.*, 1991). As the intensity of pedogenesis is predominantly driven by wet and warm conditions, magnetic susceptibility can be used as climate proxy (Evans and Heller, 2001). However, other processes may have an influence on the magnetic susceptibility values, such as parent material, pH, strength and type of pedogenic process, or detrital contributions. For example, the production of large quantities of organic matter which is non-ferrimagnetic may dilute and reduce the magnetic signal (Maher, 1986). Conversely, the signal in non-pedogenic material may be enhanced by addition of detrital magnetic material (An *et al.*, 1991b; Heller *et al.*, 1991; Kukla and An, 1989). In the past magnetic susceptibility has been used as an indicator of monsoon strength (An *et al.*, 1991b; Heller and Liu, 1982; Kukla *et al.*, 1988), a proxy for vegetation cover density (Kukla and An, 1989), and palaeorainfall (Buggle *et al.*, 2009).

Typically, low (X_{lf}) and high (X_{hf}) frequency magnetic susceptibility values are obtained. These measurements demonstrate a temporary sediment magnetisation by the application of a magnetic field in the laboratory (Evans and Heller, 2001). Low frequency data is used to investigate weathering and pedogenesis as well as sediment moisture content (Buggle *et al.*, 2009, 2014). However, the values obtained can be biased by grain size distribution and changes in the detrital inputs as outlined above, therefore frequency dependant (X_{FD}) susceptibility is an attempt to overcome these issues. This determines the contributions to the signal from superparamagnetic grains by calculating and normalising the difference between the low and high frequency measurements. This in turn can aid separation of the

weathering from the detrital inputs and therefore interpretation of the strength of the pedogenesis (Heller *et al.*, 1991).

Laboratory analysis of magnetic susceptibility (MS; χ) was conducted to investigate the strength of pedogenesis in the profiles. Sediment was oven dried (max. 40°C), gently disaggregated by hand, and packed into 10 cm³ plastic cylindrical containers. Magnetic susceptibility was measured using a Bartington MS2 Magnetic Susceptibility System with a MS2B dual frequency sensor. Data were collected at low and high frequencies, 0.465 kHz and 4.65 kHz, respectively. The measurements were corrected for sample mass and presented as mass-specific magnetic susceptibility (χ in m³kg⁻¹). The results are presented as low-frequency values (X_{lf}) and frequency dependent magnetic susceptibility (X_{FD}).

Equation 3.1 The frequency dependent magnetic susceptibility calculation

$$\chi_{FD}(\%) = \frac{\chi_{lf} - \chi_{hf}}{\chi_{lf}}$$

The X_{FD} provides an indication of the changes in concentration of ultra-fine superparamagnetic material, that is pedogenic in origin (Buggle *et al.*, 2014).

3.5. Tephrochronology

Tephrochronology (or volcanic ash isochrons) is a technique that can provide accurate synchronisation of archives across large areas (e.g. Lane *et al.*, 2011; Blockley *et al.*, 2012). It facilitates comparison of palaeoclimatic and palaeoenvironmental proxies over 10²-10⁴ km distances and between terrestrial, marine and ice core sites.

Tephra, or volcanic ash, comprises volcanic glass, lithic and crystals, smaller than 2 mm (Lowe and Alloway, 2015). It is ejected into the atmosphere during a volcanic eruption and can be transported over large distances. The almost instantaneous nature of deposition of primary tephra provides a marker for the timing of an eruption. Ash horizons preserve the

chemical signature of each eruption, which varies between e.g. a volcano's location, magma chamber, time of eruption, etc (Alloway *et al.*, 2007). Comparisons of geochemical signatures between tephra layers and known eruptions can therefore provide a reliable stratigraphic marker across sites. Tephra age is determined by independent radiometric dating, i.e. K/Ar or Ar/Ar on sanidines, of proximal volcanic material (De Vivo *et al.*, 2001), the counting of annual laminated layers such as in Greenland ice cores or varved lakes (Brauer *et al.*, 1999), or radiocarbon dating and modelling of surrounding material (Lee *et al.*, 2013).

3.5.1. Tephra sample preparation

Sample preparation followed a standard non-destructive tephra extraction method (Blockley *et al.*, 2005). To isolate tephra shards, samples were treated with 7% HCl to remove carbonates, wet sieved ($>25\ \mu\text{m}$), and density separated ($1.95\text{--}2.55\ \text{gcm}^{-3}$). Separated shards were mounted on epoxy resin stubs, and polished to expose their surfaces ready for shard-specific compositional analysis electron microprobe analysis.

3.5.2. Geochemical Analysis

The concentrations of the major and minor elements within single glass shards were analysed using a Cameca SX100 wavelength dispersive electron microprobe analyser (WDS-EPMA) in the Department of Earth Sciences, University of Cambridge. A $10\ \mu\text{m}$ diameter defocused beam spot operating at 15 kV and 6 nA was used. Counts were for sodium were collected over 10 second acquisitions, chlorine and phosphorus for 60 seconds, and all other elements for 30 seconds. Secondary standards, including a range of MPI-DING (Jochum *et al.*, 2006) fused volcanic glasses, were periodically measured to monitor analytical precision and accuracy. All raw compositional data (Appendix C Table A.2) used has been normalised to anhydrous basis.

3.6. Luminescence dating

3.6.1. Principles of OSL

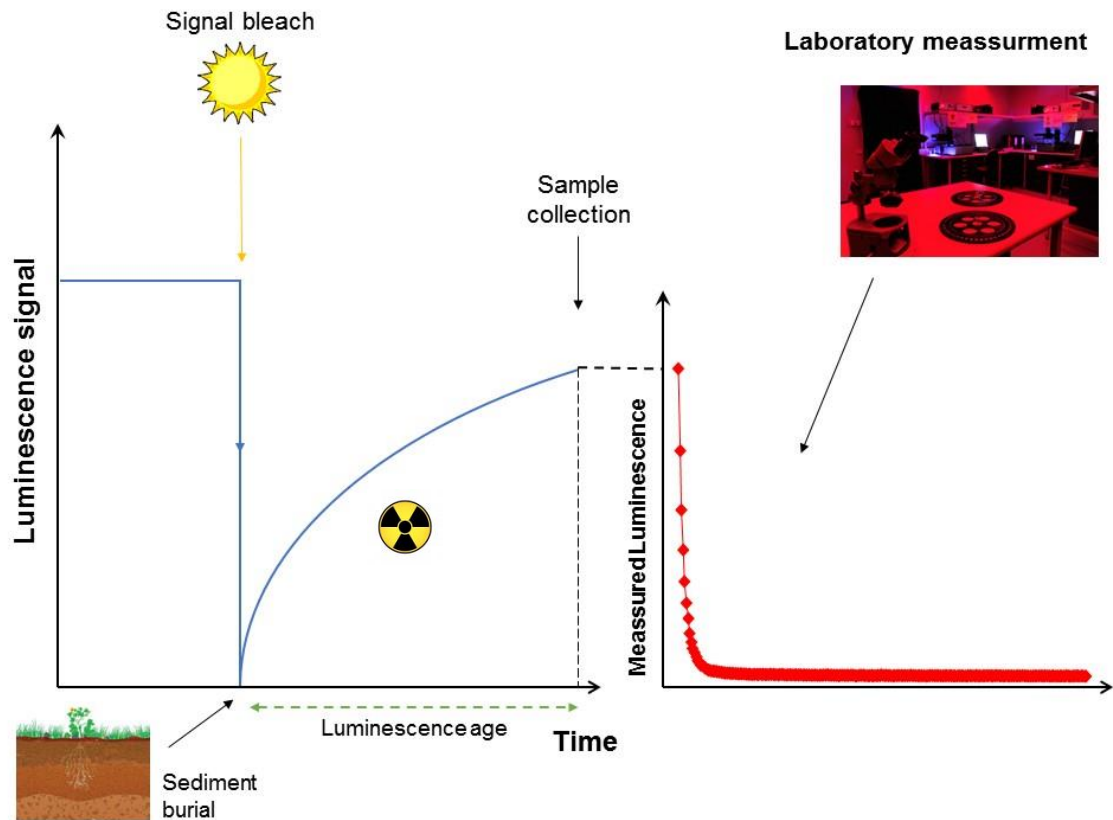


Figure 3.5 Schematic diagram of the OSL signal build-up, reset and laboratory measurement.

Optically Stimulated Luminescence is an absolute dating technique, that has its roots in thermoluminescence dating (Aitken, 1985, 1998; Huntley *et al.*, 1985; Wintle, 1988). It approximates the last time a mineral grain was exposed to sunlight or heat. Post burial grains receive natural ionising radiation from the surrounding sediment (Aitken, 1998) and cosmic rays (Prescott and Hutton, 1994). The imperfections in a mineral's crystal lattice cause the electrons to become trapped, and stored, but exposure to sunlight or heating (Roberts, 2008) causes the “trapped signal” to be removed, or “bleached” (Figure 3.5). The signal accumulated over time can be measured under controlled laboratory

conditions to determine the radiation dose (the equivalent dose). Once the rate of radiation ionisation at the sampling location (the environmental dose rate) has been measured, the luminescence age can be determined based on Equation 3.2 (Duller, 2004; Preusser *et al.*, 2008).

Equation 3.2 The age equation for calculating a luminescence age.

$$\text{Estimated Age (ka)} = \frac{\text{Equivalent dose (Gy)}}{\text{Estimated dose rate (Gy ka}^{-1}\text{)}}$$

Both quartz and feldspar, two of the most commonly occurring minerals in sediments, have been widely analysed in previous studies. Quartz is usually the mineral of choice as its dosimetric properties are better understood (Aitken, 1998; Bailey, 2001; Preusser *et al.*, 2009), however its saturation limits are much lower (~100 Gy; Wintle and Murray, 2006) than those of feldspar (>1000 Gy in some contexts; Buylaert *et al.*, (2012); Thiel *et al.*, (2011a)). This means that in the European loess context chronologies based on quartz are often limited to 30-50 ka, which approximates radiocarbon chronologies. However, some experiments on the Lower Danube quartz show that its behaviour and saturation limits are substantially different and therefore its dating range could be potentially expanded (Timar-Gabor *et al.*, 2015). While feldspar has the potential to date much older sediment, extending chronologies beyond last glacial-interglacial cycle, it is thermally unstable (Wintle, 1973). This inherent behaviour may cause age underestimation if the correct measurement protocol is not selected or the signal is uncorrected (Huntley and Lamothe, 2001; Lamothe and Auclair, 1999). Both minerals have advantages and disadvantages, therefore the selection of the appropriate mineral to use in OSL dating requires consideration (Table 3.2).

Table 3.2. Overview of the advantages and disadvantages of quartz and feldspar in the loess context.

	Quartz	Feldspar and polymineral
Signal typical used for dating	Blue stimulated UV OSL (fast component)	IR stimulated blue from K-feldspar and polymineral
Saturation	~100 Gy (Wintle and Murray, 2006) Though potential for ranges up to 500 Gy (Timar-Gabor <i>et al.</i> , 2011, 2012, 2015)	Typically 500-700 Gy (Buylaert <i>et al.</i> , 2012; Thomsen <i>et al.</i> , 2011) In some cases >1000 Gy (Thiel <i>et al.</i> , 2011a)
Average European loess dose rate	2-3 Gy ka ⁻¹	3-4 Gy ka ⁻¹
Upper dating limit in European loess	~30-50 ka	125-230 ka
Bleaching (depleting signal to ~1%)	~10 seconds (Godfrey-Smith <i>et al.</i> , 1988)	~1 hour (Godfrey-Smith <i>et al.</i> , 1988)
Residual	Negligible	As high as 40 Gy in some European loess contexts (Stevens <i>et al.</i> , 2011)
Fading	Fast component is thought not to fade	IRSL - average 2-4%/decade (Balescu <i>et al.</i> , 2003; Schmidt <i>et al.</i> , 2010; Thiel <i>et al.</i> , 2014; Wacha and Frechen, 2011) As high as 29 %/decade (Murray <i>et al.</i> , 2014) pIRIR – average 0-2%/decade

3.6.2. Sample preparation

All samples were prepared and handled under subdued orange-light conditions at the Oxford Luminescence Dating Laboratory, University of Oxford.

The light-exposed sediment from both ends of the opaque cylinder was removed and saved for dose rate and particle size analysis. In the first step carbonates and organic matter were removed from the unexposed sediment by treatment with 32% hydrochloric acid and 30% hydrogen peroxide. As different fractions were used for the equivalent dose (D_e) determination, a number of steps were used to separate required fractions.

First, through a combination of sieving and settling (calculated using Stoke's Law), a 4-11 μm fraction, typically utilised in loess research, of both quartz and polymineral was obtained. To isolate the quartz-enriched fine grained fractions a sub-sample of the polymineral separate was treated by immersion in 35 % fluorosilicic acid for up to 3 weeks, and subsequent washing with 32% hydrochloric acid to remove fluoride precipitates. Fine grained aliquots were prepared by dispensing 0.5 mg of fine grained material onto 9.8 mm diameter aluminium discs and drying.

Secondly, when a fine grained (4-11 μm) polymineral fraction proved to be too dim for feldspar analysis, a coarser fraction was prepared. This required sieving to retain fine sand (63-90 μm), and density separation using sodium polytungstate to obtain potassium feldspar (K feldspar; $\rho < 2.58 \text{ gcm}^{-3}$). For all K feldspar analyses, small aliquots (2 mm) were prepared by mounting a monolayer of sediment on the disc using silicone oil (Wintle, 1997).

3.6.3. Environmental dose rate

The denominator of the luminescence age equation (Equation 3.2), the environmental dose rate, refers to the total amount of internal and external radiation absorbed by minerals from their surroundings since burial (Duller, 2008; Guérin, 2014). The total amount of energy delivered to individual grains is the sum of cosmic radiation and alpha (α), beta (β) and gamma (γ) radiation (Equation 3.3) emitted from the radioactive decay of radionuclides.

Equation 3.3 Dose rate ($\dot{D}$) calculation. $\dot{D}_\alpha$ = alpha radiation contributions to dose rate, $\dot{D}_\beta$ = beta radiation contributions to dose rate, $\dot{D}_\gamma$ = gamma radiation contributions to dose rate, and $\dot{D}_{\text{cosmic}}$ = cosmic radiation contributions to dose rate.

$$\text{Dose rate } (\dot{D}) = D_\alpha + D_\beta + D_\gamma + D_{\text{cosmic}}$$

All dose rate calculations were carried out using the Dose Rate and Age Calculator (DRAC; v1.2) software (Durcan *et al.*, 2015) with the details of measurements and selected parameters described in detail below.

3.6.3.1. *Radionuclide concentrations*

To account for the alpha, beta and gamma radiation received by the grains, the chemical concentrations of Thorium (^{232}Th), Uranium (^{238}U), Potassium (^{40}K) and Rubidium (^{87}Rb) in all samples were measured. The decay of ^{232}Th , ^{235}U , and ^{238}U contributes alpha, beta and gamma radiation. Whereas the decays of ^{40}K contributes to beta and gamma radiation, and ^{87}Rb to beta radiation. The radionuclide concentrations were measured from the bulk sediment using quadrupole inductively coupled plasma mass spectrometry (ICP-MS) at the British Geological Survey, Keyworth. Standard (CRM-Basalt) was periodically measured as well as repeats of individual samples.

3.6.3.2. *Moisture content*

Water attenuates the radiation a mineral grain receives during burial (Aitken, 1985; Guérin *et al.*, 2012), therefore an estimation of the moisture content is critical to the dose rate equation. For quartz it is expected that a 1% change in water content will result in a 1% change in the calculated age (Roberts *et al.*, 2015). However, it is almost impossible to reconstruct moisture levels in sediments over Quaternary timescales, as they will have inevitably fluctuated. Hence one of the largest sources of age uncertainty in luminescence dating stems from estimations of the past water content in the sediment.

Despite its critical impact on the calculated ages, there is no universal protocol for estimating this value and many studies do not include this value at all (e.g. Galović *et al.*, 2009; Vasiliniuc *et al.*, 2012). A number of studies measure ‘modern’ water content from the samples collected (Constantin *et al.*, 2019; Stevens *et al.*, 2011; Veres *et al.*, 2018), but

this is unlikely to represent the past, or even average, values the sample experienced during burial. Therefore, there is no straightforward solution to the estimation of water content. Here, the $15\pm 5\%$ water content was used based on previous loess research (Antoine *et al.*, 2009a; Fuchs *et al.*, 2008; Murray *et al.*, 2014; Novothny *et al.*, 2009; Schatz *et al.*, 2012; Újvári *et al.*, 2014a).

3.6.3.3. *Conversion and attenuation factors*

Radionuclide concentrations were converted to infinite-matrix dose rates by applying Guérin *et al.* (2011) conversion factors. The infinite-matrix dose rates were also adjusted for alpha efficiency (0.04 ± 0.004 for 4-11 μm quartz, 0.08 ± 0.02 for 4-11 μm polymineral (Rees-Jones, 1995), and 0.15 ± 0.05 for coarse K-feldspar (Balescu and Lamothe, 1994)), and grain size attenuation (alpha (Brennan *et al.*, 1991) and beta (Mejdahl, 1979)). For the 63-90 μm potassium feldspars, the internal dose rate was additionally calculated using an internal potassium concentration of $12.5\pm 0.5\%$ (Huntley and Baril, 1997). Cosmogenic radiation contributions to the dose rate were corrected for sediment thickness, altitude and geographic location (Prescott and Hutton, 1994).

3.6.4. **Machine set-up**

All luminescence measurements were made using Risø TL/OSL luminescence readers using a calibrated $^{90}\text{Sr}/^{90}\text{Y}$ beta irradiation source, fitted with an EMI 9635Q bialkali photomultiplier tube. Quartz grains were stimulated with blue (470 nm) LED's and the signal was measured in a UV detection window through 7.5 mm U-340 glass filters (Bøtter-Jensen *et al.*, 2000). Potassium feldspar and polymineral grains were stimulated with infra-red emitting diodes (IR; 870 nm), and signals were detected in the blue-violet region of the electromagnetic spectrum through a combination of Schott BG39/Corning 7-59 filters.

3.6.5. Quartz

Quartz is the mineral of choice when it comes to OSL dating due to dosimetric properties and faster measurement process. The physical processes of electron movement within a crystal structure is understood better (Preusser *et al.*, 2008), quartz signals bleach more rapidly in nature (Godfrey-Smith *et al.*, 1988), and it is thermally stable over Quaternary timescales (e.g. Aitken, 1985; Spooner, 1994). However, quartz signal is dimmer and saturates at lower doses (100-200 Gy; Wintle and Murray, (2006). Combined with a typical loess environmental dose rate of $\sim 3 \text{ Gy ka}^{-1}$ this provides an approximate upper limit of $\sim 30\text{-}50 \text{ ka}$ to which quartz can be dated (Buylaert *et al.*, 2008).

3.6.5.1. The SAR Protocol

The single-aliquot regenerative-dose (SAR) measurement protocol (Table 3.3; Murray and Wintle, 2000; Wintle and Murray, 2006) was utilised to test, analyse, and date all samples. To determine the most appropriate measurement conditions, dose recovery (section 3.6.5.3) and preheat plateaus (see section 3.6.5.2) were run, details of which are provided below. Following which the preheat temperature used for PHI varied between 240 and 260°C. The cut-heat (PH2) of 160°C was used for all measurements. Both preheats were held for 10 seconds. Luminescence was measured at 125°C for 40 s and D_e s were determined by subtracting the background (last 20 s) signal from the first 0.5 s of stimulation (unless stated otherwise). Dose response curves were fitted with a single exponential and exponential plus linear functions.

Three standard luminescence signal screening criteria were used during all tests and equivalent dose determination. Signal recuperation, a ratio of a 0-dose measured at the end of the SAR cycle to a natural signal, tests for a thermal transfer between traps. Here any disk with recuperation values above 5% was rejected (Murray and Wintle, 2000). Recycling ratio determines changes in sensitivity, a signal build-up as a response to

increasing doses and heat treatment (Murray and Wintle, 2000), were accurately corrected for. This ratio is achieved by repeating the first small dose at the end of the SAR cycle, with aliquots >10% of unity rejected. Finally, an IR-depletion ratio, tests for feldspar contamination in aliquots, ensures measured signal comes from quartz grains (Duller, 2003). Quartz is inefficiently stimulated by IR at room temperature, but feldspar is, therefore another low dose measurement is added before L_x , but using an IRSL (50°C for 40 s). Aliquots with feldspar contamination that exceeded $1 \pm 10\%$ were also rejected. Feldspar contaminated aliquots were negligible and in most instances just required repeated treatment with H_2SiF_6 . Uncertainties for an individual aliquot were calculated based on 1,000 Monte Carlo reiterations of the curve fit (Duller, 2007) and propagated with a 2.5% measurement error.

Table 3.3 Step by step dating protocols for dating quartz (OSL), and polymineral and potassium feldspars (pIRIR). Details of temperatures selected for each site are given in Chapters 4, 5 and 6.

Quartz			Feldspar and polymineral	
Step	Treatment	Observed	Treatment	Observed
1	Give dose, D_i		Give dose, D_i	
2	Preheat, XX°C 10s	PH1	Preheat, XX°C, 60s	
3	Blue LED, 40s at 125°C	L_x	IR stimulation, 200s at 50°C	L_{xIR50}
4	Give test dose, D_T		IR stimulation, 200s at Elevated Temp	$L_{xpIRIRlev}$
5	Preheat, 160°C, 10s	PH2	Give test dose, D_T	
6	Blue LED, 40s at 125°C	T_x	Preheat, 250°C, 60s	
7	Return to 1		IR stimulation, 200s at 50°C	T_{xIR50}
8			IR stimulation, 200s at Elevated Temp	$T_{xpIRIRlev}$
9			Hot bleach, 200s at 320°C	
10			Return to 1	

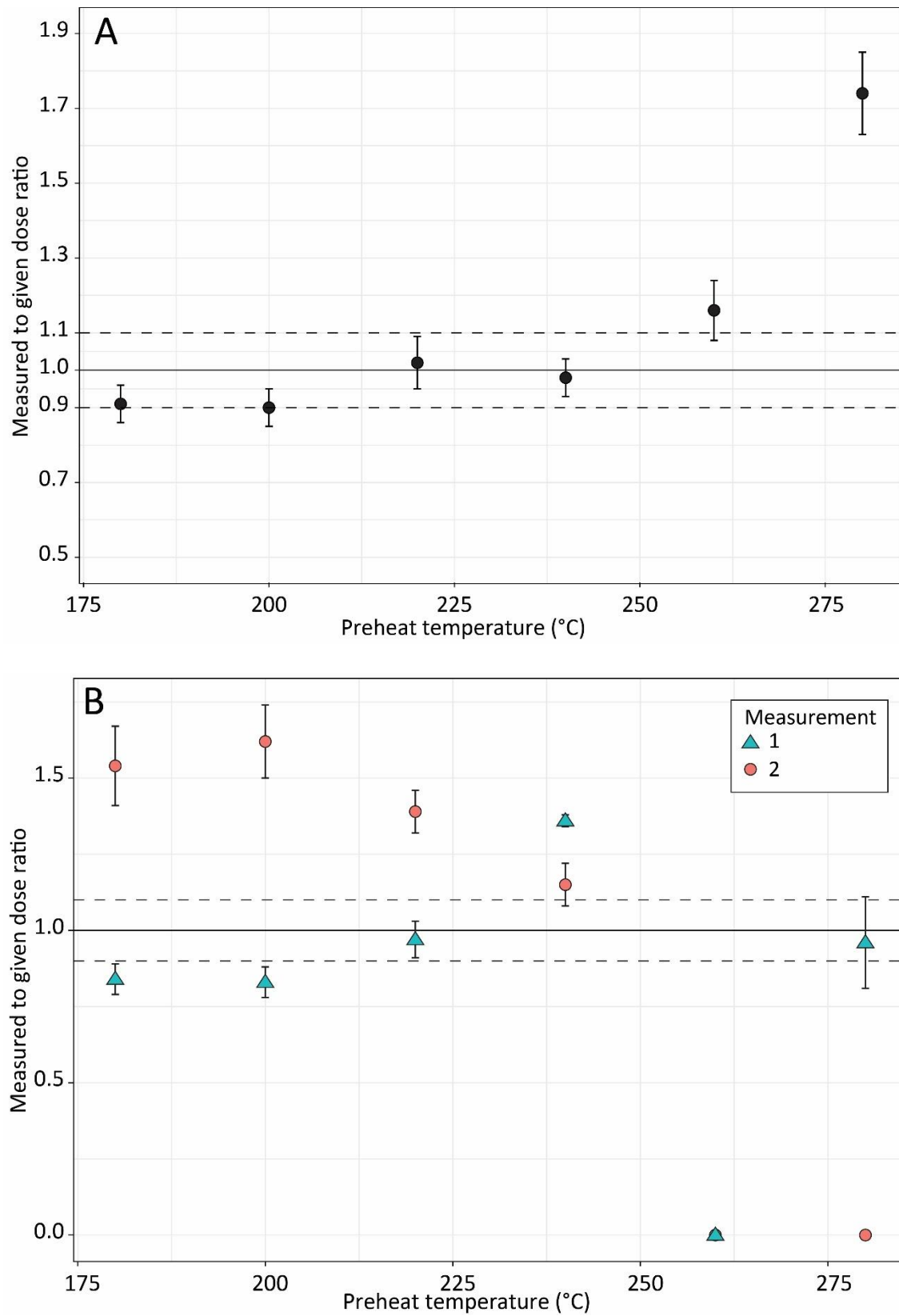
3.6.5.2. *Temperature selection*

To select optimal, preheat temperatures for the SAR protocol, combined dose recovery and preheat tests were conducted for each site. The dose recovery test is described in more detail in section 3.6.5.3.

In each case a dose approximating the natural dose was given to a subset of three aliquots. Then the same SAR protocol was applied, while varying the first pre-heat temperature (PH1) from 180-280°C, to test which temperature provides the closest match with the given dose. Figure 3.6 shows the results of the pre-heat plateaus for Croatia, Serbia and Bulgaria.

For Bulgarian samples (Figure 3.6A) the plateau for all four lower temperatures passed the dose recovery test, however the lower two temperatures were slightly underestimating the given dose by 7-14% and temperatures >240°C overestimate by as much as 220%. Although both temperatures, 220°C and 240°C appear appropriate for this site, the PH1 temperature chosen for further analysis for Slivata was 240°C because of the lower spread of values between individual aliquots.

Figure 3.6B shows the results of the preheat plateau for a sample from Croatia, Erdut. Measurements were carried out on a fine grained (4-11 µm) sample CRO16/2/15 as it was the only sample that was potentially within the age range of quartz. The plateau was never achieved, and the sample produced scattered results, especially at higher temperatures. Following first preheat-plateau (Measurement 1), dose recovery test at 200°C failed (see section 3.6.5.3). Another pre-heat test was attempted (Measurement 2), which showed completely reversed patterns. 200°C was chosen over 220°C as the data showed much greater spread at the higher temperature. Following a second pre-heat plateau, attempts at dating this sample using quartz were abandoned as there was not enough sediment to continue investigations into the sample properties.



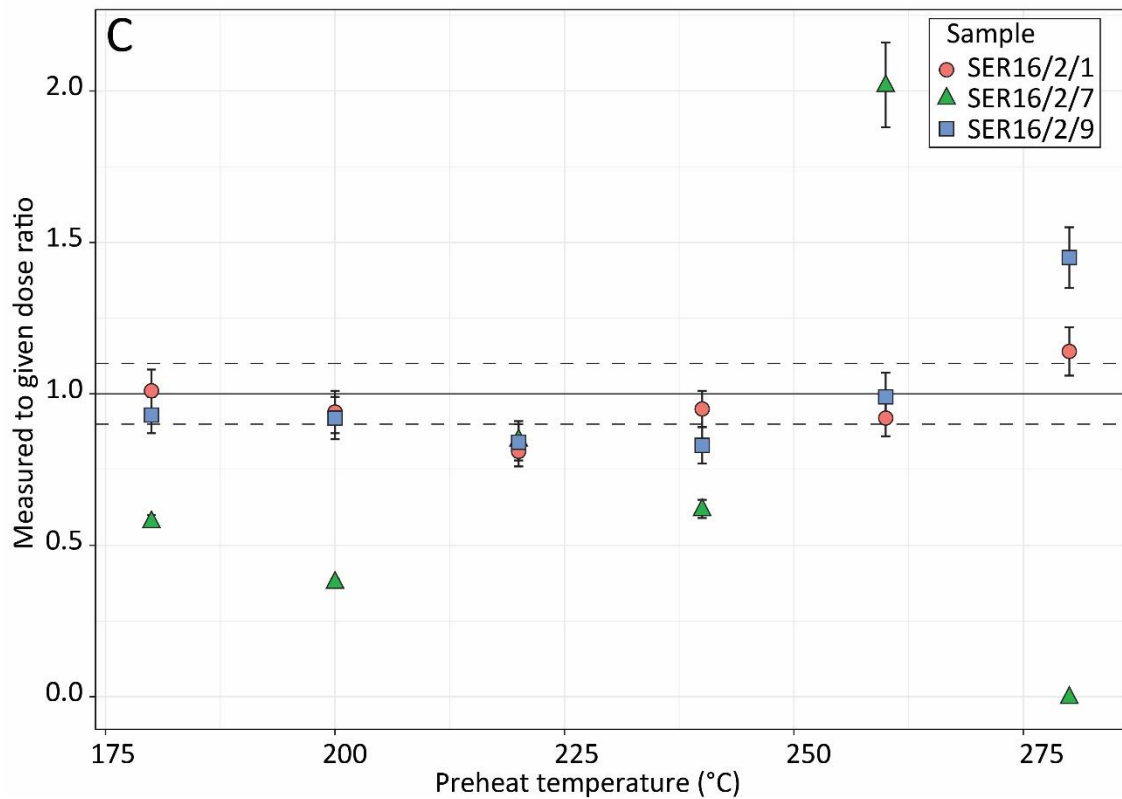


Figure 3.6 Results of quartz preheat plateau test for all sites. The average recovered dose and error of three aliquots at each temperature are shown. A) Bulgaria B) Same sample repeated twice for Croatia. C) Three samples measured for Serbia. Dotted lines mark $\pm 10\%$ from unity.

Figure 3.6C shows three preheat plateaus for samples from the Serbian site, Surduk. Initially two samples, SER16/2/1 and SER16/2/9, were investigated, both of which produced replicable patterns. Although several temperatures appeared suitable for analysis, a 260°C temperature was selected for PHI for all tests and measurements that followed. This is primarily as 180°C and 200°C were considered to produce low values, and carry a higher risk of thermal transfer. Figure 3.6 C also shows the result of the preheat plateau for sample SER16/2/7. This was run after sample failed recycling during routine D_e measurement (more detail in Chapter 6).

3.6.5.3. Dose Recovery

To test the suitability of the selected measurement temperature, a dose recovery experiment was completed. This test ensures that any sensitivity changes that occur during the heating and optical stimulation are corrected for by the test dose as a part of the SAR protocol (Galbraith *et al.*, 1999; Wallinga *et al.*, 2000; Wintle and Murray, 2006).

Dose recovery test requires the removal of the natural luminescence signal from the aliquots by bleaching. This stage is performed in three steps. First a blue LED bleach for 1000 s at 50°C, a 10,000 s pause, and a second blue LED bleach for 1000 s at 50°C. This is followed by aliquot irradiation with a known β -dose, that approximates the natural dose received by samples, and therefore each sample receives a slightly different dose. The sample is then measured using the SAR protocol, with the selected preheat temperature (PHI; Section 3.6.5.2). The measured D_e value is normalised to the value of the administered dose and presented as a ratio. The test is passed based on how closely the measured dose replicates the given one (Duller, 2008). A result of $\pm 10\%$ of unity indicates that the selected protocol can reproduce laboratory administered dose, and is therefore suitable for D_e determination.

Table 3.4 shows the average results of the dose recovery tests in all samples measured. Except for sample CRO16/2/15, from Erdut, the dose recovery tests were passed within 1 σ uncertainty, by all aliquots and samples. This provided confidence in the temperatures selected for the D_e measurements. The results of individual aliquot results can be found in Chapters 4, 5 and 6.

Table 3.4 Summary of the dose recovery tests performed on quartz samples. Except for the Croatian sample (CRO16/2/15) where 63-90 μm grains were used, all other data comes from 4-11 μm separates. Overdispersion (%) refers to the variability from the mean measured D_e .

Sample	Aliquots (n)	Given to measured dose	Given to measured dose error	Overdispersion (OD)
BUL17/1/1	12	0.97	0.05	0.0%
BUL17/1/11	12	1.01	0.05	0.0%
BUL17/2/1	12	0.92	0.05	0.0%
BUL17/2/3	12	1.00	0.07	0.0%
BUL17/2/9	12	1.02	0.05	0.5%
CRO17/2/15	12	1.42	0.10	8.5%
SER16/2/1	11	0.96	0.06	0.0%
SER16/2/3	12	0.91	0.06	5.0%
SER16/2/9	12	0.94	0.06	0.0%

3.6.6. Feldspar

Section 3.6.5 emphasized that quartz signal saturates, limiting its application to sediment younger than ~ 70 ka (Buylaert *et al.*, 2007). By comparison, the signal obtained from feldspar through the infra-red stimulated luminescence (IRSL) saturates at much higher doses and potentially extends the age range to 300-600 ka in some contexts (Buylaert *et al.*, 2012; Kars *et al.*, 2012; Li and Li, 2012; Thomsen *et al.*, 2011). This is of particular importance for this research as it attempts to investigate sites spanning the whole last glacial-interglacial cycle (e.g. Schmidt *et al.*, 2010; Schatz *et al.*, 2012; Murray *et al.*, 2014).

Although the feldspar signal offers the potential to extend the dateable age range using luminescence dating, the signal in some feldspars is unstable. This phenomena, termed

‘anomalous fading’ (Wintle, 1973), means that the signal ‘leaks’ from the grains at room temperature causing an age underestimation, if not corrected for. While attempts at correcting for the lost signal have been made (Huntley and Lamothe, 2001; Lamothe and Auclair, 1999), the process is not straightforward and mainly applicable to young samples (the linear part of the growth curve). The development of the pIRIR measurement protocol by Thomsen *et al.* (2008), provided a way of accessing a relatively more stable, signal in feldspars. Since a number of studies along the Middle and Lower Danube (Bösken *et al.*, 2019; Lomax *et al.*, 2018; Thiel *et al.*, 2011b; Vasiliniuc *et al.*, 2012) have demonstrated low fading rates (in line with laboratory fading of quartz) when applying the pIRIR protocol, therefore bypassing a need for fading correction. The results of the pIRIR approach produce more accurate ages in line with ages obtained from independent methods such as tephra (Thiel *et al.*, 2011b) and radiocarbon (Thiel *et al.*, 2011a; Újvári *et al.*, 2014a).

3.6.6.1. *The pIRIR Protocol*

The initial IRSL protocol, was based on the OSL SAR protocol to monitor and correct for sensitivity changes, but with the difference of stimulating samples at lower temperatures and within the IR, rather than blue, wavelengths. The pIRIR protocol modified the original IRSL with the addition of two steps, 4 and 8 (Table 3.3). Following the initial measurement using IR at 50°C for 200 s that removes the “unstable charge”, another 200 s measurement is carried out, still by stimulation in the IR wavelengths but at an elevated temperature. The elevated temperature is selected through the preheat plateau described in more detail in Section 3.6.6.3. Lastly, the “hot bleach” step (9; Table 3.3) is added at the end of each SAR cycle. This ensures no signal is carried out from one SAR cycle to the next one as feldspars are harder to bleach. D_e s were determined by subtracting the background (last 100 s) signal from the first 1 s of stimulation. Dose response curves were fitted with a single exponential and exponential plus linear functions.

As in the case of quartz measurement, the feldspar SAR cycle was screened using the standard rejection criteria, though signal recuperation ($<5\%$) and recycling ratio ($1\pm 10\%$) were used (Murray and Wintle, 2000).

3.6.6.2. Prior IR Stimulation Plateau

Jain and Ankjærgaard, (2011) suggested that the first IRSL stimulation at 50°C could have an impact on the stability of the pIRIR signal. To test the relationship between the first and second stimulation, and therefore the influence of the first IRSL measurement on the D_e values obtained from the pIRIR signal, a prior-IR stimulation plateau test was conducted (Buylaert *et al.*, 2012). This test should identify the appropriated temperature for the first IRSL measurement. As a result of this test 50°C temperature was selected, discussed in more detail in Chapter 4.

3.6.6.3. Temperature selection

Table 3.5. Preheat and stimulation temperature pairings for the feldspar preheat plateau analysis.

Preheat	200°C	225°C	250°C	280°C	300°C	320°C
1 st IRSL	50°C	50°C	50°C	50°C	50°C	50°C
IRSL elevated	180°C	200°C	225°C	250°C	270°C	290°C

The selection of temperature can have a great impact on the measured D_e values (Roberts, 2012), yet preheat plateaus for the pIRIR protocols are not commonly applied in loess research. At the same time a number of studies reported problems with dose recovery when applying only pIRIR₂₉₀ (Schatz *et al.*, 2012; Thiel *et al.*, 2011b, 2011a, 2014; Újvári *et al.*, 2014a). A very similar procedure to the OSL preheat, applies in the selection of temperature for the pIRIR protocol. Here however the analysis is not combined with dose

recovery tests, and it tests temperatures in pairs (Table 3.5). Six preheat temperatures (from 200°C to 320°C) and an elevated pIRIR temperature (25-30°C lower than the pre-heat) pairings were tested.

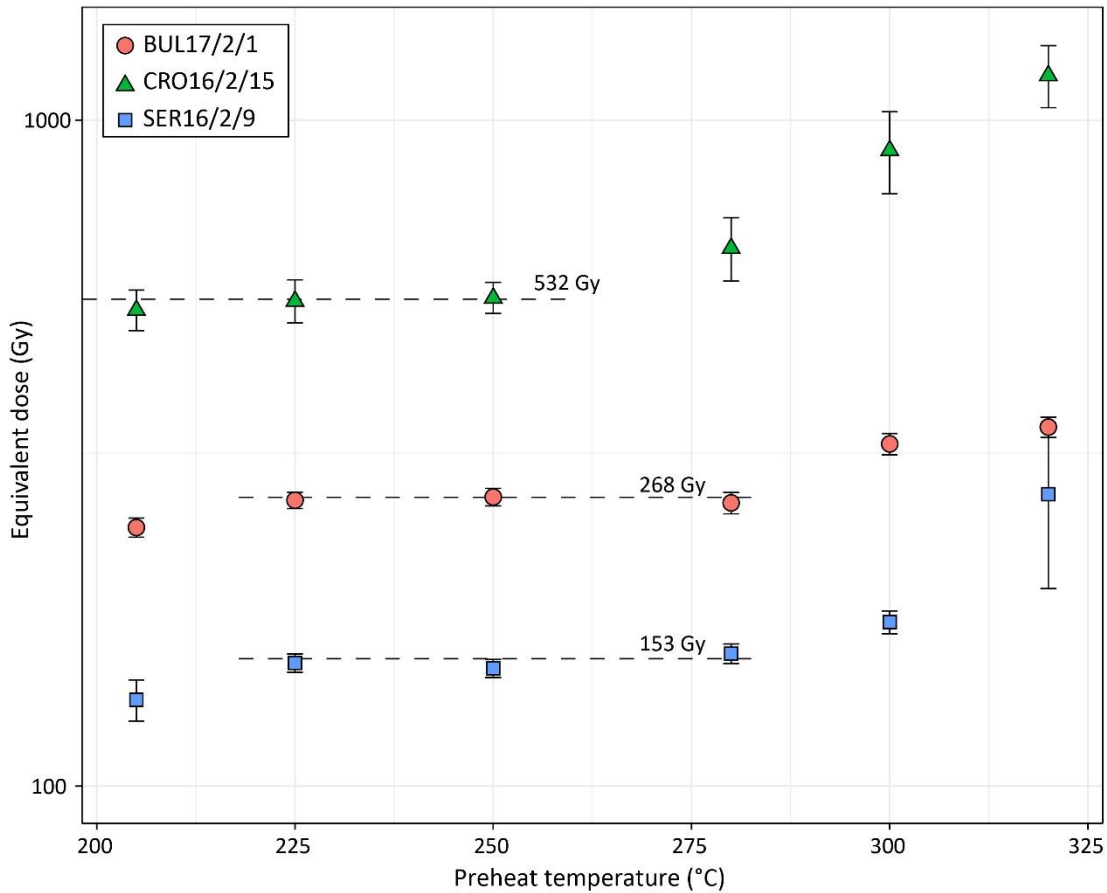


Figure 3.7 D_e dependency on pre-heat temperature for three sites. The average D_e value and standard deviation of three aliquots at each temperature are shown. Pre-heat plateaus are marked by the dashed lines, as well as the average D_e values for the plateau. Please note the y-axis is logged.

Figure 3.7 shows the results of the preheat plateau for three sites, which are discussed in detail in Chapters 4, 5 and 6. However, it is important to note that in all three cases there is a rise in the D_e values obtained from higher temperature stimulations. This is particularly dramatic in the case of the Croatian sample, where the pIRIR₂₉₀ protocol

produces values almost twice as high as those produced at lower temperatures. While the selection of the temperature should be independently verified, through comparison with tephra, radiocarbon or even quartz results, that is not always possible. Given the consistency in D_e s measured using lower temperatures (between 205°C and 250°C), a pIRIR₂₂₅ protocol with a 250°C preheat was selected for use in Croatia and Bulgaria, whilst a pIRIR₂₂₀ combination was used in Serbia. The selected temperatures are additionally examined through the dose recovery tests (Section 3.6.6.4).

3.6.6.4. *Residual test and Dose Recovery*

As indicated in Section 3.6.6.3, feldspars may in some contexts not bleach well. There is a component to all feldspar signals that is not removable, i.e. is unbleachable, that is known as residual signal (Buylaert *et al.*, 2011). If this component is large enough it could lead to an age overestimation, as it will be measured when the D_e is determined (Murray and Olley, 2002). Therefore, it is critical to test for the size of this component to assess its potential impact on final ages.

Theoretically in aeolian sediments (including loess), feldspars have a very high likelihood of being well bleached during sediment transport in the atmosphere, and therefore are likely to have a relatively small residual signal (Buylaert *et al.*, 2011). However, some studies in European loess deposits have reported quite large residual components e.g. 15-20 Gy in Austria (Thiel *et al.*, 2011a), 7-25 Gy in Ukraine (Veres *et al.*, 2018), and as high as 40 Gy in Serbia (Stevens *et al.*, 2011). With the average dose rates at each of these sites, this equates to ~4-5 ka, ~2-8 ka, and ~12 ka, age overestimation respectively. This highlights the importance of testing for residual signal.

Four samples from Croatia and Serbia and one from Bulgaria were bleached in daylight for 7-10 days (in March, April and May in the UK). Samples were then measured using the pIRIR_{elevated} protocol selected during the preheat plateau to determine the size of the

unbleachable signal. The results of this test are presented in Table 3.6 and discussed in more detail in Chapters 4, 5 and 6. It is worth noting, that residual signal in all cases is quite low and corresponds only to a small fraction of the final age; Croatia 4.71 ± 0.19 Gy ($\sim 1.51 \pm 0.06$ ka), Bulgaria 4.06 ± 0.15 Gy ($\sim 1.53 \pm 0.06$ ka), and Serbia 1.41 ± 0.20 Gy ($\sim 1.1 \pm 0.16$ ka).

Table 3.6. The residual dose and dose recovery results summary for all sites. All data are shown with 1σ errors. Please note that all dose recovery tests were conducted on 12 aliquots and residual tests on 6 aliquots.

Sample	Fraction	Grain size	Residual dose (Gy)	Dose recovery*	Overdispersion (OD)
CRO16/2/9	K-feldspar	63-90 μm	6.31 ± 0.27	1.07 ± 0.09	0%
CRO16/2/10	K-feldspar	63-90 μm	4.60 ± 0.18	1.05 ± 0.08	0%
CRO16/2/17	K-feldspar	63-90 μm	4.11 ± 0.16	1.04 ± 0.07	0%
CRO16/2/27	K-feldspar	63-90 μm	4.37 ± 0.17	0.98 ± 0.07	0%
BUL17/2/1	K-feldspar	63-90 μm	4.06 ± 0.15	0.92 ± 0.05	1.4%
SER16/2/9	Polymineral	4-11 μm	1.10 ± 0.16	1.08 ± 0.04	0%
SER16/2/10	Polymineral	4-11 μm	1.25 ± 0.31	0.87 ± 0.05	0%
SER16/2/17	Polymineral	4-11 μm	2.07 ± 0.17	0.87 ± 0.04	0%

*Residual subtracted dose recovery ratio

The suitability of the selected temperature pairing for the pIRIR_{elevated} SAR protocol was tested using the dose recovery test.

Four samples from Croatia and Serbia were selected, and one from Bulgaria. Unless stated otherwise 12 aliquots were used for all measurements. The aliquots were bleached in the same daylight conditions as the aliquots used for the residual tests, and irradiated with a β -dose approximating their natural dose. Following D_e the measurement using the

selected pIRIR_{elevated} protocol, the average residual signal for each site was subtracted from that measured, before calculation of the dose recovery ratio. All samples recovered administered doses within 10% uncertainty.

3.6.6.5. *Anomalous Fading*

IRSL signal in feldspar grains is known to be affected by signal loss at room temperature (Wintle, 1973), which can in turn lead to erroneous age calculations. To overcome this issue the pIRIR protocol, that accesses more a signal stable over longer geological timescales, has been developed (Buylaert *et al.*, 2012; Thomsen *et al.*, 2008). Nonetheless, it is necessary to assess fading to determine if an appropriate correction is required (Huntley and Lamothe, 2001; Kars *et al.*, 2008) as even the pIRIR protocol has been shown to suffer from fading rates (Schmidt *et al.*, 2010; Thiel *et al.*, 2014; Vasiliniuc *et al.*, 2012). While quartz grains are known to be athermally stable in nature, when subjected to laboratory fading test (g-values) they yield a fading rate of $0.98 \pm 0.08\%$ /decade (Buylaert *et al.*, 2012), showing that the laboratory test may produce “artificial” fading rate. It is therefore accepted that low fading rates, in the range of 1–1.5%/decade, measured using the pIRIR protocol are likely an artefact of laboratory procedures and do not require a fading correction (Thiel *et al.*, 2011a). Fading rates ($g_{2\text{days}}$) were measured using three aliquots per sample. A standardised protocol was used to assess fading rates, a fixed β -dose of 170 Gy was administered and the luminescence signal measured after a pause (Auclair *et al.*, 2003). This cycle was followed with pauses increasing in length each time (0h, 1h, 10h, 100h and 1000h). The pause time was plotted against the sensitivity corrected luminescence signal (L_x/T_x) and fitted with an exponential function to determine the fading rate (%/decade normalised). This was done for pIRIR and the IR₅₀ signal to determine the differences in fading and assess if the pIRIR protocol accesses the non-

fading signal. All fitting and calculation of g-values were done using the *analyse_FadingMeasurement* function (Kreutzer and Burow, 2017) in R Studio.

Table 3.7. Fading test (norm. 2 days) results for IR₅₀ and pIRIR signals. Each value is an average of data from three aliquots.

Sample	IR ₅₀ g-value (%/decade)	pIRIR g-value (%/decade)
CRO16/2/5	3.23±1.22	0.31±0.88
CRO16/2/9	4.66±1.53	3.30±1.37
CRO16/2/10	2.82±1.26	1.62±1.12
CRO16/2/15	3.18±1.19	1.55±1.19
CRO16/2/17	2.41±1.13	1.90±1.14
CRO16/2/21	1.79±1.20	1.38±1.09
BUL17/2/1	5.35±1.37	2.06±1.67
SER16/2/7	13.0±0.9	2.1±1.1
SER16/2/10	16.3±0.9	0.9±1.1
SER16/2/12	11.9±1.0	2.1±1.2
SER16/2/17	10.2±0.9	2.5±1.1
SER16/2/23	5.4±1.2	1.8±1.0

3.6.7. Age calculation

The final equivalent dose determination per sample requires the selection of an appropriate age model, i.e. common age, central age, minimum age or finite mixture model, to ensure correct and precise calculation of appropriate overall D_e (Figure 3.8). The Central Age Model (CAM; Galbraith *et al.*, 1999) acknowledges that the measurement uncertainties account for all of the observed D_e variability and provides a measurement of

the data spread around the central D_e (overdispersion), beyond variability estimated from measurement errors and machine replicability. The model assumes normally distributed D_e s (Figure 3.8A) and the calculated value can be interpreted as the mean of the true D_e . The Common Age Model (Figure 3B) assumes measurement errors explain all of the observed variability (Galbraith *et al.*, 2005). When this model is applied, D_e distributions are thought to represent a common value (Galbraith *et al.*, 1999). The Minimum Age Model (Figure 3C) is commonly used in samples that have not been fully bleached during sediment transport (e.g. fluvial, colluvium) (Galbraith and Laslett, 1993). This model assumes that some signals have been fully bleached, whilst others (with higher D_e s) have not. In this model a series of parameters with errors are used, including a number of fully bleached grains or the truncation point of the distribution. This model can be further separated into MAM-3 and MAM-4 following the suggestion of Bailey and Arnold (2006), depending on the bleaching extent, burial dose variance, and the size of errors. Finally the Finite Mixture Model (Figure 3D) was adopted into luminescence dating from fission track dating (Galbraith and Green, 1990). This model is applied in cases where a number of discrete D_e populations are found in samples that are consistent with each other. However, this model assumes a normal distribution of each of the populations. The choice should be guided by understanding the sedimentary nature of samples and their expected overdispersion values (Jacobs *et al.*, 2006).

The logged CAM assumes normally distributed D_e s and the calculated value can be interpreted as the mean of the true D_e . This method also provides a measurement of the data spread around the central D_e (overdispersion), beyond variability estimated from measurement errors and machine replicability. This model was chosen following the Bailey and Arnold (2006) decision tree, but also due to relative homogeneity of aeolian samples, and their fine grain nature (the signal is averaged, often over millions of grains).

Analyst v4.14.6 (Duller, 2013), v4.31.7, and v.4.31.9 (Duller, 2015) was used for processing the D_e values and calculation of the CAM. To ensure all sources of error associated with both components of the age equation (dose rate and equivalent dose) are included and propagated in quadrature to produce final age and uncertainty estimation, DRAC v1.2 software (Durcan *et al.*, 2015) was used.

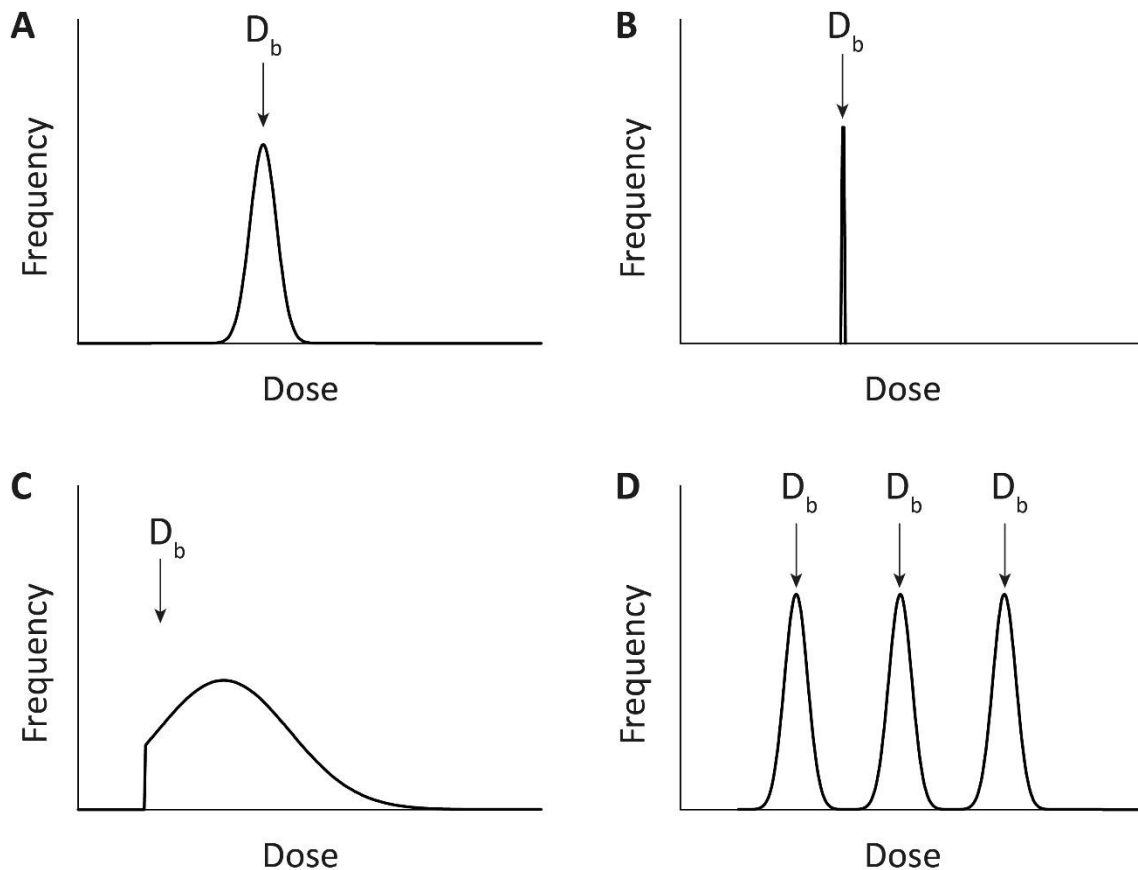


Figure 3.8. Examples of theoretical D_e value distributions for a sample and commonly applied models for these types of datasets. A) Central Age Model. B) Common Age Model. C) Minimum Age Model. D) Finite Mixture Age model (adopted from Duller, 2008).

3.6.7.1. Age – depth modelling

Luminescence ages often provide chronological information where no other chronological tool can be used, either due to the environment of deposition or timescale covered

(Fitzsimmons *et al.*, 2012). With the popularisation of the technique, studies with numerous luminescence ages in a single stratigraphic sequence are becoming a norm (Moska *et al.*, 2019; Perić *et al.*, 2019; Stevens *et al.*, 2018; Thiel *et al.*, 2014; Veres *et al.*, 2018). Typically, basic age-depth plots are provided, but integrating age using modelling approaches (e.g. Bayesian) is not yet widespread. The application of modelled ages can provide a better insight into the depositional history of a site than single ages, or in fact age depth plots. While simple age-depth models can be constructed by fitting ages with linear functions, the age inversions may make this approach problematic. Especially in situations where the age including uncertainties fits the model but the “mean” age is inversed. Moreover, luminescence ages inherently suffer from quite large uncertainties resulting from some assumptions surrounding age calculation (in particular water content) that affects the age’s precisions.

Bayesian statistics have been long used to both calibrate and improve accuracy and precision of radiocarbon ages (Buck *et al.*, 1991, 1992). By incorporating pre-existing information about datasets such as changes in stratigraphy, stratigraphic position, and sampling resolution, Bayesian modelling recalculates uncertainty using Markov Chain Monte Carlo (MCMC) simulations for ages (age probability density functions) which overlap. It can provide a likelihood for each modelled age. Especially in the context of constructing age-depth model Bayesian models offer much more sophisticated approach than linear interpolation. Therefore, Bayesian modelling is now an integral element of radiocarbon dating (Niu *et al.*, 2013; Ramsey *et al.*, 2010) especially since the development of user friendly software Oxcal (Bronk Ramsey, 1995) and Bacon (Blaauw and Christeny, 2011).

The Bayesian approach has great potential for improving the uncertainties of luminescence ages, especially where large number of samples were collected in

stratigraphic succession and age errors overlap. A growing number of luminescence studies have been using one of the two most common Bayesian age-depth models, Bacon or OxCal, in their analysis especially where luminescence ages are combined with radiocarbon ages (Leighton *et al.*, 2013; Li *et al.*, 2015; Perić *et al.*, 2019; Rhodes *et al.*, 2003). However, these approaches do not fully capture the complexity of luminescence ages as they were developed for calibration and modelling of radiocarbon ages. The main challenge stems from the structure of luminescence age error, which is composed of systematic (e.g. source calibration, conversion factors) and random (e.g. D_e spread, counting statistics) component (Wallinga and Cunningham, 2015). The proportions of systematic and random errors are often unquantified, which is why these methods are unable to separate the two errors and model them as one. Yet only the random error should be used for modelling luminescence, otherwise an artificial error reduction can be caused.

Recently, a new approach has been proposed by Zeeden *et al.* (2018), combining inverse modelling and a Bayesian age-depth model to recalculate luminescence ages. This technique creates probability density functions for both systematic and random errors and models errors by only applying the random portion of the error. In turn this provides the basis for age recalculation, improving their precision. Based on the tests runs potential chronology improvements of up to 30% have been suggested, with the approach already used in several studies (Noppradit *et al.*, 2019; Perić *et al.*, 2019; Veres *et al.*, 2018).

Therefore, to better visualise the age distributions, improve the resolution, and reduce the uncertainty estimates, age-depth models based on Zeeden *et al.* (2018) approach were developed for each site. Where possible additional chronological information such as tephra was included.

3.7. Provenance

3.7.1. Bulk sample vs single grain

Geochemical investigations are among the most common approaches when investigating loess provenance. Traditionally this focused on bulk sample analysis due to relatively low cost and the speed of analysis (Von Eynatten *et al.*, 2003). This is also true for the majority of European loess provenance research, with elemental composition and their various ratios (Bösken *et al.*, 2018; Buggle *et al.*, 2008; Galović, 2014; Hošek *et al.*, 2015; Obreht *et al.*, 2016; Újvári *et al.*, 2008, 2014b), and Sr-Nd isotope (Schatz *et al.*, 2015; Újvári *et al.*, 2012) forming the bulk of the provenance research.

While there are many benefits to characterising the elemental and isotopical composition of a sediment, in mixed sedimentary bodies such as loess, this data may not identify the source of material. As sediment gets entrained, transported, deposited, and buried in a number of cycles, its chemical composition can be altered (Morton, 1991). This process can be enhanced by climate, vegetation, and weathering (Weltje and von Eynatten, 2004). Therefore, bulk sediment may not reflect the true source signal, but a sum of processes undergone by the sediment and the amount of time spent “in transit”. An additional complication can be caused by the incorporation of sediment from multiple sources in a final deposit, with the bulk geochemical signature representing anything from an average to a mixing line between multiple sources. A number of loess provenance studies both in China (Bird *et al.*, 2015; Licht *et al.*, 2016; Maher *et al.*, 2009) and Europe (Schatz *et al.*, 2015; Újvári *et al.*, 2008) have already argued that while loess may have a dominant source, any deposit is unlikely to contain sediments derived from a single source. This is supported by geochemical analysis results which suggest that loess bulk composition often approximates Upper Continental Crust values (UCC; Gallet *et al.*, 1998; Buggle *et al.*, 2008;

Újvári, Varga and Balogh-Brunstad, 2008), suggesting that this approach will struggle to identify differences between samples that are quite similar.

Detrital single-grain provenance analysis offers potentially more accurate identification of source, as in principle one grain can only have source (i.e. parent rock). Single-grain research can explore various approaches, such as grain morphology, geochemical composition (including Rare Earth Elements (REE), and isotopic composition) and geochronology and thermochronology, to fingerprint source regions. Moreover, advances in geochemical techniques, especially when small grain sizes are concerned, through methods such as LA-ICP-MS (laser ablation ICP-MS) or electron microprobe have increased the precision and speed of single-grain analysis (Hietpas *et al.*, 2011). These developments saw the first application of single-grain detrital zircon dating in Chinese loess (Stevens *et al.*, 2010) and the following expansion of the application of the technique, especially in a Chinese context (Bird *et al.*, 2015; Che and Li, 2013; Licht *et al.*, 2016; Nie *et al.*, 2015; Pullen *et al.*, 2011; Stevens *et al.*, 2013a, 2013b; Xiao *et al.*, 2012). Additionally some researchers explored the application of other single grain provenance proxies in loess e.g. garnet types (Fenn *et al.*, 2018), Hf isotopes in zircons (Újvári and Klötzli, 2015), or rutile (Újvári *et al.*, 2013). Crucially, the method selected needs to take into consideration the research question, as while single-grain approaches offer many advantages, they may still suffer from the same issues as bulk methods approaches e.g. multiple recycling of the material, source signals having very indistinguishable signatures, or not be sufficient to explore questions such as erosion patterns and sediment flux (Vezzoli *et al.*, 2016). Finally, as with any palaeoinvestigation, the most information is gained when a multiproxy approach is taken. Given the above considerations, detrital zircon U-Pb dating combined with Hf isotopical was selected as the provenance approach. Work was conducted at the British Geological Survey, Keyworth, with the following discussion outlines key principles and the methods used.

3.7.2. Zircon

Zircon (ZrSiO_4) predominantly forms in intermediate to felsic igneous, especially plutonic, rocks. This orthosilicate mineral is classed as heavy mineral due to its density at 4.6-4.7 gcm^{-3} (Deer *et al.*, 1992). Zircons are able to withstand mechanical abrasion, weathering, burial and metamorphic events (Morton and Hallsworth, 2007), therefore making them an abundant heavy mineral in sedimentary rocks.

During crystallisation zircons incorporate Hf, U, Th, and REE (Dill, 2010). Therefore their trace element content, isotopes (Hf, O, Li), and morphology are often used in geological setting discrimination and provenance studies (von Eynatten and Dunkl, 2012). However, the most common approaches focus on both high and low temperature chronology, i.e. U-Pb and fission track dating, respectively.

While zircon geochronological approaches have been central to the tectonic and geological studies (Gehrels, 2014), only recently they have become the methodological approach of choice in provenance studies, especially loess research. The advances in understanding of loess provenance on the Chinese Loess Plateau (e.g. Stevens *et al.*, 2013; Nie *et al.*, 2014; Bird *et al.*, 2015; Licht *et al.*, 2016; Fenn *et al.*, 2018) would not be possible without zircon single-grain dating.

3.7.2.1. Sample preparation

Clay grain size fractions were removed from bulk sediment (~1 kg) in settling columns (calculated using Stoke's Law). The remaining sediment was processed through a super-panner to concentrate heavy minerals.

Heavy minerals were separated from the concentrated fractions using heavy liquid (diiodomethane; 3.3 gcm^{-3}). Magnetic separation was carried out to remove the most magnetic material, while avoiding losing any high-U, relatively magnetic zircons using a

Frantz Isodynamic Separator. Zircon-enriched separates were mounted on epoxy disks (Figure 3.9), without picking to avoid identification bias (Figure 3.10). Finally, stubs were polished to reveal the grains' centres.



Figure 3.9 Fully prepped and polished stub of sample CRO16/2/27.

3.7.2.2. *Cathodoluminescence imaging (CL)*

The zircon crystallisation process often results in a polyphase structure (zonation) that represents periods of mineral growth. Zonation analysis provides a record of a magma's geochemical condition, and timing of growth (Hanchar and Miller, 1993). However, the robust nature of zircon means that it can survive cycles of erosion and re-melting, and crystals may exhibit xenocrystic cores surrounded by rims reflecting new magmatic zircon growth. Zircon may also grow during high-grade metamorphism, forming rims on pre-existing crystals (Hietpas *et al.*, 2011). As a result, ages between rims, zones and centres can vary, from a few Ma to thousands of Ma. These internal structures can be revealed through cathodoluminescence imaging (Figures 3.10 and 3.11).

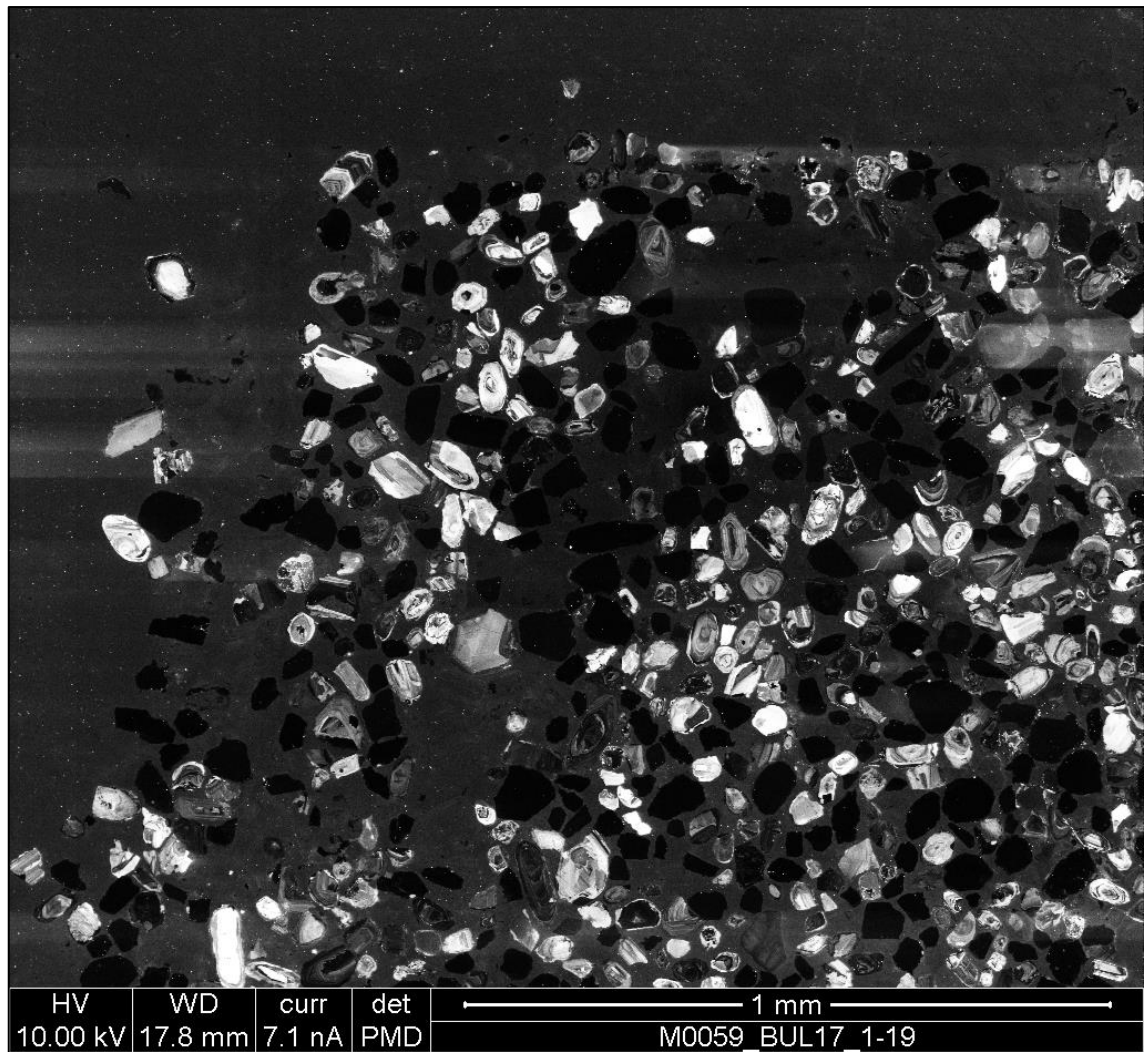


Figure 3.10 CL image of part of the BUL17/1/9 stub, showing zircon grains available for analysis. While not visually appealing in comparison to the approach in which grains are hand-picked prior to analysis, the inclusion of all zircon grains combats the identification bias.

To ensure a systematic approach across the study and meaningful comparison between samples, every grain was CL imaged prior to selection for U-Pb analysis and the creation of stub maps to help identify grains for U-Pb and Hf measurement. Analysis was carried out on a Quanta FEI scanning electron microscope at the British Geological Survey (BGS), Keyworth. This approach also allowed identification of zircons present on the stub, regardless of their size, cathodoluminescence or morphology (Figure 3.10). The grains

available for analysis were generally small, usually not much larger than the size of the smallest laser spot size (20 μm). Therefore, grains with complex internal structures or obvious metamorphic overgrowths were avoided to prevent from obtaining meaningless, mixed ages between rim and core.

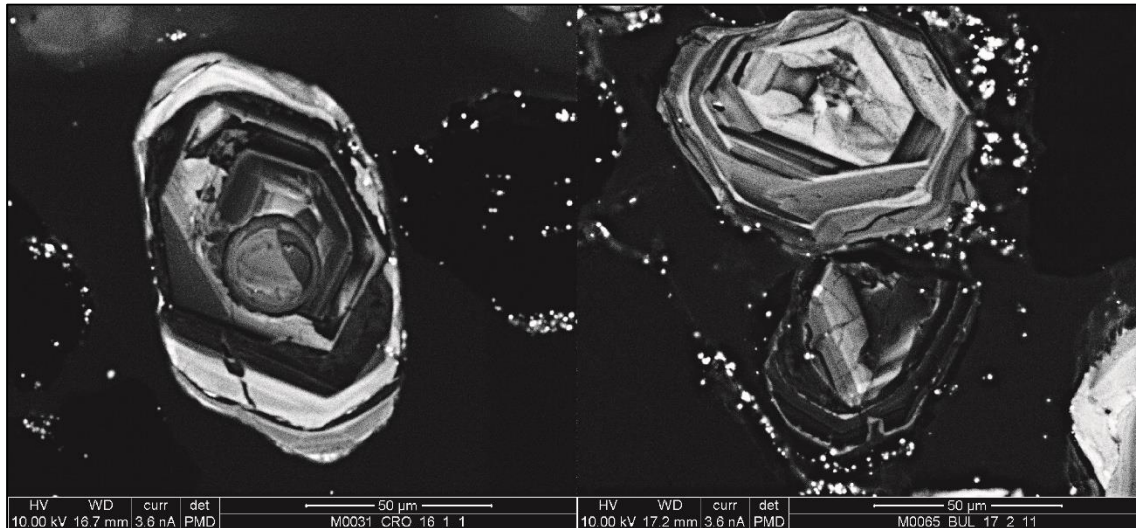


Figure 3.11 CL images of examples of zircon grains observed in two samples CRO16/1/1 and BUL17/2/11.

3.7.2.3. *Uranium-Lead dating*

Rock dating through the application of radiogenic U-Pb isotopes is one of the oldest, most reliable and precise, geochronological approaches (von Eynatten and Dunkl, 2012). It is based on the decay chain of two uranium isotopes, ^{238}U and ^{235}U , and uses the ratio of parent to daughter isotopes (Figure 3.12). Due to the relative abundance of uranium bearing minerals and their long half-life, this geochronological technique is applicable to a range of timescales and geological systems. In this research the geochronological information preserved by zircons, i.e. the timing of formation, is used as the proxy for source area identification. It provides a means of establishing links between the zircons in the loess samples and the zircon in parent rocks.

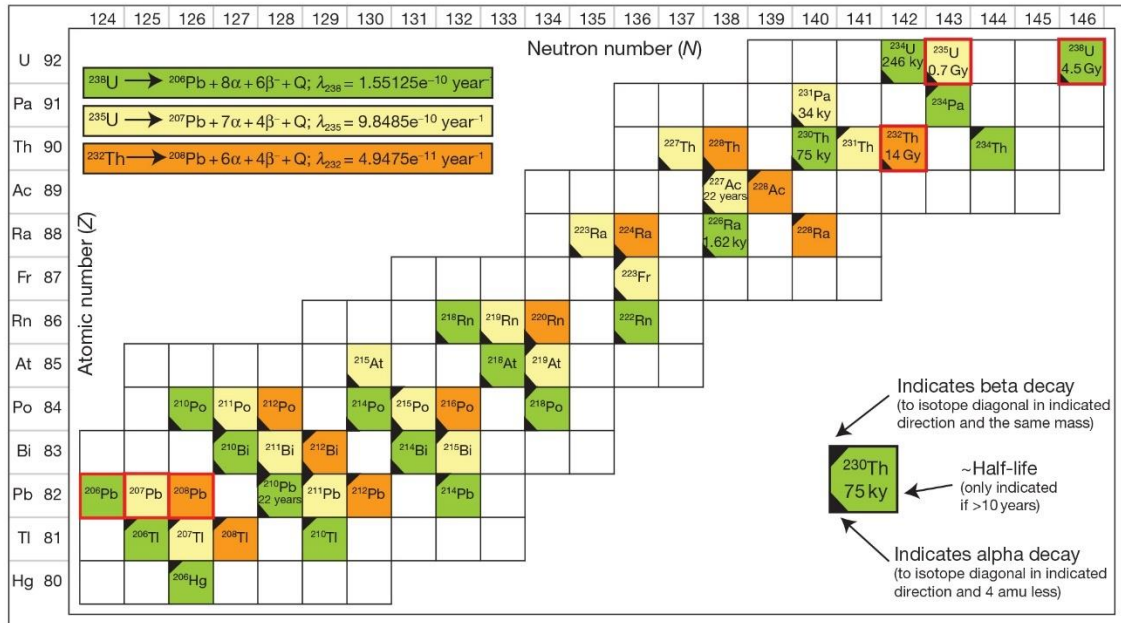


Figure 3.12 U-Th-Pb decay chains with each decay chain colour coded. Both parent and daughter isotopes are highlighted in red (Schoene, 2014).

Zircon is by far the most commonly selected mineral for a U-Pb geochronology, due to its abundance and relatively high U-content. Zr^{4+} and U^{4+} atoms have the same ionic charge and relatively similar ionic radius (0.9 Å and 1.05 Å, respectively), therefore uranium easily substitutes for zirconium atoms and is incorporated into the crystal lattice during the crystallisation process (Deer *et al.*, 1992). Conversely, Pb^{2+} is much larger, 1.32 Å, and has a lower charge making it relatively incompatible with the zircon's structure. Therefore, after the crystallisation process is concluded, zircon becomes a closed system with a initially low non-radiogenic lead content (Faure, 1986). As the parent isotopes follow a sequence of alpha and beta decays to create daughter isotopes, age equations can be developed based on separate and independent decay systems, and used to calculate ages.

$$\left(\frac{^{206}\text{Pb}}{^{238}\text{U}} \right) = (e^{\lambda_{238}t} - 1)$$

Equation 3.4. $^{206}\text{Pb}/^{238}\text{U}$ isochron equation, t is the time since system closure and λ_{238} is a decay constant of ^{238}U .

$$\left(\frac{{}^{207}\text{Pb}}{{}^{235}\text{U}}\right) = (e^{\lambda_{235}t} - 1)$$

Equation 3.5. ${}^{207}\text{Pb}/{}^{235}\text{U}$ isochron equation, t is the time since system closure and λ_{235} is a decay constant of ${}^{235}\text{U}$.

A crucial requirement in deriving reliable ages is that the system remains closed on geological timescales. By plotting the results of equations 3.4 and 3.5, i.e. ${}^{206}\text{Pb}/{}^{238}\text{U}$ against ${}^{207}\text{Pb}/{}^{235}\text{U}$, a concordia curve can be constructed. This tests, if the system in fact remained closed since formation as data will fall on the concordia line where both chronometers agree. The concordia diagram provides a way of screening and rejecting datapoints which are discordant due to mixing, loss of radiogenic Pb (open-system behaviour) or contamination with common Pb.

Imaged zircon mounts were analysed using two mass spectrometer systems: a Nu Instruments AttoM single-collector inductively coupled plasma mass spectrometer (SC-ICP-MS), and a Nu Plasma HR multi-collector mass spectrometer (MC-ICP-MS). Samples were ablated using a New Wave Research 193SS solid state laser ablation system. Ablation parameters, tuned to the U and Pb content of the analysed detrital zircons and standards, were as follows: 10 Hz repetition, with fluence of 2-2.5 Jcm⁻² and a 600 ml/min helium flow. All samples were analysed using a 20 µm laser spot, with a 20 second laser warmup/sample washout, and a 30 second laser ablation dwell time (full analysis parameters are presented in Table 3.8).

Instrument mass bias and depth dependent inter-element fractionation of U, Pb, and Th were corrected for by regular measurement of three standards; 337.13±0.37 Ma Plešovice zircon (Sláma *et al.*, 2008); 1065.4±0.3 Ma 91500 (Wiedenbeck *et al.*, 1995); and GJ-1 (unpublished TIMS analysis, see Table 3.8). All data were processed using a combination of Iolite data reduction software and IsoplotR.

For grains < 1.2 Ga, the $^{206}\text{Pb}/^{238}\text{U}$ age was used, whereas for older grains, the $^{207}\text{Pb}/^{206}\text{Pb}$ age was preferred. Data was screened for concordance as follows. For grains <1.2 Ga analyses with < $\pm 5\%$ discordance were accepted, whereas for grains >1.2 Ga a wider $\pm 10\%$ discordance was accepted, accounting for a higher degree of Pb-loss in older, especially Archaean populations. Raw data including element concentrations, ratios, and ages are presented in Appendix E Table A.3.

Table 3.8. Machine protocol used during the LA-ICP-LA U-Pb zircon analysis.

Laboratory & Sample Preparation	
Laboratory name	Geochronology and Tracers Facility, British Geological Survey
Sample type/mineral	Zircon
Sample preparation	Conventional mineral separation, 1 inch resin mount, 1 μm polish to finish
Imaging	CL, 10nA, 16mm working distance
Laser ablation system	
Make, Model & type	ESI/New Wave Research, UPI93SS
Ablation cell & volume	NIGL low volume cell, with low effective volume (ca. 3-4 cm^3), washout time ca.1sec
Laser wavelength (nm)	193 nm
Pulse width (ns)	3-4 ns
Fluence ($\text{J}\cdot\text{cm}^{-2}$)	2.0-2.5 $\text{J}\cdot\text{cm}^{-2}$
Repetition rate (Hz)	10 Hz
Ablation duration (secs)	30 secs
Ablation pit depth/ablation rate	16 μm pit depth, measured using an optical microscope and by SEM, equivalent to 0.08 μm /pulse
Spot size (μm)	20 μm
Sampling mode/pattern	Static spot ablation
Carrier gas	100% He, Ar make-up gas
Cell carrier gas flow (l/min)	0.6 l/min
ICP-MS Instrument	
Make, Model & type	Nu Instruments HR MC-ICP-MS

Sample introduction.	Free air aspiration of desolvator
RF power (W)	1200W
Make-up gas flow (l/min)	0.6l/min Ar
Detection system	Discrete dynode MassCom ion counters / Faraday array
Masses measured	202, 204, 206, 207, (+/-208), (+/-232), 235 or 238
Integration time per peak (ms)	ca. 200 ms
Integration time/reading	Ca.1 sec
Sensitivity /	Not determined
IC Dead time (ns)	15 ns
Data Processing	
Gas blank	>30 second on-peak zero subtracted using Iolite
Calibration strategy	91500, GJ1, Plešovice (zircon)
Reference Material info	91500 (Wiedenbeck <i>et al.</i> , 1995); Plešovice (Sláma <i>et al.</i> , 2008); GJ1 $^{206}\text{Pb}/^{238}\text{U}$ $602.3 \pm 1\text{Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}$ $609.2 \pm 0.7\text{Ma}$ (in-house TIMS, unpublished)
Data processing package used	Nu Instruments TRA acquisition software, Iolite v3.6, IsoplotR
Mass discrimination	$^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ normalised to ref. material
Common-Pb correction	No common-Pb correction applied to the data
Uncertainty level & propagation	Ages in the data table are quoted at 2-sigma absolute, propagation is by quadratic addition.
Quality control / Validation	See data table for validation results

3.7.2.4. Hafnium isotopes

Geochronological data recorded in zircon grains has been key in loess provenance studies, however it provides only a one-dimensional source information. The addition of a second line of evidence, such as the Lu-Hf isotope system recorded within zircon grains, can be critical in distinguishing between grains of similar ages but originating from different crustal settings (Veevers *et al.*, 2005).

Zircons are predominantly composed of ZrO_2 and SiO_4 (98%), but HfO_2 and trace elements and REE may make up to several percent (Knudsen *et al.*, 2001). The relative high concentration of hafnium means that it is possible to investigate the Lu-Hf isotope system using laser ablation. Through β emission the unstable ^{176}Lu decays into stable ^{176}Hf . The differences in $^{176}\text{Hf}/^{177}\text{Hf}$ values and Lu/Hf can be used both as an additional geochronological technique and geochemical tracer (Vervoort, 2013). Both Lu and Hf are quite immobile and incompatible. However, Lu substitutes easier than Hf ions and as the mantle melts, a fractionation of Lu from Hf occurs. This process results in a mantle depleted in Hf, with a higher Lu/Hf ratio and a high time-integrated $^{176}\text{Hf}/^{177}\text{Hf}$ ratio. Continental crust material, on the other hand, becomes enriched in Hf relative to Lu, and therefore has low Lu/Hf and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios (Kinny and Maas, 2003). Zircon has very low Lu/Hf ratios, and so it preserves the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of magma from which the mineral crystallised. It is therefore possible to discriminate between zircons derived from primitive, mantle-derived melts from those derived by melting of ancient crust using the isotope composition of hafnium within the crystal. The Lu and Hf isotopic composition of mantle has evolved through time as low Lu/Hf melt has gradually been extracted. An estimate of the hafnium isotope composition of bulk earth is based on the composition of chondritic meteorites, referred to as the chondritic uniform reservoir (CHUR). ϵHf can be calculated (Equation 3.6) as a reference to CHUR, to provide a deviation baseline for samples.

$$\epsilon\text{Hf}_t = \left[\frac{\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}} \right)_t}{\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}} \right)_{\text{CHUR}}} - 1 \right] \times 10000$$

Equation 3.6. Epsilon Hf equation.

Zircons that have crystallised from depleted magma (high Lu/Hf and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios) will therefore have positive ϵHf values. This indicates a juvenile crust, effectively derived straight from the mantle. Examples include oceanic crust sources, such as island arcs (e.g. 4.2-16.9 ϵHf ; Iizuka *et al.*, 2013), ocean island basalts or mid-ocean ridge basalts (mean 14-15 ϵHf (Chauvel *et al.*, 2008; Iizuka *et al.*, 2017; Vervoort *et al.*, 1999)). On the other hand, zircons originating from continental crust material (low Lu/Hf and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios) will have negative ϵHf values. This is particularly evident when analysis ϵHf from basement melts, with average $\epsilon\text{Hf} = -13.2 \pm 2$ calculated for the upper continental crust (based on bulk sample; Chauvel *et al.*, 2014). Therefore the combination of values from the same age population can help imply whether source had pure mantle inputs, continental, or mixture of both and recycling of older crust was taking place (Reid and Payne, 2017).

Hf-isotope analysis was conducted at BGS, using a Thermo Scientific Neptune Plus MC-ICP-MS coupled to a New Wave Research 193UC Excimer laser ablation system. Measurements were carried out with helium as the carrier gas. A static 30 second ablation was used to simultaneously analyse lutetium (^{175}Lu), ytterbium (^{172}Yb , ^{173}Yb), and hafnium (^{176}Hf , ^{178}Hf , ^{179}Hf and ^{180}Hf) isotopes. The spot size used was 25 μm ; fluence = 7-10 J cm^{-2} .

The terrestrial ^{176}Lu decay constant ($\lambda^{176}\text{Lu}$) of $1.867 \times 10^{-11} \text{yr}^{-1}$ (Söderlund *et al.*, 2004), CHUR $^{176}\text{Lu}/^{177}\text{Hf}$ value of 0.0336 and $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.282785 (Bouvier *et al.*, 2008), were used in all ϵHf calculations. To correct for instrument error and normalise the data throughout the analysis standards were measured at regular intervals. The mean $^{176}\text{Hf}/^{177}\text{Hf}$ values for the standards are as follows: 0.282313 ± 0.000008 (2σ) for 91500 (Blichert-Toft, 2008); 0.282507 ± 0.000006 for Mud Tank (Woodhead and Hergt, 2007); and 0.282482 ± 0.000013 (2σ) for Plešovice (Sláma *et al.*, 2008).

Hf-isotope data processing was conducted using an Iolite data reduction package. All raw and standard data can be found in the Appendix F Table A.4.

3.7.3. Major and trace elements

While single-grain approaches form the core of the provenance analysis in this thesis, bulk sample geochemistry has formed the basis of provenance research in European loess (Buggle *et al.*, 2008; Galović, 2014; Obreht *et al.*, 2016; Újvári *et al.*, 2008, 2014b). The results of bulk sample analysis are not comparable with zircon U-Pb and Hf analysis. Therefore in order to aid a comparison with previous provenance studies a bulk sample geochemical analysis is also attempted. This could also add a source of information, and potentially discrimination, to the provenance analysis conducted as a part of this thesis.

Inductively coupled plasma–mass spectrometry is a destructive elemental analysis method. It uses high temperature argon plasma to dry out samples (introduced into the machine as an aerosol) and separates molecules into ions which are then separated and measured according to their mass-ratio by the mass spectrometer. This approach was chosen because it only requires small sample sizes, yet the detection limits can reach ppt at a relatively high level of precision.

ICP-MS was carried out at the BGS to measure concentrations of major and trace elements within bulk sediment samples. Prior to measurement samples were oven-dried overnight and powdered using a pestle and mortar.

Measurements included 9 major and minor elements (Al, Ca, Mg, Na, K, Fe, Ti, Mn, P) as percentage oxides and 44 trace elements (V, Cr, S, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Cs, Ba, Tm, Hf, Ta, W, Tl, Pb, Bi, Th, U, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Yb, and Y) at ppm levels (full data included in Appendix F Table A.5). Standards (CRM- Basalt) were periodically measured as well as repeats of individual samples.

3.7.4. Data visualisation and statistical analysis

3.7.4.1. Zircon age distribution

Once processed, all zircon data were plotted using IsoplotR statistical software (Vermeesch, 2018a) and Compare Detrital Zircon Suites ‘*detzrcr*’ R-package (Andersen *et al.*, 2018).

In detrital zircon studies, age distributions aim to characterise numerous source populations in often very large datasets (Bird *et al.*, 2015; Fenn *et al.*, 2018; Stevens *et al.*, 2010). This presents serious data visualisation and summary challenges, that are not encountered in metamorphic and igneous studies. In those instances zircon ages from a single sample constrain an age of one event (Drost *et al.*, 2011; Gehrels *et al.*, 2011; Kebede *et al.*, 2005; Sláma *et al.*, 2008) and Wetherill or Tera-Wasserburg concordia plots are more commonly used. The two most encountered plots in detrital zircon studies are Probability Density Plots (PDPs) and Kernel Density Estimation (KDE) (Figure 3.13).

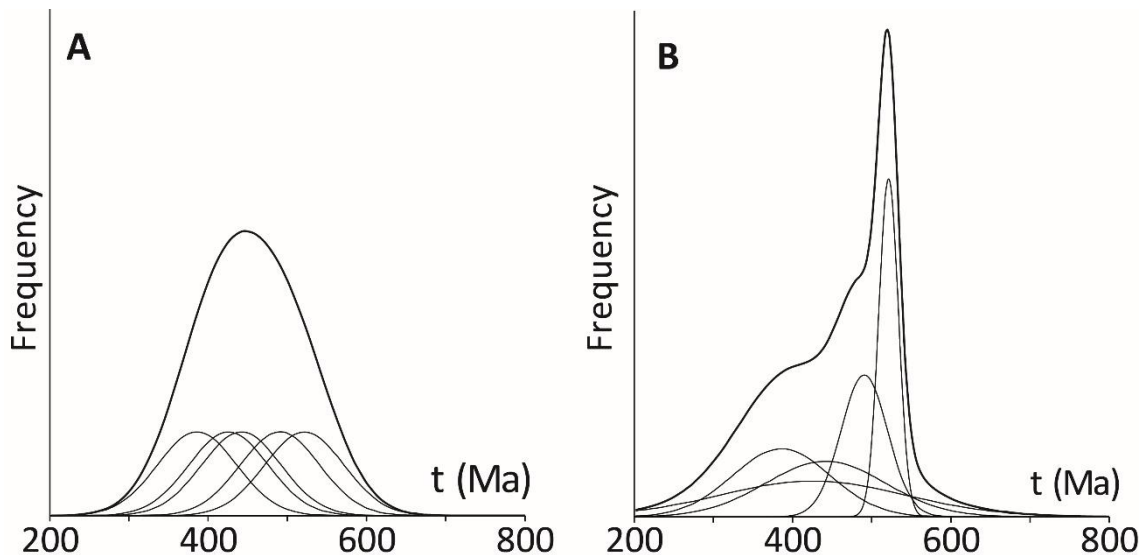


Figure 3.13. Theoretical stacked normal distributions A) Kernel Density Estimation B) Probability Density Plots (Vermeesch, 2012).

Probability Density Plots (PDPs) are a graphic method that in their simplest form are a smoothed histogram of the observed age(s). They became very popular through the user friendly software Isoplot and AgeDisplay (Ludwig, 2003; Sircombe, 2004), though the statistical method behind these plots has still not been explored (Galbraith, 2010). PDPs are produced by stacking Gaussian distributions on top of each other (Figure 3.13B), with the bandwidth representing measurement uncertainty (Vermeesch, 2012). While at first glance it may appear useful to include analytical errors, it has been shown that by doing so the PDPs can instead obscure the true ages and lead to erroneous interpretations (Galbraith, 1998). The standard deviation used by the plot is different for each measurement, and therefore each datapoint does not influence the shape of the PDP in the same way. In the simplest terms this method adds weight to measurements with high precision. However the PDPs density function averages the precision between the “datapoints” to create the shape of the curve (Galbraith, 2010), and oversmooths the diagram (Figure 3.14C bottom). This may not be an issue if all measurements are precise but, in the situations where a mixture of precise and imprecise analysis are included, the true age will be offset (Figure 3.14C bottom row). Additionally, the second population is also oversmoothed. Even when the bi-modal distribution is composed of two precise analyses, PDPs can also produce a series of spikes (Figure 3.14C top row).

A Kernel Density Estimation (Vermeesch, 2012) also provides a probability plot of zircon U-Pb age distributions. This approach also stacks Gaussian distributions on top of each other, however here the standard deviation represents the local probability density (Figure 3.12A). The approach itself is also grounded and supported by statistical literature (cf Vermeesch, 2012). Figure 3.14B shows that in the case of two precise measurements KDE (top row) represents the true age distribution very well. The bottom row of Figure 3.14B shows that in the scenario where a mixture of precise and imprecise ages are included, the population estimates are approximated very well. Vermeesch (2012) argued that an

analytical error does not have to be included in the density analysis as sampling and measurements have already accounted for this. Therefore, KDE has been chosen in the research as the most appropriate visualisation methods for the zircon age distributions.

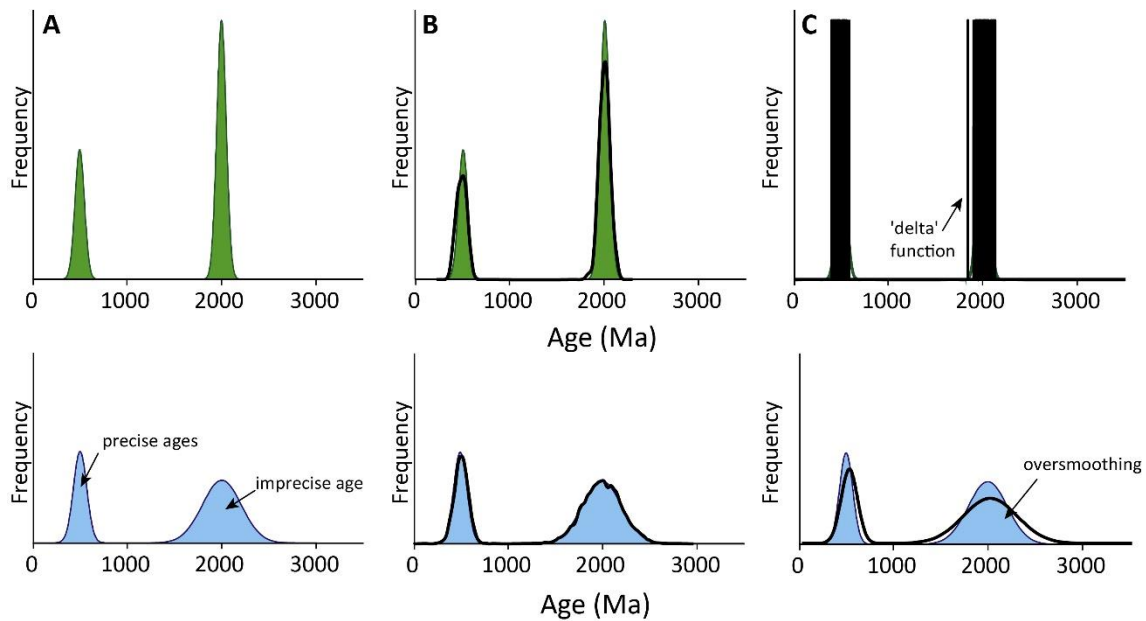


Figure 3.14 A comparison of the age distribution by the PDP and KDE diagrams in two case scenarios; two high precision measurements (top row) and a mixture of precise and imprecise ages (bottom row). A) True age distribution B) Kernel Density Estimation C) Probability Density Plot. In both cases the bottom row in B and C is based on 10000 randomly selected analyses (adapted from Vermeesch, 2012).

There are several parameters that can be adjusted by the user. The type of the 'kernel' can be chosen as e.g. triangle, normal (Gaussian), or Epanechnikov; it has been shown that the choice of kernel does not impact the results greatly in detrital zircon research (Vermeesch, 2012). However, the choice of bandwidth (the width of the kernel) has been shown to be crucial and will affect whether the function is under- or over- smoothed (Figure 3.15). In most software the bandwidth can be specified manually by the user or selected automatically by the programme based on best fit (Andersen *et al.*, 2018; Vermeesch *et al.*,

2016). In this research a bandwidth of 25 Ma was selected for all samples as this achieved a balance between under- and over- smoothing (Figure 3.16).

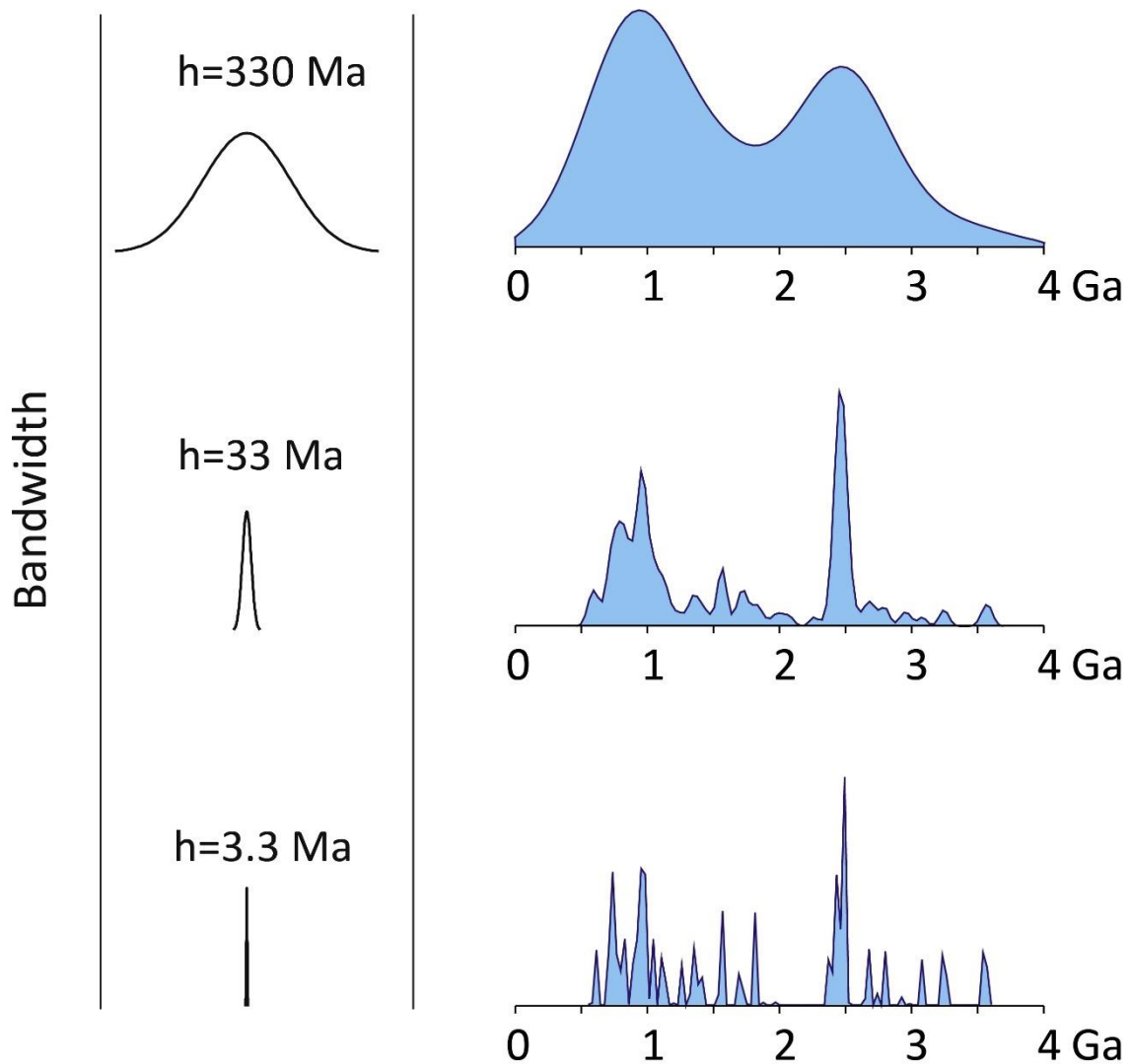


Figure 3.15 The impact of bandwidth selection on the shape of KDEs (adapted from Vermeesch, 2012).

Additionally, both IsoplotR and detzrc provide an option to plot Cumulative Age Distributions (CADs) which are just simple cumulative distribution plots (Vermeesch, 2007). These plots provide a visual measure of distribution without smoothing and are recommended to support the KDE diagrams as they add insights into the ages where the diagrams diverge (Vermeesch *et al.*, 2016).

These steps alone cannot identify similarities between samples, as the datasets are too big and neither of these approaches incorporate uncertainties (Vermeesch, 2018a), they are both valuable tools. They help to understand the individual distributions, and provide clues as to the dominant ages and groupings between datasets.

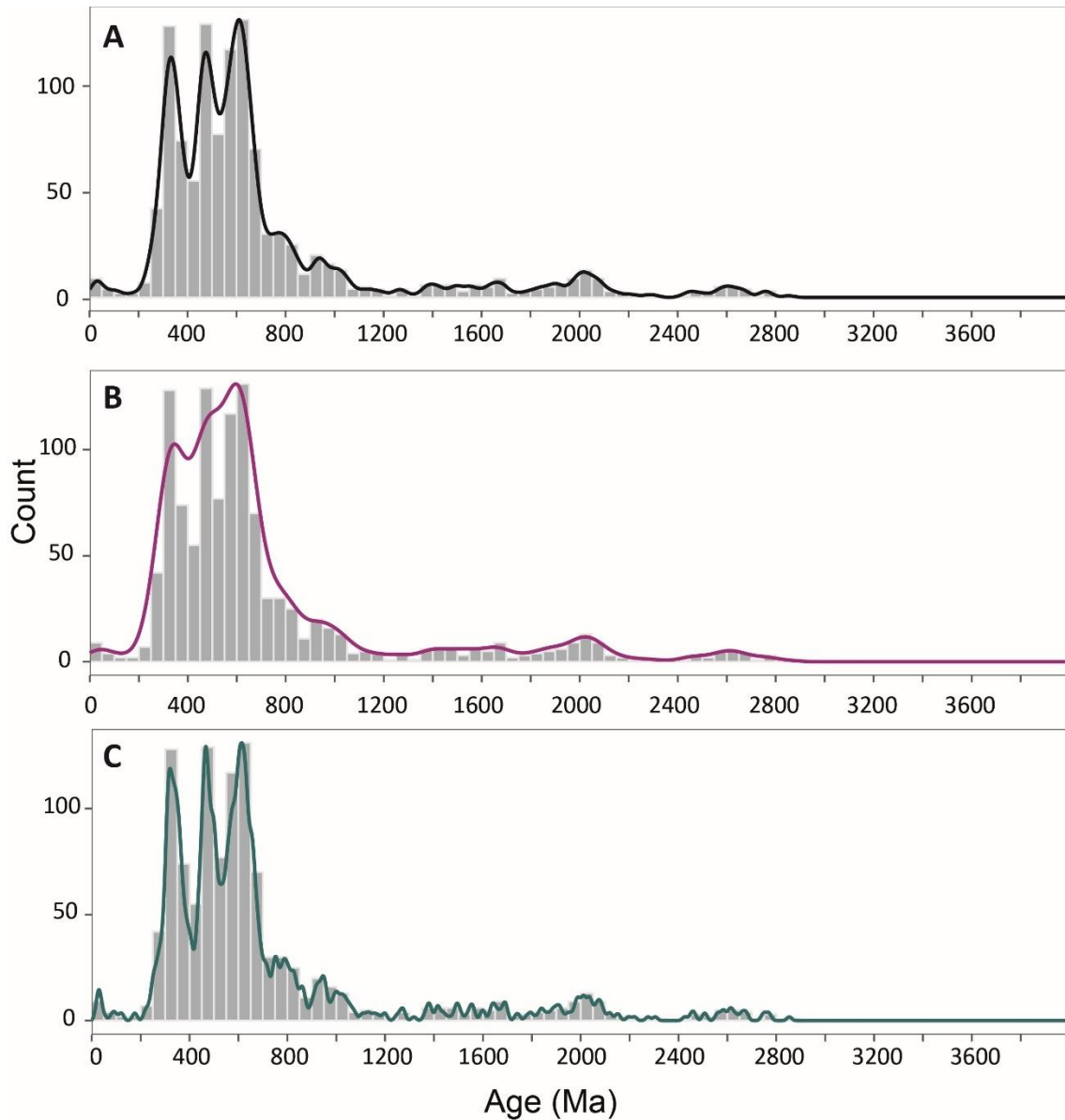


Figure 3.16. Kernel Density Estimation for Slivata based on A) 25 Ma bandwidth, B) 50 Ma bandwidth, C) 10 Ma bandwidth. Diagram is based on 1309 grains.

3.7.4.2. Comparing zircon ages – Multidimensional Scaling (MDS)

While KDEs and CADs provide a very helpful visual first step in understanding detrital zircon populations within individual samples, a visual approach of a large number of datasets is both impractical and imprecise. This study has produced 31 zircon datasets which includes analysis of over 3337 grains. The addition of published source, loess and sedimentary features datasets requires a comparison and discrimination of over 13193 grains. This shows how complex and unreliable a visual only assessment would be.

A number of ways to statistically assess differences between samples have been proposed (c.f. Andersen, Kristoffersen and Elburg, 2018). Multi-dimensional scaling (MDS; Vermeesch, 2013) and 3-way MDS (Vermeesch and Garzanti, 2015) statistical techniques were developed to provide a more objective way of comparing datasets, as well as combining a number of provenance techniques into a single assessment of similarities in a visually appealing way. MDS has been readily utilised in loess provenance studies, especially since the increased speed of the ICP-MS methods which lead to the production of vast datasets (Bird *et al.*, 2015; Fenn *et al.*, 2018; Nie *et al.*, 2015; Rittner *et al.*, 2016).

This approach is closely related to Principal Component Analysis (PCA) but makes fewer assumptions about the structure of datasets. MDS statistically simplifies datasets by reducing them into two-dimensional ‘maps’, where similar data points are plotted in clusters and dissimilarities are mapped as far apart (Figure 3.17). The distance between points is calculated based on a Kolmogorov-Smirnov (KS) statistic (Vermeesch, 2013), which approximates distance in a mathematical sense (Vermeesch, 2018a, 2018b). The “non-metric” algorithm is used in all MDS configurations used in this research as dissimilarities are ranked rather than approximated. The results are plotted on the dimensionless MDS plot and range from -1 to 1. Additionally, lines of similarity can be

added (Figure 3.17) where solid lines represent the most similar age distributions and dashed lines point to the second most similar sample.

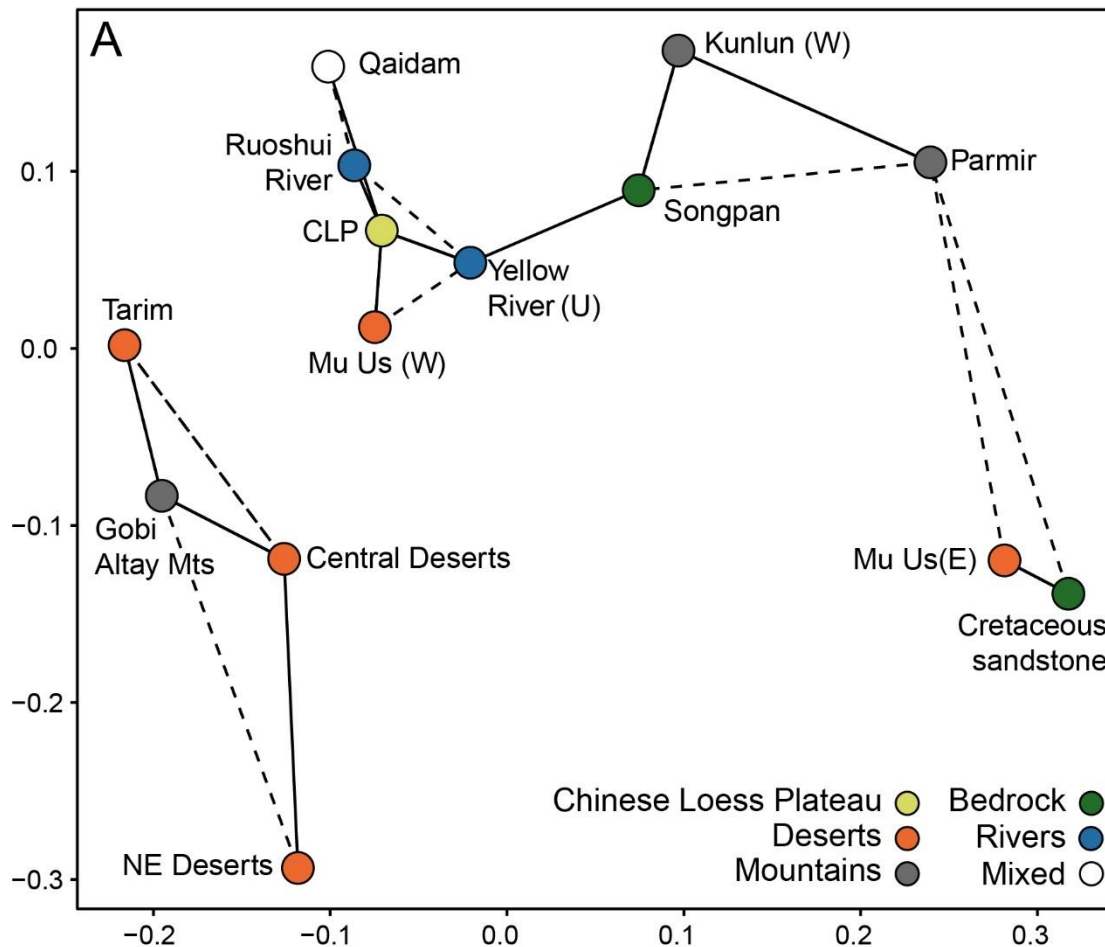


Figure 3.17 Example of an MDS plot (adopted Fenn *et al.*, 2018).

The modes of the age distributions strongly influence the KS statistics, meaning that this approach is not so sensitive to the tails of the distributions. Based on the analysis of the Chinese Loess Plateau deposits Fenn *et al.* (2018) argued that, that it is the tails that are likely to be responsible for the variability between loess samples, rather than the peaks. Therefore, it is worth noting that MDS maps may not provide a full picture of the differences between samples. When plotting MDS maps that included published samples, datasets with a small number of grains were removed (if they could not be combined) as

these would statistically appear different and therefore skew the MDS maps. Samples with grains $n < 50$ were excluded.

3.7.4.3. Hafnium isotopic-age distributions

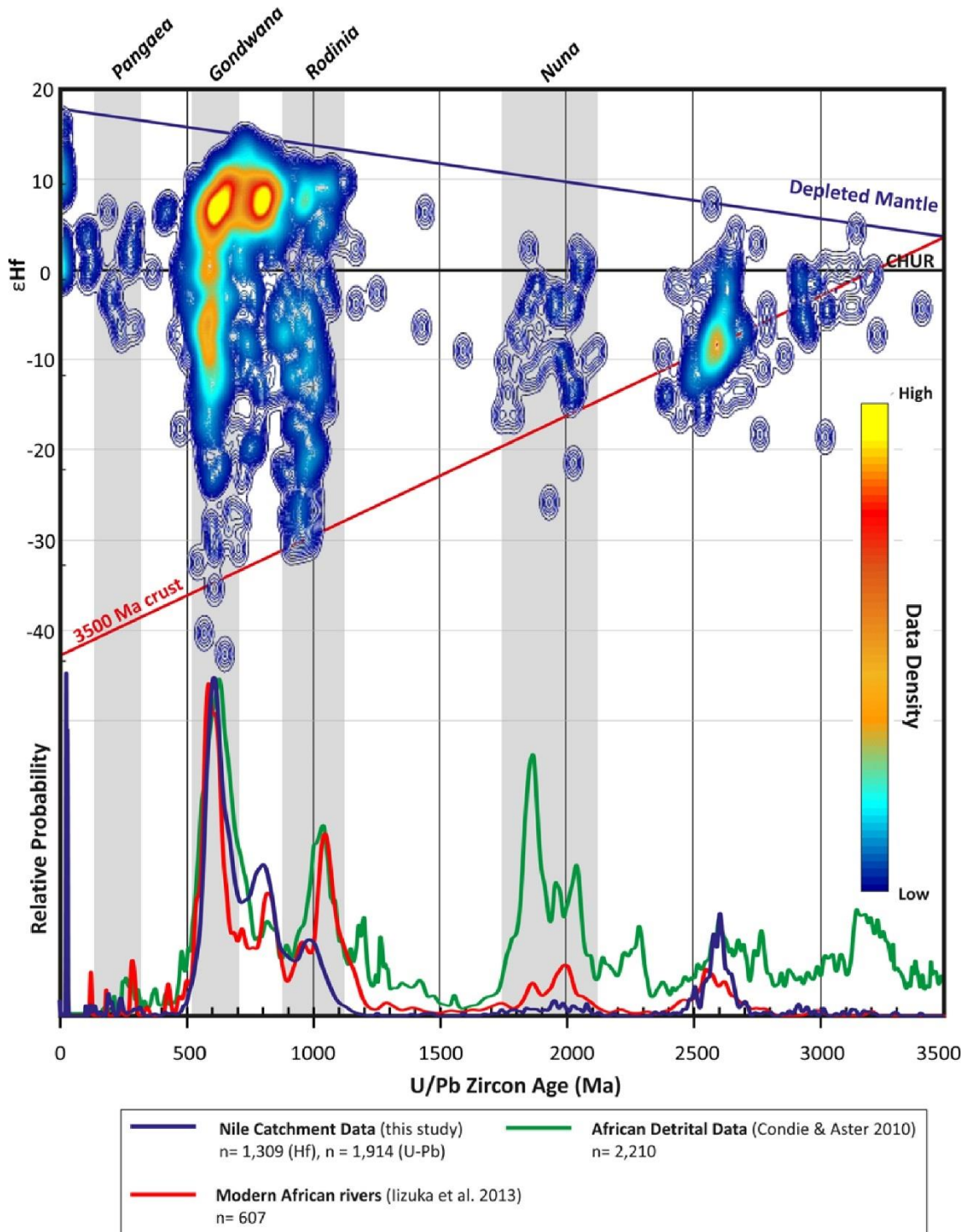


Figure 3.18 An example of a probability density plot for Hf isotope evolution through time (adopted from Fielding *et al.*, 2017).

Hafnium isotopic results can be combined with U-Pb dating results to construct isotopic evolution over time, where the ϵHf value from each grain is plotted against its age. The data are assessed with respect to the CHUR and depleted mantle (DM) lines (Figure 3.18). The depleted mantle line plots the modelled evolution of the Earth's mantle ϵHf values over geological time from the “primitive” chondritic composition, using the decay constant. This shows that since its formation the mantle's ϵHf has been increasing and the crust formed from modern melts have strongly positive ($\epsilon\text{Hf} > 15$) values. As Chondritic Uniform Reservoir values are used to normalise Hf, points with a value of zero fall on the CHUR line. This means that zircons with $\epsilon\text{Hf}=0$ crystallised from magmas that have a composition similar to the chondritic unfractionated reservoir or ones derived from older crust. Grains that fall between the CHUR and DM lines (i.e. $+\nu \epsilon\text{Hf}$) are interpreted as sourced from juvenile magmas, such as mid-oceanic ridges and oceanic island arcs, while grains that plot underneath the CHUR line (i.e. $-\nu \epsilon\text{Hf}$), represent zircons crystallised from re-melted crust. Moreover, lines of ϵHf evolution for rocks crystallised at a specific point in time can be added to determine the source of the negative value contributions. For example, Figure 3.18 shows that the very strongly negative ϵHf cluster values at 900 Ma can be explained by contributions from melting of the 3500 Ma crust.

Where large numbers of analyses were investigated (e.g. overall Danubian loess provenance or variability at each site), individual data points were converted into bivariate Kernel Density Estimation plots in R following (Botev *et al.*, 2010). This is a relatively recent method (Armistead *et al.*, 2018; Fielding *et al.*, 2017; Spencer *et al.*, 2019; Wang *et al.*, 2020; Yao *et al.*, 2018) which is particularly useful where datasets with >1000 grains are compared (Figure 3.18). Some of the results of this study aim to compare results of

~3000 Hf analyses with published datasets, therefore KDE plots were selected for the analysis. This is the same kernel density estimation as the one used for the zircon U-Pb data, however two bandwidths can be specified. Here one epsilon was selected for ϵ_{Hf} (y-axis) and 20 Ma for U-Pb ages following the suggestion of Spencer *et al.* (2019).

SUMMARY

This Chapter outlines the detailed methods used to conduct this research. To provide a chronology, multiple approaches are explored, including tephrochronology, quartz OSL, feldspar pIRIR IRSL, and polymineral pIRIR IRSL dating. To understand the sediment source, single grain zircon U-Pb dating is utilised and supplemented by *in-situ* Hf isotopical analysis. These results are complemented by bulk sample elemental geochemical analysis. Finally, at the Bulgarian site, detailed particle size and magnetic susceptibility investigations were carried out to aid in the understanding of the Quaternary environmental and climatic signal at the time of deposition.

Therefore, this Chapter presents the diversity of methods applied in both geochronological and provenance lines of investigation, indicating the thorough approach of this research.

Chapter 4: Paper 1

A 180 ka record of environmental change at Erdut (Croatia): a new chronology for the loess-palaeosol sequence and its implications for environmental interpretation.

Paper 1: Fenn Kaja, Durcan, Julie A., Thomas, David S.G., Banak Adriano

Status: Published in *Journal of Quaternary Science* (5th May 2020)

Abstract

While there are numerous thick, loess-palaeosol sequences preserved across the Carpathian Basin, well dated sites that provide terrestrial palaeoenvironmental records extending beyond last glacial-interglacial cycle are scarce. Robust chronologies are essential for correlations of loess with other long-term Quaternary records and furthering understanding of the palaeoenvironment and climate of this important region beyond the last 125 ka. Here a new geochronology based on 13 post-infrared infrared (pIRIR) stimulated luminescence ages focused on the lower part of the loess-palaeosol sequence at Erdut is presented. The results show that the lower part of the Erdut profile spans the penultimate glacial cycle (MIS 7 to MIS 5). The considerable sediments overlaying the investigated part of the profile suggest this section spans two glacial cycles, rather than the previously suggested one. The most likely source of the discrepancy is the use of uncorrected infra-red stimulated luminescence (IRSL) signal, which can cause age underestimation if not accounted for. This study demonstrates the need to revisit sites such as Erdut, re-date them using updated measurement protocols, and update existing palaeoenvironmental interpretations.

4.1. Introduction

Loess-palaeosol sequences are important terrestrial archives often preserving near-continuous and high-resolution sedimentary records. They often span multiple glacial-interglacial cycles and offer long term Quaternary records in regions where other long-term archives are frequently absent. Therefore they provide a unique insight into the Earth's past and an opportunity to compare and correlate terrestrial signals with ice- and marine- core records (Antoine *et al.*, 2009a; Kukla, 1977; Stevens *et al.*, 2018).

Central European loess deposits, especially along the Danube River, are particularly thick, with a number of sites extending beyond the last glacial-interglacial cycle, including in Bulgaria (Jordanova *et al.*, 2008), Croatia (Galović *et al.*, 2009; Wacha and Frechen, 2011), Hungary (Thiel *et al.*, 2014; Újvári *et al.*, 2014a), Romania (Balescu *et al.*, 2010; Vasiliniuc *et al.*, 2012), and Serbia (Murray *et al.*, 2014; Schmidt *et al.*, 2010). Consequently, in terms of capacity to generate long palaeoclimate and palaeoenvironment signals in Central and Southeastern Europe, loess archives are only matched by a very limited number of lacustrine records, e.g. Lake Ohrid, Macedonia (Lacey *et al.*, 2016), Tenaghi Philippon, Greece (Tzedakis *et al.*, 2006), or Lake Ioannina, Greece (Roucoux *et al.*, 2011).

Despite their potential as palaeoarchives, loess-palaeosol sequences often suffer from a lack of robust, high-resolution, absolute chronologies. Traditionally, researchers have relied on broad stratigraphy e.g. position and number of palaeosols (Marković *et al.*, 2015), geomagnetic polarity reversal tie points (Marković *et al.*, 2011; Sümegi *et al.*, 2018), and sedimentological correlations with distant ice cores (An, 2000; Antoine *et al.*, 2009a; Rousseau *et al.*, 2002). However, these methods assume continuous deposition and the absence of erosion, which has since been shown to be erroneous (Stevens *et al.*, 2006, 2018). In addition, stratigraphic correlations has proven more complicated than originally thought, for example single soils corresponding with multiple soils at other sites (Marković

et al., 2008), and has led to ambiguous links (cf Thiel *et al.*, 2014). Reliable and independent chronology is therefore accepted as a critical underpinning of studies covering last glacial-interglacial period, and by extension wherever possible the same requirement should be applied to studies extending beyond 125 ka.

In theory, infra-red stimulated luminescence (IRSL) dating of feldspar provides the potential to date 300-500 ka old material (Thomsen *et al.*, 2011), because feldspars' higher saturation limit. They therefore provide the opportunity to construct chronologies for loess profiles extending beyond the last interglacial period (e.g. Novothny *et al.*, 2002; Schmidt *et al.*, 2010; Wacha & Frechen, 2011). However, some feldspar signals are athermally unstable, a phenomena termed 'anomalous fading' (Wintle, 1973). This process causes feldspars to "leak" signal and results in age underestimation if not corrected for. Although corrections for the signal loss are possible (Huntley and Lamothe, 2001; Lamothe and Auclair, 1999), they can be problematic and are mainly applicable to younger samples. In 2008, Thomsen *et al.* published a post-infrared infrared (pIRIR) measurement protocol for potassium feldspar signals, which allows for a more stable signal to be accessed. Subsequently, a number of studies across the region have tested the pIRIR protocol and when compared to independent age controls such as tephra (Thiel *et al.*, 2011b), radiocarbon ages within the last 50 ka (Thiel *et al.*, 2011a; Újvári *et al.*, 2014a), or a semi-independent quartz OSL ages (Buylaert *et al.*, 2011; Schatz *et al.*, 2012), they showed the ability to accurately date loess sites extending beyond 70 ka.

Here a new pIRIR luminescence geochronology based on thirteen ages for the loess-palaeosols section at Erdut, Croatia is presented. A nearby section was investigated by Galović *et al.* (2009), but their study relied on only five luminescence ages, calculated using an additive-dose IRSL protocol. This protocol can result in large age uncertainties (Novothny *et al.*, 2010; Wacha *et al.*, 2011), and in their study, Galović *et al.* (2009) did not

investigate or correct their IRSL signals for fading, generating the potential for age underestimation.

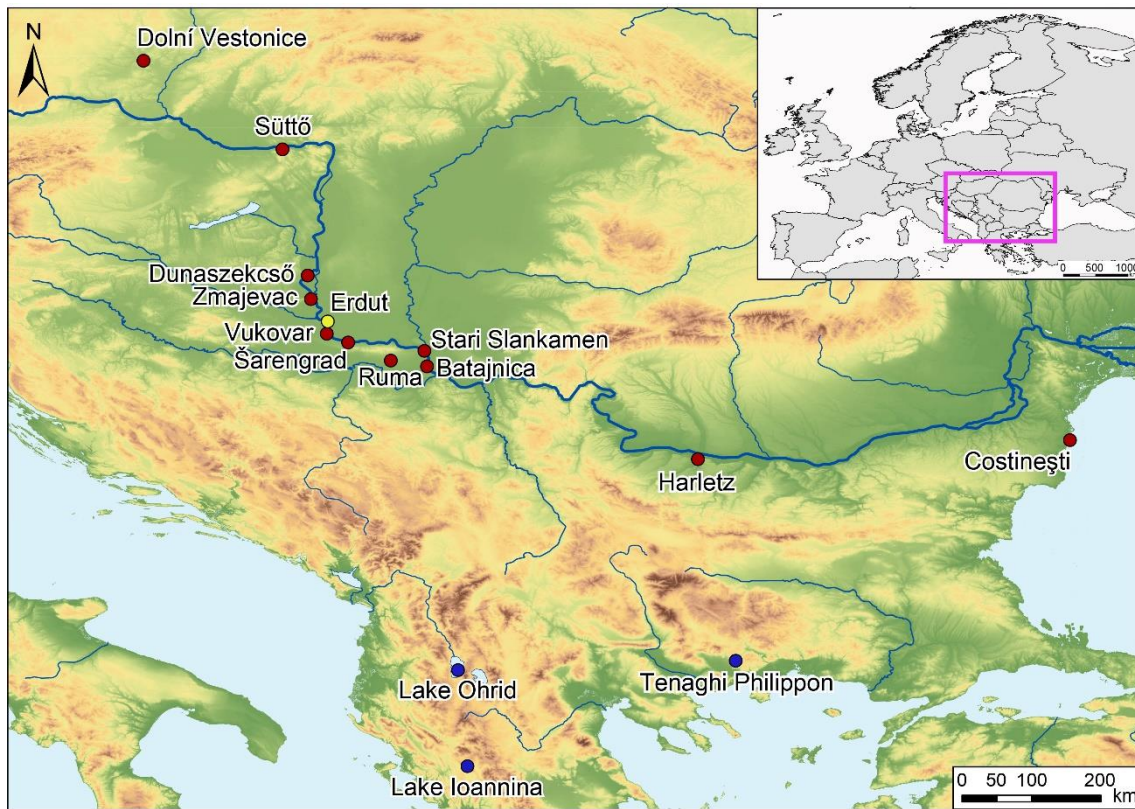


Figure 4.1 Map of the study region, study site (Erdut) and other sites discussed in the text. Yellow denotes Erdut, red other loess profiles, and blue lake sites (DEM Source: ©JAXA).

4.2. Geological setting and site description

Loess deposits in Eastern Croatia are primarily found along the Danube River valley where a number of thick sequences have been reported (Banak *et al.*, 2012; Wacha *et al.*, 2013; Wacha and Frechen, 2011). Erdut (45°30'49.78"N, 19°4'39.072"E, 97 m a.s.l) is located on the western bank of the Danube (Figure 4.1), 150 meters away from an abandoned channel and 1.2 km from the modern river. Loess-palaeosol sequences at the site are associated with a very small (~30 km²) plateau-like feature, which follows the bend of the Danube River. The feature is heavily incised by gullies on the northern side, whilst on the southern

side, exposures are not as extensive or thick. The loess outcrops on the southern side are situated on a gentle slope towards the river, with individual unit thickness decreasing in the same direction.

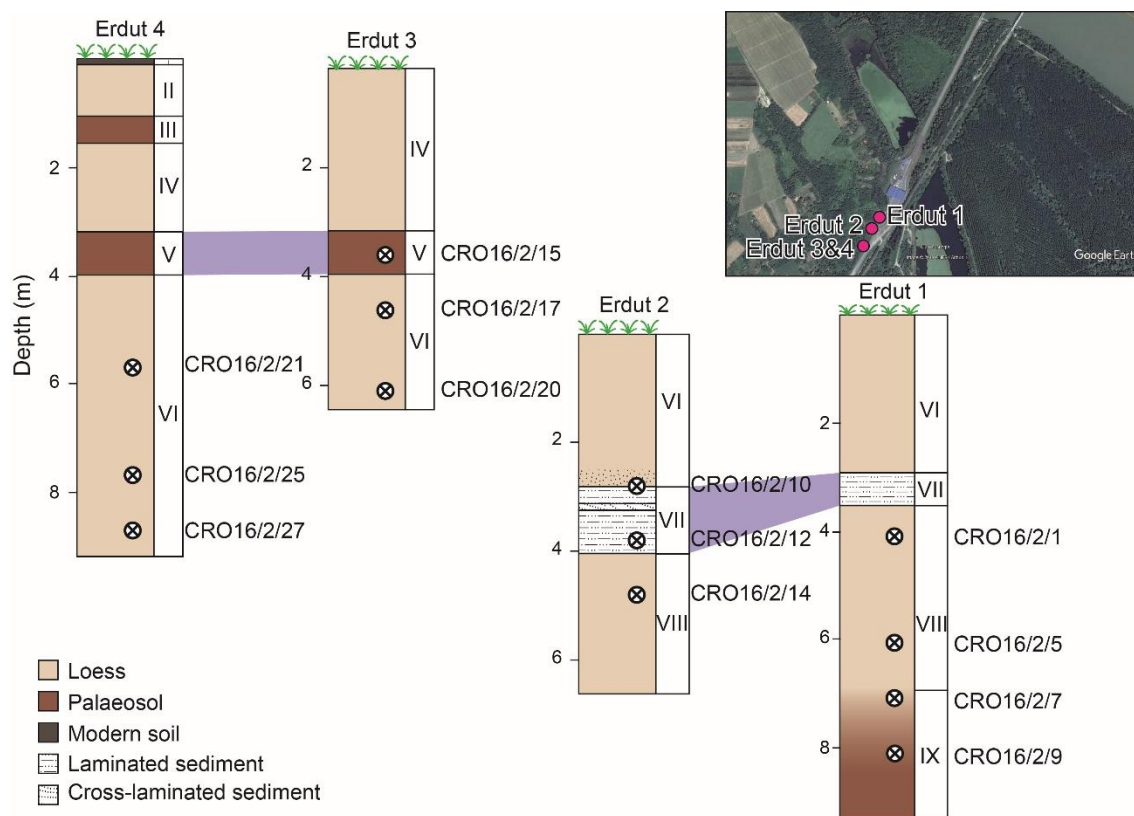


Figure 4.2 Stratigraphic logs of four profiles along a 100-meter stretch of the exposure at Erdut. Sequences are 6, 60 and 20 meters apart. Correlations between sections are based on the field observations and luminescence ages. Circles mark the position of the luminescence samples, and the field description of units I-IX are given in Table 4.1. Insert shows the location of all four profiles in relation to each other (Source: ©GoogleEarth).

This outcrop comprises three palaeosol, and three loess units one of which is punctuated by a laminated sediment (Table 4.1 and Figure 4.2). The top four units (Unit I - modern soil, Unit II, Unit III, and Unit IV) were not sampled in this study. Unit V comprises a pale brown soil (10YR 6/3) with small, granular peds and numerous small shells. Unit VI, a

thick loess layer, has a high concentration of well-preserved gastropods, 1 mm-2 cm in size, especially in its upper 2.5 meters (Figure 4.3B). The sediment is pale yellow (2.5Y 7/3), though it gradually becomes yellowish brown (2.5YR 6/4) within the first meter. The field assessment suggests that the unit coarsens downwards from silt to sandy silt. The laminated sediment, Unit VII, comprises three sub-layers: horizontal lamination (30 cm), cross lamination (10 cm) and horizontal lamination (80 cm) again. In both cases, horizontal laminations comprise a few mm thick, sheets of alternating silt and very fine sand (Figure 3A). The cross laminations are also a few mm in thickness.

Table 4.1. The field description of the sedimentary units of all profiles at Erdut.

Unit	Section and depth (m)	L-P stratigraphy	Field description
I	Erdut 4: -	SO	<i>Modern Soil</i>
II	Erdut 4: -	LILL1	<i>Loess</i>
III	Erdut 4: -	LISS1	<i>Palaeosol</i>
IV	Erdut 4: - Erdut 3: -	LILL2	<i>Loess</i>
V	Erdut 4: 3.3-4 Erdut 3: 3.2-4	SI	<i>Palaeosol</i>: At both profiles (Erdut 3 and 4) unit's structure is made of small granular peds (Figure 4.3D). <i>Palaeosol</i> is pale brown (10YR 6/3), clayey, and compacted. Small (<1 cm) unidentified gastropod shells (Figure 4.3D) abundant throughout, while small insect burrows become abundant from 3.7 m. Both boundaries are irregular but quite sharp. At Erdut 4 the unit is slightly thinner (70 cm). Top and bottom boundaries are sharp and irregular.
VI	Erdut 4: 4-9.2 Erdut 3: 4-6.5	L2	<i>Loess</i> : At Erdut 3 the loess is pale yellow (2.5Y 7/3) dry and silty. The sediment is very compacted and cemented in the top 10 cm.

	Erdut 2: -		Sediment shifts to light yellowish brown (2.5YR 6/4) at ~5.7 m.
	Erdut 1: -		An assemblage of large gastropods (2-3 cm; Figure 4.3C) is observed between 4-5 m. While a second assemblage of much smaller gastropod shells (max 1 cm) is noted between 5.6-6.1 m. At Erdut 4 the same colour changes from pale yellow (2.5Y 7/3) to light yellowish brown (2.5YR 6/4) are observed. As with Erdut 3 gastropod assemblages of varying sizes (mm to 2 cm) are abundant between 5.7-6.4 m. Additionally, between 7.5-8.2m small (1 cm) to large (>30 cm) carbonate concretions are observed. While visible at Erdut 1 and 2 these units have only observed at distance. Therefore thickness, sedimentological description is unavailable.
VII	Erdut 2:	N/A	<i>Sandy and laminated complex:</i> At Erdut 1 a 50 cm unit of horizontally laminated silt and very fine sand with sharp top and bottom boundary is observed. The unit's thickness is not uniform laterally and quickly shifts to 70 cm away from the river.
	2.4-4		At Erdut 2 Unit VII is 1.6 m thick comprise four sub-units: sandy layer (VIIa), horizontal laminations (VIIb), cross laminations (VIIc), and horizontal laminations (VIId).
	Erdut 1:		2.4-2.8 m. VIIa subunit comprise 40 cm thick of very fine, light olive brown (2.5Y 5/4)
	3.1-3.8		2.8-3.1 m. VIIb preserves 30 cm thick horizontal laminations of silt and very fine sand - mm in size and pale yellow (2.5Y 7/4) in colour. Sharp boundary with subunit above and below
			3.1-3.2 m. VIIc comprise cross laminated silt and very fine sand (10 cm). Sharp boundary with subunit above and below

			3.2-4 m. VIId subunit contains 80 cm thick horizontally laminated silt and very fine sand, pale yellow (2.5Y 7/4). At ~3.7 m multiple large (20-30 cm) multiple calcrete precipitations are seen. Sharp boundary with loess below.
VIII	Erdut 2: 4-6.6 Erdut 1: 3.8-7.1	L2	<i>Loess:</i> At Erdut 1 profile unit comprise predominantly lightly yellowish brown (2.5Y 6/4) silt though very fine sand is also present especially within the first 10 cm from the boundary. Dark Fe/Mn and lighter CaCO₃ mottles present though the unit though they increase gradually down section. At Erdut 2 unit VIII is also predominantly silty with no obvious structures. Below 5m insect burrows become very abundant
IX	Erdut 1: 7.1-8.7	S2	<i>Palaeosol:</i> Gradual transition into palaeosol (7.1-7.6 m). Fairly clay, lightly reddish brown (2.5YR 6/4) silt with dark Fe/Mn and lighter CaCO₃ mottles. Main palaeosol noted from 7.6 m based on the gradually increasing clay content to silty clay and shift in colour to lightly yellowish brown (10YR 6/4). The boundary between the two parts is defused but straight.

The final light yellowish, brown loess (2.5Y 6/4) layer (Unit VIII) is mottled throughout and full of calcified root holes. The section culminates in a light reddish brown to lightly yellowish brown clayish palaeosol (10YR 6/4 to 2.5YR 6/3). The unit grades over 1m from loess to a full soil. The total thickness of this unit could not be established as the profile could not be excavated fully.

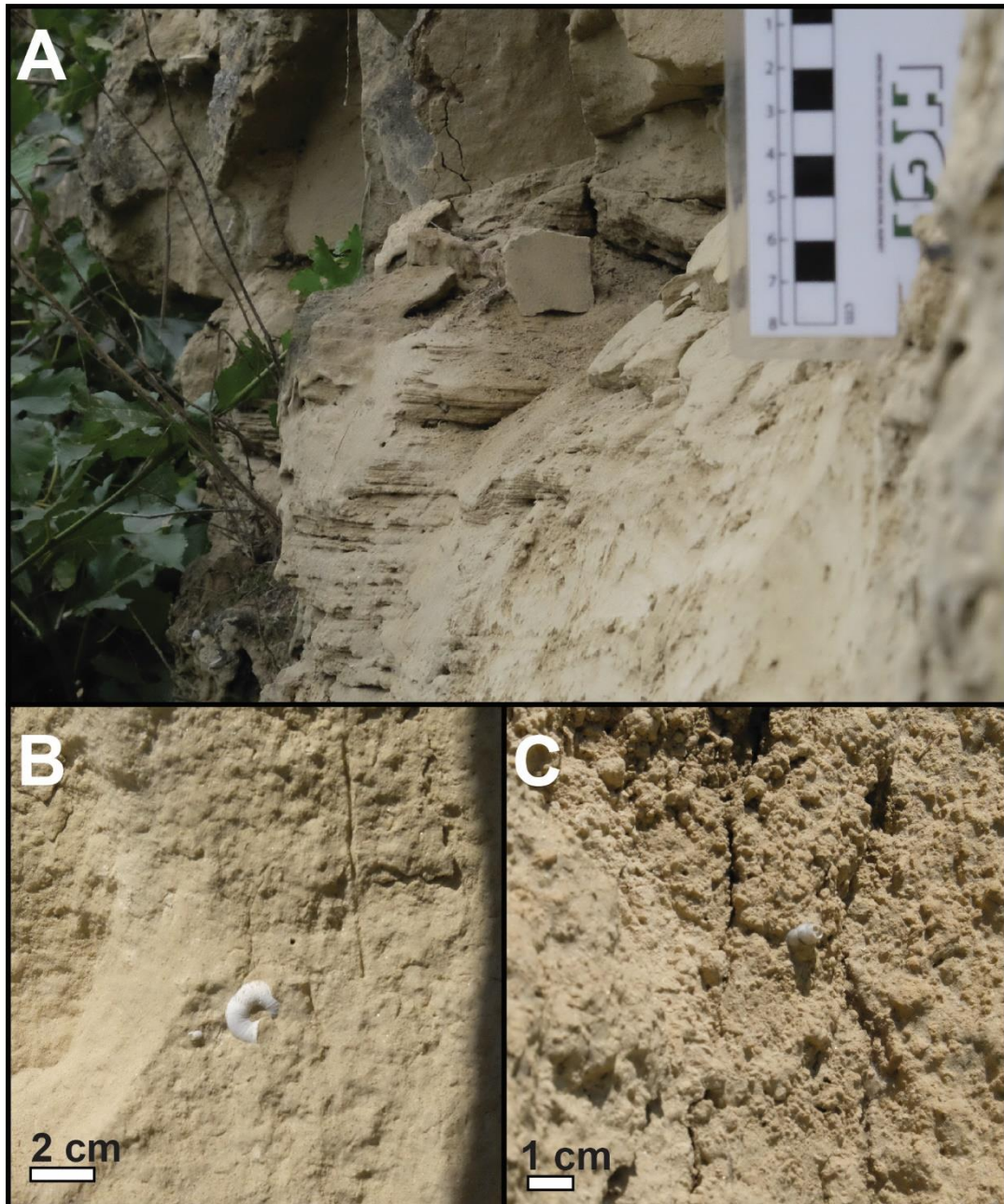


Figure 4.3 A) Erdut 3 and 4 loess-palaeosol profile. B) Horizontal laminations at profile 2 (unit VII). C and D) Examples of gastropod shells found within Unit VI.

4.3. Sampling, preparation and equipment

Due to access restrictions, only the lower parts of the Erdut profiles were accessible. Thirteen samples for grain size analysis (Appendix K Figure SI) and age determination were collected (Figure 4.2) using light-tight plastic cylinders. All samples for luminescence

dating were handled under subdued orange-light conditions at the Oxford Luminescence Dating Laboratory, University of Oxford. The light-exposed sediment from both ends of the cylinder was removed, and retained for dose rate and particle size analysis. Prior to sieving all samples were pre-treated with 32% HCl to remove carbonates, and 30% H₂O₂ to remove organic matter. Samples were sieved to retain fine sand (63-90 µm), and density separated using sodium polytungstate to obtain potassium feldspar ($\rho < 2.58 \text{ g cm}^{-3}$). Small (2 mm) coarse-grained aliquots were made by mounting a monolayer of sediment on the disc using silicone oil. All measurements were carried out using a Risø TL/OSL luminescence reader with a calibrated ⁹⁰Sr/⁹⁰Y beta source, and a bialkali photomultiplier tube. Potassium feldspar grains were stimulated with infra-red emitting diodes emitting at 870 nm, and signals were detected in the blue-violet region of the electromagnetic spectrum through a combination of Schott BG39/Corning 7-59 filters.

Thomsen *et al.* (2008) and Buylaert *et al.* (2012) have shown that the pIRIR signal measured at an elevated temperature is more stable over Quaternary timescales, and typically fades substantially less than the IR signal. Therefore, a pIRIR single aliquot regenerative dose (SAR) protocol was used for all measurements and D_e determination (Appendix K Table SI). After a 250°C pre-heat, IR₅₀ and pIRIR_{elev} signals were measured for 200 seconds, followed by the measurement of a test dose to monitor sensitivity change. A 290°C ‘hot-bleach’ was performed at the end of each SAR cycle for 200 seconds. The signal was integrated from the first 2 seconds of the stimulation time subtracting the last 100 seconds of the background. The dose response curves were fitted with an exponential function.

4.3.1. Dose rate determination

Environmental dose rates were calculated from radionuclide concentrations (U, Th, K, and Rb) measured using inductively coupled plasma mass spectrometry (ICP-MS) at the

British Geological Survey, Keyworth. Secondary standards were periodically measured to monitor analytical precision and accuracy. Radionuclide concentrations for each sample were converted to infinite-matrix dose rates using the conversion factors of Guérin *et al.* (2011). The infinite-matrix dose rates were adjusted for alpha efficiency using an a -value of 0.15 ± 0.05 (Balescu and Lamothe, 1994), grain size attenuation using the data set of Brennan *et al.* (1991) for alpha dose rates and Mejdahl (1979) for beta dose rates, and a commonly used loess moisture content of $15 \pm 5\%$ (Novothny *et al.*, 2009; Schatz *et al.*, 2012; Stevens *et al.*, 2011; Újvári *et al.*, 2014a). Cosmogenic radiation contributions were corrected for sediment thickness and altitude (Prescott and Hutton, 1994). The internal dose rate was calculated in addition to the external dose rate using an internal potassium concentration of $12.5 \pm 0.5\%$ (Huntley and Baril, 1997). Dose rate calculation was carried out using DRAC (v1.2) software (Durcan *et al.*, 2015).

4.4. Equivalent dose determination

4.4.1. Pre-heat test/temperature selection

It has been suggested that the first IRSL stimulation temperature may impact pIRIR signal stability (Jain and Ankjærgaard, 2011). To test this, a prior-IR stimulation plateau test was conducted (Buylaert *et al.*, 2012), to ascertain the dependence of pIRIR D_e on the first IRSL measurement. Five temperatures (50-170°C) were tested for the first IRSL stimulation while the pIRIR stimulation temperature was kept at 225°C. Figure 4.4 demonstrates that D_e is insensitive to the prior-IR stimulation temperature. However, because signal intensity diminishes with an increased IRSL temperature (Figure 4.4, inset), 50°C was selected for the IRSL stimulation in this study.

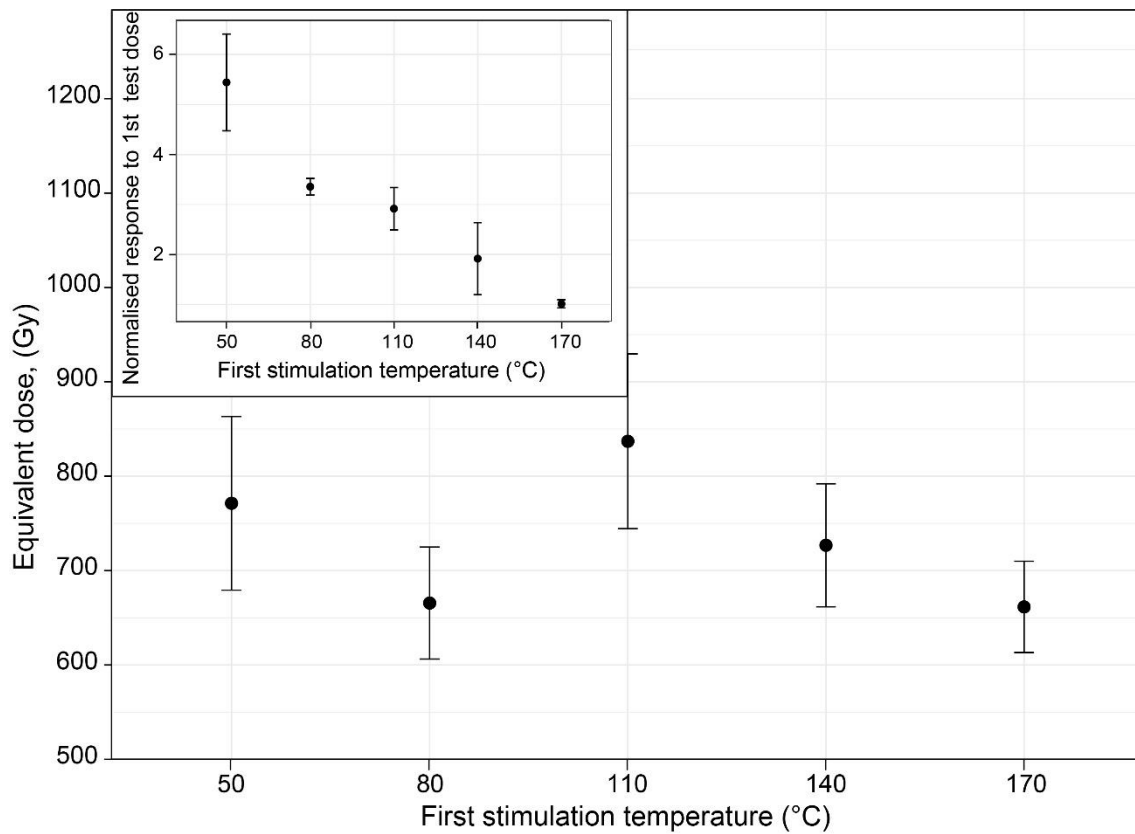


Figure 4.4 D_e as a function prior-IR stimulation temperature for sample **CRO16/2/10**. The average and standard deviation of 3 aliquots is shown. Inset, the pIRIR₂₂₅ response normalised to the natural test dose plotted against the first stimulation temperature.

Roberts (2012) showed the importance of testing the preheat temperatures, as they can have an effect on the final D_e values. They argued for conducting a preheat plateau for feldspar to determine the most appropriate preheat and measurement temperature combination for the samples, as in the case of quartz. This step seems particularly imperative in Central European loess as a number of researchers have reported problems with dose recovery when applying only pIRIR₂₉₀ signals (Murray *et al.*, 2014; Schatz *et al.*, 2012; Thiel *et al.*, 2014; Újvári *et al.*, 2014a). Therefore, six preheat (205-320°C) and elevated pIRIR temperature (25-30°C lower than the pre-heat) pairings were tested. Figure 4.5 shows the results of the preheat plateau conducted on the sample CRO16/2/10. A plateau is observed at the three lower temperatures (205-250°C), with an average D_e value

of approximately 590 Gy. D_e s increased with higher pre-heat temperatures ($>280^\circ\text{C}$), with the pIRIR₂₉₀ protocol producing D_e values more than twice as large (1108 ± 129 Gy, Figure 4.5). This is consistent with the trends observed by both Roberts (2012) and Zhang *et al.* (2015), who also saw a tendency for D_e to increase as higher pre-heat temperatures were applied. Given the consistency in D_e s measured using lower temperatures (Figure 4.5), a pIRIR₂₂₅ protocol with the 250°C preheat was selected.

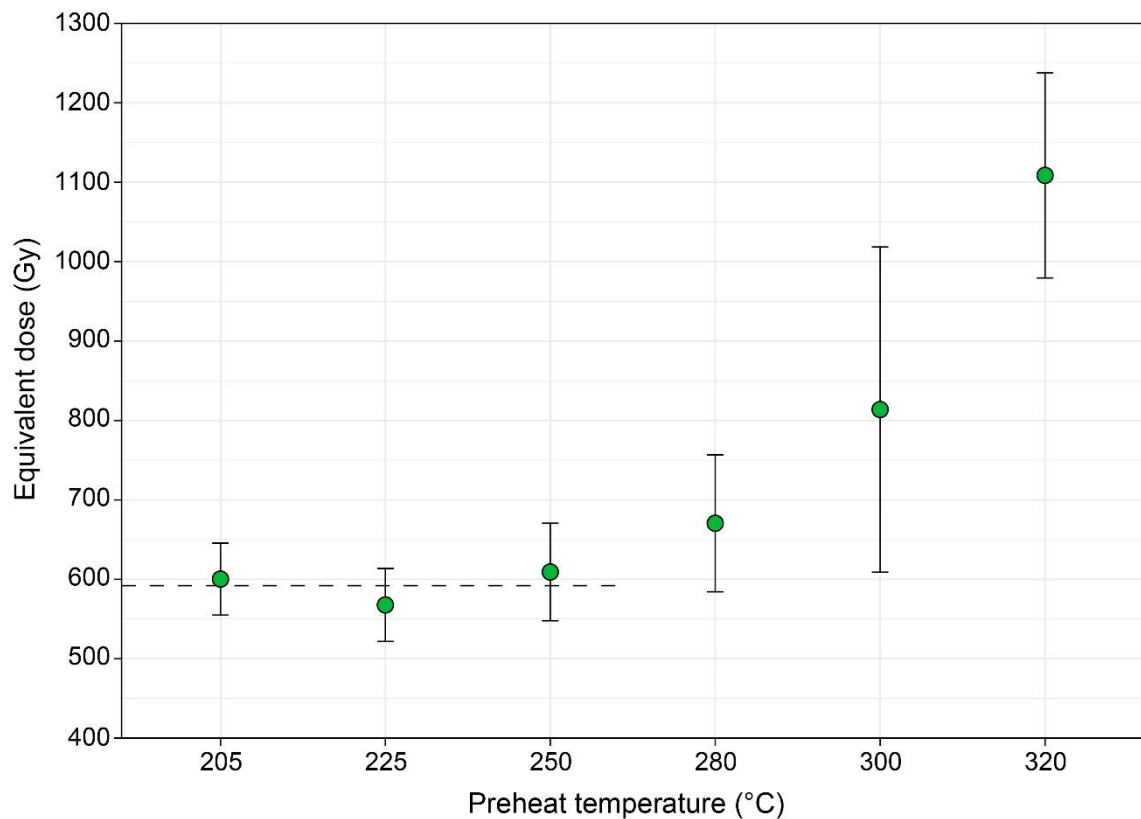


Figure 4.5 D_e dependency on pre-heat temperature for sample CRO16/2/10. The average D_e and standard deviation of three aliquots at each temperature are shown. Note, the pre-heat plateau at lower temperature (dashed line).

4.4.2. Dose Recovery

The suitability of the selected temperature pairing was tested through the dose recovery experiments, which examined the ability of the pIRIR₂₂₅ protocol to recover an administered laboratory dose. The test was applied to four samples CRO16/2/9,

CRO16/2/10, CRO16/2/17 and CRO16/2/27. 12 aliquots per sample were used for the first three samples and 6 aliquots for the last sample due to sediment availability. The aliquots were bleached in daylight, irradiated in the laboratory with a beta-dose approximating their natural dose and measured using the pIRIR₂₂₅ protocol (Appendix K Table S1). The average residual signal (see section 4.4.4) from the 42 discs was subtracted from the measured equivalent dose prior to calculating the dose recovery ratio. In initial dose recovery tests, the test dose constituted ~20% of the given dose, which resulted in underestimation of the given dose by 12%. A similar trend was reported by Colarossi *et al.* (2018) who showed that low test doses (as a percentage of the given dose) suppress the shape of the dose response curve, causing D_e underestimation. To improve the performance of our SAR protocol the test dose was increased to ~30% (170 Gy) of the given dose. All discs passed the dose recovery test within uncertainty (Appendix K Figure S2). The average dose recovery ratio for pIRIR₂₂₅ per sample was 1.04 ± 0.07 ($n = 42$, Table 4.2).

Table 4.2 Results of the residual, dose recovery and fading tests carried out on selected samples. All data are shown with 1σ errors.

Sample	Potassium feldspars			
	Residual dose (Gy)	Dose recovery*	IR ₅₀ g-value (%)	pIRIR ₂₂₅ g-value (%)
CRO16/2/5	-	-	3.23 ± 1.22	0.31 ± 0.88
CRO16/2/9	6.31 ± 0.27	1.07 ± 0.09	4.66 ± 1.53	3.30 ± 1.37
CRO16/2/10	4.60 ± 0.18	1.05 ± 0.08	2.82 ± 1.26	1.62 ± 1.12
CRO16/2/15	-	-	3.18 ± 1.19	1.55 ± 1.19
CRO16/2/17	4.11 ± 0.16	1.04 ± 0.07	2.41 ± 1.13	1.90 ± 1.14
CRO16/2/21	-	-	1.79 ± 1.20	1.38 ± 1.09
CRO16/2/27	4.37 ± 0.17	0.98 ± 0.07	-	-
Average	4.71 ± 0.19	1.04 ± 0.07	3.02 ± 1.25	1.68 ± 1.13

*Residual subtracted dose recovery ratio

The $2D_0$ value has been suggested as a prudent upper limit for dating (Wintle and Murray, 2006). To ensure that D_e values used for the age calculation are not saturated the D_0 values of each disk were checked. Figure 4.6 shows a typical dose response curve for sample CRO16/2/5, which has a $2D_0$ of 842 Gy. Taking into consideration the average dose rate at this site (3 Gy ka^{-1}) this suggests that sediment at this site can be dated to $\sim 280 \text{ ka}$.

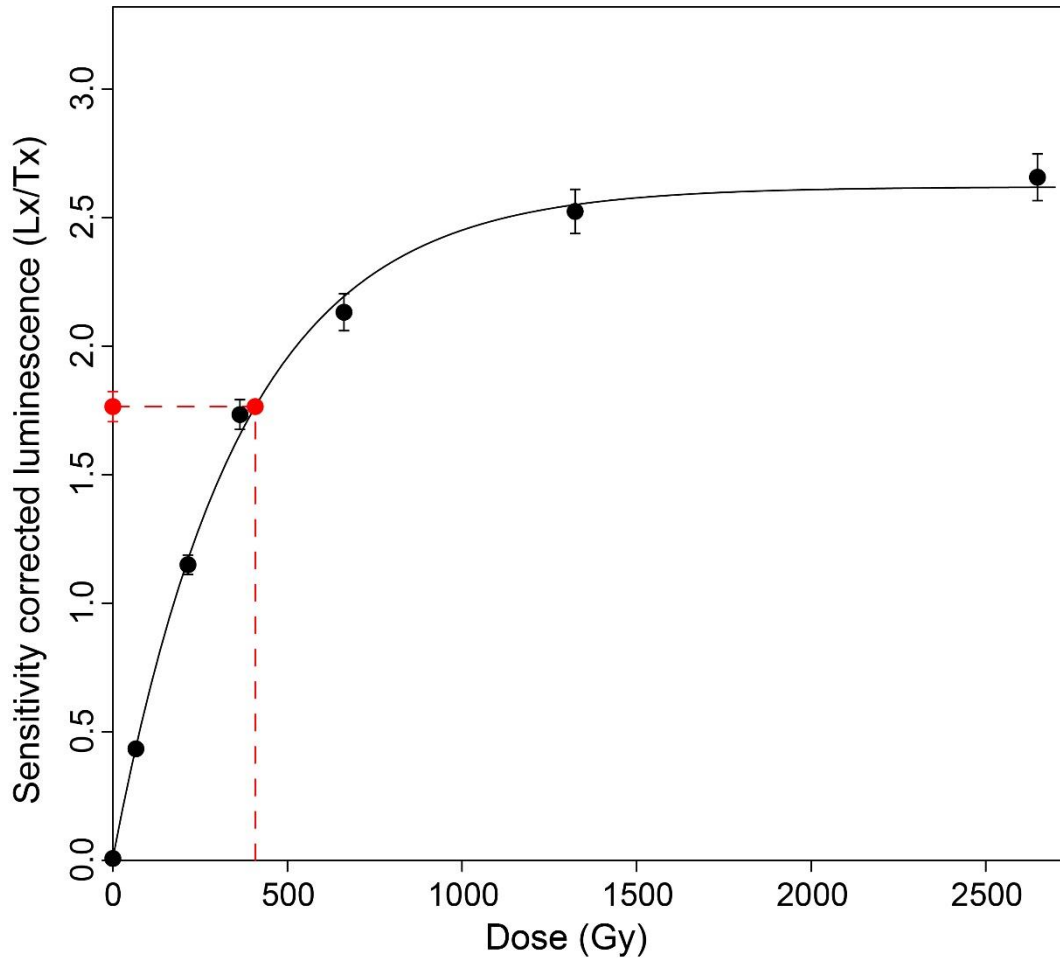


Figure 4.6 The $pIRIR_{225}$ dose response curve from an aliquot of CRO16/2/5. The natural signal is shown by the red circle and dashed red line.

4.4.3. Anomalous fading

It has been suggested that all feldspars regardless of the signal and measurement protocol suffer from signal loss termed anomalous fading (Wintle, 1973), which can result in D_e underestimation and therefore erroneous ages. However the $pIRIR$ protocols has been

shown to utilise more geologically stable, non-fading signal in feldspars (Buylaert *et al.*, 2012; Thomsen *et al.*, 2008). To assess the extent to which the pIRIR₂₂₅ signals from Erdut samples fade, and whether fading corrections are required (Huntley and Lamothe, 2001; Kars *et al.*, 2008) fading tests were performed. To measure the fading rates (g_{2days}) three aliquots per sample were irradiated with a fixed dose of 170 Gy repeatedly and the luminescence signal measured following a series of pauses (0, 1, 10, 100 and 1000 h) following the protocol of (Auclair *et al.*, 2003). Sensitivity corrected luminescence was plotted against hold time, and data were fitted with an exponential function to determine the fading rate (%/decade normalised). The range of the fading rates for the IR₅₀ signal varies between 1.14 ± 0.96 %/decade and 6.91 ± 1.76 %/decade (mean of 3.02 ± 1.25 %/decade), whereas pIRIR₂₂₅ results range from 0.06 ± 0.85 %/decade and 7.52 ± 1.81 %/decade with a mean of 1.68 ± 1.13 %/decade (Table 4.2 and Figure 4.7). The results show that pIRIR₂₂₅ fades less than the IR₅₀ signal. This relationship also holds true for sample CRO16/2/9 where the average pIRIR₂₂₅ fading rate is slightly higher than the other samples (3.30 ± 1.37 %/decade). The fading rate for this sample is a result of an unusually high fading rate recorded for one aliquot, 7.52 ± 1.81 %/decade (Figure 4.7), which increases the average fading result for this sample. Out of the remaining two aliquots, one is found within the accepted range fading range for pIRIR protocol (0.09 ± 0.86 %/decade), while the other one is only borderline (2.29 ± 1.43 %/decade). Given the general low fading rates calculated, fading correction was not applied to majority of the samples as recorded pIRIR₂₂₅ fading is in line with previously reported laboratory fading rates for non-fading quartz signals (Buylaert *et al.*, 2012). Nonetheless, as sample CRO16/2/9 was found to be borderline acceptable, the age was corrected for fading and presented alongside the uncorrected age. The correction was performed in the R Luminescence package using the `calc_FadingCorr` script (Kreutzer, 2019a) which is based on the Huntley & Lamothe (2001) calculation.

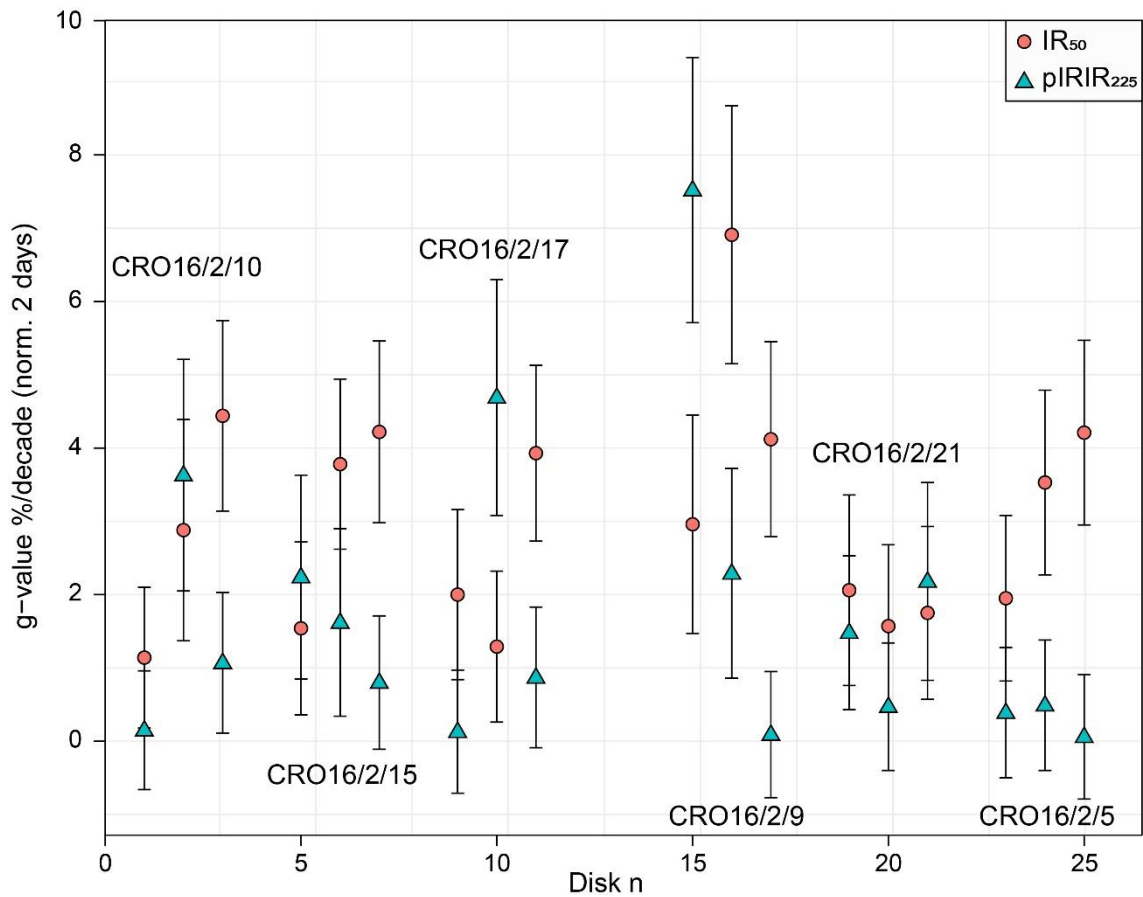


Figure 4.7 Calculated fading rates for the IR₅₀ and pIRIR₂₂₅ luminescence signals for all measured samples (three disks per sample). All data are shown with 1 σ errors.

4.4.4. Residual test and signal resetting

Sunlight exposure during aeolian transport should almost completely bleach signal in feldspar (Buylaert *et al.*, 2011). Nonetheless testing for the size of the residual component is important in aeolian samples because feldspars may have an unbleachable ‘residual’ component which, if large enough, could cause age overestimation (Stevens *et al.*, 2011). Sets of 6–12 aliquots from samples CRO16/2/9, CRO16/2/10, CRO16/2/17 and CRO16/2/27, were bleached in daylight for 10 days (in May in the UK). Samples were then measured using the same pIRIR₂₂₅ protocol to determine the residual signal remaining after bleaching. The average residual component in all measured samples is 4.71 ± 0.19 Gy (3.38–6.81 Gy range; Table 4.2), which is relatively small in comparison to some reported

European loess studies. Thiel *et al.* (2011a) for example presented a 15-20 Gy unbleachable component in Austrian loess, and Stevens *et al.* (2011) found residuals as high as 40 Gy in Serbian loess.

Given that the IR signals are much harder to bleach in nature than quartz (Godfrey-Smith *et al.*, 1988), samples were further investigated to eliminate the possibility that the signals were not fully reset prior to the burial. To test this IR₅₀ signals, which bleach more rapidly in nature, were compared to pIRIR signals (Appendix K Figure S3). Fading corrected IR₅₀ ages are slightly lower than pIRIR₂₂₅ ages, with an average ratio between the two of $0.86 \pm 0.09 \sigma$, although if the individual ratio of 0.58 for sample CRO16/2/25 is excluding, the overall ratio increases to $0.89 \pm 0.04 \sigma$. Given that in all cases the IR₅₀ fading correction is applied to relatively old ages, and therefore the non-linear portion of the dose response curve these results were accepted as indicative of reasonable signal resetting of both the IR₅₀ and pIRIR₂₂₅ signals. For sample CRO16/2/25 the underestimation is much greater (~58%), which could suggest that signal was not fully reset in nature and therefore the age of this sample maybe overestimated. However, the age is stratigraphically consistent with the sample above and below, and therefore is accepted.

4.4.5. D_e calculation

Luminescence signals were screened using typical rejection criteria, i.e. signal recuperation (<5% of the natural), and recycling ratios of $1 \pm 10\%$ (Murray and Wintle, 2000). For all measured signals (n=193), all disks passed the recycling ratio (1.03 ± 0.05), and recuperation was less than $0.57 \pm 0.03\%$. Overdispersion values recorded varied between 0 and 6.7%, with the majority of samples recording no overdispersion. Therefore, equivalent doses were calculated by applying Central Age Model (Galbraith *et al.*, 1999).

4.4.6. Age depth model and mass accumulation rates

To assist with the investigation of the age change with depth, and calculation of accumulation rates, an age-depth model was constructed based on the pIRIR₂₂₅ ages. Zeeden *et al.* (2018a) R package was utilised to Bayesian and inverse model luminescence ages. This approach is able to separate systematic and random errors of luminescence age by creating probability density functions for both, and include only the later in the uncertainty calculations. All ages discussed in text refer to modelled ages (Appendix K Table S2).

To investigate dust fluxes and interpret sedimentary deposition, mass accumulation rates (MARs) were calculated based on modelled luminescence ages, following the equation of Kohfeld & Harrison (2003):

Equation 4.1 Mass accumulation rate equation.

$$\text{MAR (g m}^{-2} \text{ a}^{-1}) = \text{SR} \times f_{\text{eol}} \times \rho_{\text{dry}}$$

Where, SR denotes the sedimentation rate (m a⁻¹), f_{eol} is the fraction of the sediment that is aeolian in origin, and ρ_{dry} represents the bulk density of dry sediment (g m⁻³). The sediment was interpreted to be aeolian in origin, therefore f_{eol} value of 1 was used. The commonly applied loess bulk density value of 1.5 g cm⁻³ (Perić *et al.*, 2019; Újvári *et al.*, 2010a) was used. Minimum and mean MARs were calculated based on a minimum and mean sedimentation following the suggestion of Leighton *et al.* (2014).

Table 4.3. Samples, depths, radionuclide concentrations, dose rates, D_e values and the final luminescence ages obtained using pIRIR₂₂₅ protocol applied to 63-90 μm potassium feldspars. In bold are highlighted ages used for modelling.

Sample	Depth (m)	Unit	U (ppm $\pm 1\sigma$)	Th (ppm $\pm 1\sigma$)	Rb (ppm $\pm 1\sigma$)	K (% $\pm 1\sigma$)	Cosmic dose rate (Gy/ka)	Total dose rate (Gy/ka)	Aliquot s (m/a) *	OD (%) **	D_e (Gy)	Uncorrected pIRIR ₂₂₅ age (ka)
PROFILE 1												
CRO16/2/1	4.1	VIII	1.95 ± 0.19	9.79 ± 0.98	79.74 ± 7.97	1.62 ± 0.16	0.13 ± 0.01	3.18 ± 0.19	15/15	2.5	484.55 ± 9.57	152.58± 9.58
CRO16/2/5	6.1	VIII	1.80 ± 0.18	9.21 ± 0.92	83.28 ± 8.33	1.67 ± 0.17	0.10 ± 0.01	3.11 ± 0.19	15/15	0	500.96 ± 9.15	162.01± 10.22
CRO16/2/7	7.1	IX	1.97 ± 0.20	10.73 ± 1.07	89.97 ± 9.00	1.79 ± 0.18	0.09 ± 0.01	3.38 ± 0.21	15/15	2.3	521.80 ± 11.0	154.48± 9.92
CRO16/2/9	8.1	IX	2.02 ± 0.20	11.69 ± 1.17	101.08 ± 10.1	1.86 ± 0.19	0.09 ± 0.01	3.52 ± 0.22	13/13	0	592.40 ± 16.2	168.37 ± 11.27 233.99± 49.69 ***
PROFILE 2												
CRO16/2/10	2.8	VII	1.88 ± 0.19	10.55 ± 1.06	59.99 ± 6.00	1.24 ± 0.12	0.15 ± 0.02	2.91 ± 0.17	15/15	8.7	592.28 ± 12.1	203.73± 12.80
CRO16/2/12	3.8	VII	1.89 ± 0.19	10.06 ± 1.01	84.57 ± 8.46	1.77 ± 0.18	0.13 ± 0.01	3.32 ± 0.20	15/15	0	501.82 ± 9.0	151.27± 9.47
CRO16/2/14	7.8	VIII	1.99 ± 0.20	10.42 ± 1.0 4	81.66 ± 8.17	1.67 ± 0.17	0.12 ± 0.01	3.27 ± 0.20	15/15	0	477.21 ± 8.4	145.81± 9.11
PROFILE 3												
CRO16/2/15	3.6	V	2.00 ± 0.20	10.05 ± 1.01	84.85 ± 8.48	1.82 ± 0.18	0.14 ± 0.01	3.40 ± 0.20	15/15	6.8	254.77 ± 3.9	75.01± 4.67
CRO16/2/17	4.6	VI	1.75 ± 0.17	7.95 ± 0.79	60.48 ± 6.05	1.37 ± 0.14	0.13 ± 0.01	2.74 ± 0.16	15/15	8.3	382.80 ± 6.1	139.61± 8.54

CRO16/2/20	6.1	VI	1.87±0.19	8.44±0.84	67.44±6.74	1.54±0.15	0.10±0.01	2.94±0.18	15/15	6.3	413.00±6.4	140.42±8.66
PROFILE 4												
CRO16/2/21	5.7	VI	1.84±0.18	8.43±0.84	65.31±6.53	1.51±0.15	0.11±0.01	2.92±0.17	15/15	0	418.46±6.9	143.29±8.86
CRO16/2/25	7.7	VI	1.64±0.16	8.39±0.84	68.30±6.83	1.56±0.15	0.09±0.01	2.88±0.17	15/15	0	422.27±7.63	145.08±9.09
CRO16/2/27	8.7	VI	1.91±0.19	9.57±0.96	71.44±7.14	1.54±0.15	0.08±0.01	3.03±0.18	15/15	6.7	515.5±13.0	170.14±11.13

*M – measured. A – accepted **Overdispersion ***Corrected pIRIR₂₂₅

4.5. Results and discussion

4.5.1. A new chronology for the Erdut loess-palaeosol section

Thirteen unmodelled and modelled pIRIR₂₂₅ luminescence ages from Units V to IX are presented in Figures 4.8 and 4.9, and Table 4.3 and Appendix K Table S2. The top of the Unit IV was dated to 75.01 ± 5.44 ka. Five ages were measured from the underlying thick loess, Unit VI. The uppermost sample, collected at the Erdut 3 profile, 40 cm below the palaeosol-loess boundary provided an age 139.18 ± 8.75 ka. The remaining three ages from both Erdut 3 and 4 are quite closely spaced at 140.48 ± 7.52 ka, 143.29 ± 7.76 ka, 145.47 ± 9.33 ka. While the bottom sample from the Erdut 4 profile was dated to 170.14 ± 13.49 ka. This could indicate a sediment gap contained in a metre of sediment, however the size and the exact position of this hiatus requires further investigation.

Ages from profiles 3 and 4 differ markedly from those in the chronology of Galović *et al.* (2009). Based on the stratigraphic position it is likely that one of the ages presented by Galović *et al.* (2009), 53.8 ± 5.4 ka, corresponds to Unit VI. However, it is not possible to establish the relationship between the depth of their samples and the depths of the samples presented here. Therefore, while underestimation is observed, there are a number of factors that can be contributing to this discrepancy including for example use of an uncorrected IR₅₀ signal for the equivalent dose estimation (Galović *et al.*, 2009) or use of different grain size fractions (63-90 μ m potassium feldspar here vs 4-11 μ m polymineral (Galović *et al.*, 2009)) between two studies. The uncorrected IR₅₀ ages (Appendix K Table S3) for the Unit VI show ages in a similar range (53.19-98.96 ka) to those reported by Galović *et al.* (2009). This suggests that the use of uncorrected IR₅₀ signal for the equivalent dose estimation is likely the largest source of age underestimation, however this requires further investigation and is beyond the scope of this paper. Galović *et al.*

(2009) did not obtain ages from the palaeosol (Unit V), however they attributed ages 46.9 ± 4.8 and 46.5 ± 4.7 ka to the loess above it. While these ages cannot be verified, in view of the rest of the chronological results, they are likely to be underestimated.

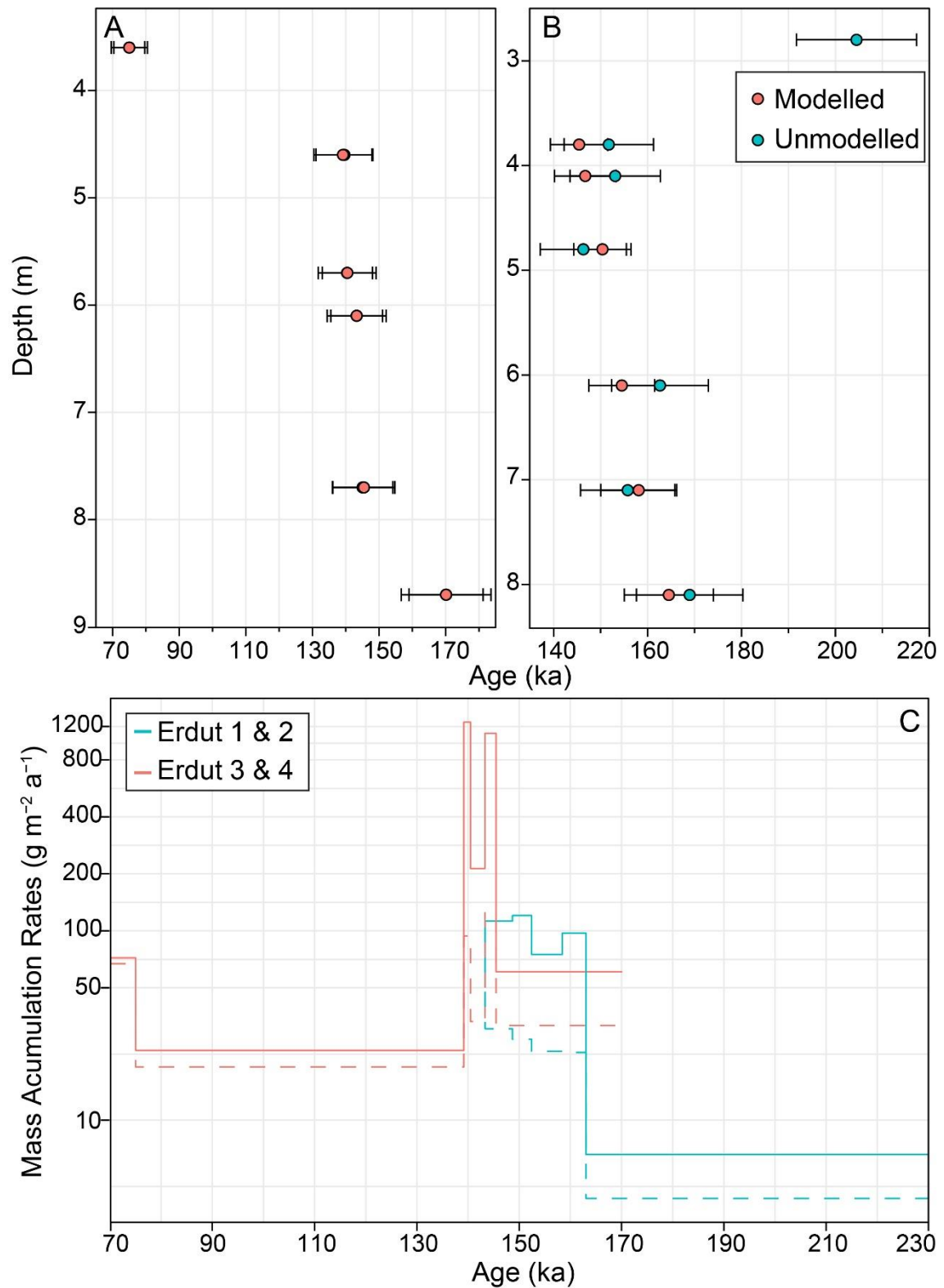


Figure 4.8 A comparison of the modelled and unmodelled pIRIR₂₂₅ ages for Erdut profiles A) 3 and 4 B) 1 and 2. Please note that the top age in 9B (CRO16/2/10) is only presented as a unmodelled value as it is an outlier. C) Mass accumulation rates ($\text{g m}^{-2} \text{a}^{-1}$) for Erdut presented as mean (solid line) and minimum (dashed values) values based on the modelled ages.

At profiles 1 and 2 the luminescence ages provide chronology for laminated sediment (Unit VII), loess (Unit VIII) and bottom palaeosol (Unit IX). Sample CRO16/2/10 (203.73 ± 12.8 ka) from the top of the laminated unit, appears to be significantly overestimating the depositional age and is the only age inconsistent with the rest of chronological record (within uncertainties). Based on stratigraphy, field observations, and grain size analysis (Figures 4.2, 4.3 and Table 4.1) this sample is fluvial in origin. Therefore, a ~60 ka age reversal could potentially be explained by incomplete bleaching of the sediment. Partial bleaching is not unusual in fluvial sediments as complete exposure to light may be restricted in sediment-lain water (Wallinga, 2002). However, it is unclear why the discrepancy is recorded only in one sample and without further investigation using single grain approaches it is difficult to interpret this age.

Four ages from the lowest loess Unit (VIII), at Erdut 1 and 2, fall in the 148.69 ± 6.98 - 158.42 ± 7.77 ka age range, covering a period of 10-16 ka (based on mean and minimum ages). As with Unit VI it is not possible to correlate more precisely the depth at which Galović *et al.* (2009) sample from this Unity, and therefore compare with results of this study. Nonetheless their results provide an uncorrected IR₅₀ age of 61.5 ± 6.2 ka which corresponds with 85 ± 5.6 - 92.9 ± 6.2 ka IR₅₀ age range (Appendix K Table S3). As highlighted above there are potentially other sources of the discrepancy including mineral fraction and grain size though the largest driver appears to be the use of uncorrected IR₅₀ signal. The Erdut 1 profile culminates in a thick palaeosol (Unit IX), dated to 231.29 ± 40.63 ka

(uncorrected 168.37 ± 11.27 ka). These results suggest that this section spans two glacial-interglacial cycles, rather than just one as was previously proposed.

Despite a large overlap between ages from two parts of the profile (Figures 4.8 and 4.9), the lateral disappearance of the palaeosols and the laminated fluvial sediments prevents from consolidating this record into one. Further the chronological gap recorded at the bottom of the profile 4 requires further attention.

4.5.2. Mass accumulation rates

High-resolution loess chronologies extending beyond the penultimate interglacial are limited, as a result so are mass accumulation rate for this period. Figure 4.8C shows the MARs based on the modelled pIRIR₂₂₅ ages for the Erdut outcrop. While most commonly taken approach relies on calculation of MARs based on only the mean age, it has been shown in aeolian context that this may lead to misleading interpretations of luminescence ages (Leighton *et al.*, 2014). Therefore, the results presented here also show the minimum MARs values.

Palaeosol Unit IX records the lowest accumulation rate in the whole section; $6 \text{ g m}^{-2} \text{ a}^{-1}$ and $4 \text{ g m}^{-2} \text{ a}^{-1}$, mean and minimum respectively, though the Unit V's rates are also low ($19\text{--}23 \text{ g m}^{-2} \text{ a}^{-1}$). Conversely rates within loess are not only high but also quite variable. The top part of the loess Units VI shows very rapid accumulation $94\text{--}1265 \text{ g m}^{-2} \text{ a}^{-1}$. However, between 143 and 140 ka MARs drop to the average $213 \text{ g m}^{-2} \text{ a}^{-1}$ (minimum $33 \text{ g m}^{-2} \text{ a}^{-1}$). These shifts could indicate change(s) in a number of factors including sediment production at source(s), sediment transport (either by the Danube River or the wind), preservation potential, in wind direction, and activation/deactivation of an additional or new source.

Importantly Figure 4.8 shows that loess deposition has been neither uniform nor continuous, which are common assumptions in loess research. By nature, loess is a very homogenous sediment in which depositional gaps or erosional events are not obvious when assessing the stratigraphy. Furthermore, the homogeneity also means that even if an erosional event occurred the new sediment is likely to have a similar grain size and magnetic susceptibility to the one deposited before. Therefore, unless a change in source or material delivered to a site occurred as well, hiatuses will be difficult to identify from the proxy record. At Erdut the erosional gap is represented by fluvial sediments in profiles 1 and 2. However, fluvial sediments are not preserved in profile 4, yet the dates suggest a sedimentary gap. This hiatus should be further investigated as its size may vary between 1.85 and 47.5 ka, depending on whether a minimum or maximum error is used.

With more high-resolution dating studies conducted, the size of hiatuses in loess records could be better constrained and investigated in the context of climatic and/or local influences on the loess deposition. Whether climatically or locally driven a number of gaps in loess records been reported at multiple locations (e.g. Dong *et al.*, 2015; Stevens *et al.*, 2018), highlighting the danger of the loess continuity assumption. The profiles at Erdut provide a unique view of the issue as profile 4 shows a hiatus that would not be recognised due to the lack of lithological changes. However, 100 meters away profiles 1 and 2 preserve the likely cause of the gap. This not only shows a need for high-resolution chronological approaches but also investigation of sedimentological sections in a wider spatial context.

4.5.3. Environmental implications

Samples CRO16/2/9 and CRO16/2/7 from the middle of the gradational boundary and the top of Unit IX at Erdut, provide modelled ages of 231.29 ± 40.63 ka and 163.05 ± 7.77 ka, respectively (Figure 4.9). This thick, dark and well-developed palaeosol reportedly has relatively high Total Organic Carbon (TOC) content and proportion of clay and fine silts

(Galović *et al.*, 2009). Although the corrected age for the palaeosol has a very large uncertainty it falls well within the bounds of MIS 7 and therefore is identified as S2 soil. The luminescence age from the stratigraphic boundary between loess and palaeosol, likely represents the transition period between MIS 6 and MIS 7 stages. Other detailed and dated climatic archives for this period are scarce, with the majority located near the south Balkans and Mediterranean Sea.

As only the transitional zone and top of this palaeosol is exposed, it is not possible to determine the full thickness and appearance of Unit IX palaeosol in Erdut. In the Danubian loess, S2 is represented as a double or triple palaeosol pedocomplex with a strongly developed S2SI palaeosol that has enhanced magnetic susceptibility values (Bugge *et al.*, 2009; Marković *et al.*, 2006, 2009; Wacha *et al.*, 2013). Currently it is not possible to determine how many palaeosols are preserved at Erdut and therefore how this site fits into the regional loess stratigraphy.

Based on the modelled luminescence ages Units VIII and VI, likely represent the same period of loess deposition (Figure 4.9); however, at present it is impossible to precisely combine them into a single stratigraphic unit. Loess accumulation at Erdut begun at 170.14 ± 13.49 ka and conclude by 139.18 ± 8.75 ka, showing that site experienced semi-continuous loess deposition for 9-53 ka, based on minimum and maximum ages respectively (Figure 4.9). Chronology suggest that this Units provide a record of the MIS 6 and are therefore classified as L2 loess. Further a drop in the TOC associated with decreased biological productivity, as well as an increase in the proportion of coarse silt and sand is noted in this unit (Galović *et al.*, 2009). These changes suggest increased windiness and/or a change in wind direction, a change in sediment supply, or new source activation; all likely possibilities during glacial periods.

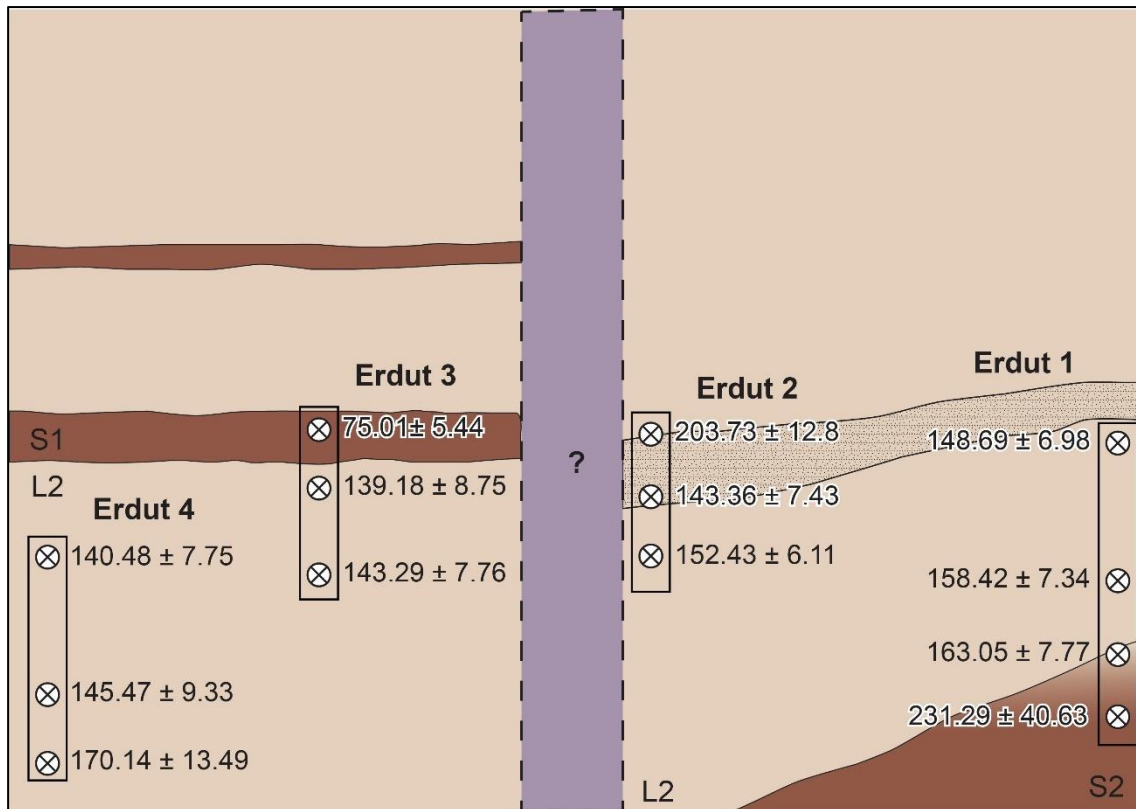


Figure 4.9 A schematic stratigraphy diagram for the four profiles at Erdut with modelled luminescence ages shown. The blue rectangle marks the area of stratigraphical uncertainty.

The sites extending beyond last interglacial are often located near the Danube (Figure 4.1). Along the Danube the L2 loess is not as well preserved or exposed as the L1 (the record of the last glacial period). In many cases just the top of the L2 unit is exposed at the base of profiles (cf Fitzsimmons *et al.*, 2012). Nonetheless, the thickness of the exposed L2 unit at Erdut, Vukovar (Wacha and Frechen, 2011), Ruma (Marković *et al.*, 2006), Batajnica (Marković *et al.*, 2009), Süttő (Novothny *et al.*, 2011), Costinești (Constantin *et al.*, 2014), Harletz (Lomax *et al.*, 2018), indicates large quantities of sediment available for transport and deposition along the Danube corridor. This is not surprising as the MIS 6 stage is considered as one of the most climatically severe periods in Europe, with the farthest extent of the glaciers (Ehlers and Gibbard, 2007; Francke *et al.*, 2016). The glacial action

producing the sediment, increased fluvial and aeolian transport, in combination with a cold and dry climate and predominantly dry steppe and/or forest steppe like conditions (Marković *et al.*, 2006, 2007, 2018b) supports increased sediment availability in the system.

Figure 4.8 shows this period is marked by a highly variable accumulation rates. All Erdut's profiles indicate that in the early parts of the MIS 6 rates were relatively low; 32-60 g m⁻² a⁻¹ (Erdut 1 and 2) and 23-97 g m⁻² a⁻¹ (Erdut 3 and 4). This is followed by a temporary drop to 75 g m⁻² a⁻¹ (mean) between 158.42±7.34 and 152.43±6.11 ka and rise to ~120 g m⁻² a⁻¹ (mean). At Erdut 1 and 2 rates increase rapidly (mean 1104 g m⁻² a⁻¹ and 125 g m⁻² a⁻¹) after 145.47±9.33 ka, drop to 213 g m⁻² a⁻¹ (mean) at 143.29±7.76 ka, and increase to their highest mean value (1265 g m⁻² a⁻¹; minimum 94 g m⁻² a⁻¹) between 140.48±7.52 and 139.18±8.75 ka after which the rates drop until the beginning of MIS 5. This further supports the suggestion that MIS 6 can be divided into two parts at around 155 ka (Margari *et al.*, 2010); with the first part resembling more of an interstadial, while the full glacial conditions beginning after 155 ka, as the global ice volume increases to reach glacial maximum. The division at Erdut is seen in both minimum and mean MARs and occurs after ~152 ka in agreement with Margari *et al.* (2010). This again highlights that loess accumulation is not uniform and continuous during glacial periods and suggests that the sediment dynamics were highly susceptible to change and continued to respond to climatic and/or geomorphological changes.

At the profiles closest to the modern river channel (Erdut 1 and 2), the L2 is punctuated by a series of horizontally- and cross- laminated sand and silt. These are absent from profiles 3 and 4, only 100 m further away. Laminated deposits were previously interpreted as fluvial (Galović, 2014; Galović *et al.*, 2009), which is supported by field observations conducted during this research. The deposition of the Unit VII commenced between

148.69±6.98 ka and 143.36±7.43 ka. However, its termination is unclear as the unmodelled luminescence age from the top of the unit, dates it to 203.73±12.8 ka. This age is not consistent with the rest of the stratigraphic and chronological record at Erdut and a likely overestimation based on the sample's stratigraphic position (see discussion in section 4.5.1). While profiles 3 and 4 do not contain laminated sediments a hiatus in ages (170.14±13.49–145.47±9.33 ka), corresponding to the onset of fluvial sediment, suggests whole site may have been subject to fluvial influence.

This temporary shift to fluvial sedimentation could indicate changes to the Danube's main channel or a development of a small branching channel. Fluvial sediments also punctuate L2 unit at Stari Slankamen (Marković *et al.*, 2011), and Zmajevac (Banak *et al.*, 2012; Galović *et al.*, 2009) either as a series of laminated sediment or as an erosional feature. Further fluvial features at Šarengrad (Galović *et al.*, 2009) could also be of the same age. However, this cannot be confirmed until the chronologies for these sections are verified and more detailed sedimentological investigations are conducted. Nonetheless, this could indicate a basin wide hydrological event, potentially restricted to the sites found along the main Danube corridor. However, the exact timing and cause of this event cannot be resolved due to the uncertainty on luminescence dates.

The relatively thin palaeosol (Unit V) dates to 75.01±5.44 ka, with the loess sample below providing a bracketing age of 139.18±8.75 ka, suggesting that this palaeosol represents the last interglacial (MIS 5) (Rasmussen *et al.*, 2014). The bottom age estimate is in line with the onset of Termination II (Moseley *et al.*, 2015), the transition from the MIS 6 into MIS 5, supporting its identification as the last interglacial soil (SI). This is also supported by an increase in clay particles and TOC to the highest values in the section (Galović *et al.*, 2009). It is possible that Erdut experienced a locally driven, favourable conditions for the pedogenesis to occur over ~50 ka (Figure 4.9), that resulted in low MARs rates (Figure

4.8). Therefore, Unit V could be preserving record of the whole interglacial period, including all of the substages in a single palaeosol.

However, the SI palaeosol at Erdut is relatively thin in comparison to palaeosols of that age across the region (cf Fitzsimmons *et al.*, 2012), e.g. the three times thicker SI palaeosol at Vukovar (Wacha and Frechen, 2011), a few km downstream. Furthermore, other SI palaeosols in the Carpathian Basin e.g. Dunaszekcső (Újvári *et al.*, 2014a), Süttő (Novothy *et al.*, 2011), and Dolní Věstonice (Fuchs *et al.*, 2013) are represented by double or triple palaeosols. Consequently, partial erosion of the other the pedocomplex at Erdut is likely.

Nevertheless, SI pedogenic complexes are heterogenous across the region (cf Fitzsimmons *et al.*, 2012), and palaeosol at Erdut could reflect pedogenic processes driven by local conditions such as palaeotopography (including drainage), vegetation, proximity to the river, and micro-climate (Lehmkuhl *et al.*, 2016; Vandenberghe *et al.*, 2014). This could be pointing to regional and/or local drivers preserved in the loess records on the sub-orbital level. Therefore, SI palaeosol at Erdut requires further high-resolution chronological analysis combined with the detailed sedimentological and micromorphological investigation.

4.6. Conclusions

A review of the chronology for the loess-palaeosol sequence at Erdut is presented, based on coarse-grain (63-90 μm) potassium feldspar and pIRIR₂₂₅ measurement protocol. The modelled uncorrected pIRIR₂₂₅ ages range from 75.01 ± 5.44 to 231.29 ± 40.63 ka, which suggest a semi-continuous loess accumulation at this site since the MIS 7. The results show that Erdut preserves much longer climatic and environmental records than originally thought and could therefore greatly contribute to understanding of the long-term Pleistocene changes in the region. A fluvial event, which disturbed L2 loess accumulation

is also reported. This could be pointing to a wider hydrological that affected loess deposits along the main Danube channel (e.g. Stari Slankamen (Murray *et al.*, 2014)). Other sites in Croatia (Zmajevac and Šarengrad) that preserve fluvial sedimentary sequences in L2 were dated using uncorrected IR₅₀ protocol, which this research shows is likely underestimating ages. Therefore it is not possible to compare and provide more detailed picture of the fluvial event. Consequently chronologies at Zmajevac and Šarengrad should be revisited. Finally, this research shows that more high-resolution approaches based on the pIRIR protocols are needed to better understand the timing of the climatic and environmental changes during the penultimate glacial-interglacial stage.

SUMMARY: Paper 1

Chapter 4 addresses **Objective 1** for site one, i.e. it produces an up to date chronology and provides a basis for re-assessing the palaeoenvironmental history, through the application of luminescence dating and particle size techniques.

At present not much is known about the palaeoclimate and palaeoenvironment of Central Europe beyond the last 125 ka, as most sites preserving long term Quaternary records are restricted lakes. While a number of loess-palaeosol sequences are thought to extend beyond the last glacial-interglacial cycle, not many have independent and robust chronologies.

Paper 1, therefore, seeks to address this gap by constructing a relatively high resolution chronology for the loess-palaeosol sequence at Erdut (Croatia) using post-IR infrared (pIRIR) stimulated luminescence dating of feldspars. This chapter shows that that previously constructed chronology for this site underestimated the ages, likely due to the use of an uncorrected dating protocol, which did not account for anomalous fading in feldspars. It demonstrates that Erdut preserves the last 180 ka of loess deposition and is therefore a record of the last two glacial-interglacial cycles.

This chapter also shows that loess deposits at Erdut contain a hiatus in the form of a fluvial event preserved within sediment. This has implications not only for the typical interpretation of loess-palaeosol deposits as continuous, but may also suggest a widespread fluvial event along the Danube after ~150 ka.

Chapter 5: Paper 2

Local or global signal? Multiproxy, dating and provenance investigations of complex Late Pleistocene loess sequences, Bulgarian Lower Danube

Paper 2: Fenn, Kaja, Thomas, David S.G., Durcan, Julie A., Millar, Ian L., Veres, Daniel, Piermattei, Alma, Lane, Christine S.

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Abstract

Loess-palaeosol sequences are an important archive of past climate and environmental conditions, especially as they are often found in areas where other terrestrial archives are lacking. It is therefore important that they are utilised to the best of their potential. We present the results of a high-resolution sedimentological investigation of two loess profiles, 2km apart, at Slivata (Bulgaria), supported by independent chronological approaches; luminescence dating and tephra. The records span 95-14ka, with sedimentological research focused on the last ~52ka. We identify unusual thin soil-like features, previously reported at only in a handful of sites in Central and Eastern Europe (Veres *et al.*, 2018). Using a combination of sedimentology, accumulation rates, and provenance we suggest that these features are likely colluvial in nature. The findings demonstrate that loess deposits can be strongly influenced by local/regional factors, and can preserve much more complex records than would result from global, large scale, drivers alone. Identification at Slivata of the Cape Riva (Y-2) tephra horizon, previously only recorded in a few terrestrial locations further south, provides a new tephrostratigraphic marker for eastern European loess during LGM.

5.1. Introduction

Loess-palaeosol sequences (LPS) are one of the key long-term terrestrial climate archives that can be found on every continent, including in central-eastern Europe (Buggle *et al.*, 2009; Fitzsimmons *et al.*, 2012; Novothny *et al.*, 2011; Stevens *et al.*, 2011). They may provide insights into past climatic and environmental changes in regions where other palaeoarchives are rare and often temporally limited to the Last Glacial Maximum (LGM). Due to the nature of their formation, loess deposits provide an opportunity to investigate past environmental conditions (Antoine *et al.*, 2009b; Marković *et al.*, 2007; Moine *et al.*, 2017; Schatz *et al.*, 2011; Újvári *et al.*, 2017; Zech *et al.*, 2013), as well as mechanisms of dust emissions (Albani *et al.*, 2015; Sima *et al.*, 2009; Stevens *et al.*, 2013b; Újvári *et al.*, 2012) and fluxes (Mahowald *et al.*, 2006; Újvári *et al.*, 2010b).

To date, the majority of central-eastern European LPS investigations have focused on so called “typical” loess sections. These provide a record of large-scale, orbitally driven climate changes, comprising thick glacial loess units, separated by well-developed interglacial and, in some sites, weakly developed interstadial palaeosol(s) (Buggle *et al.*, 2009; Fitzsimmons and Hambach, 2014; Fuchs *et al.*, 2008; Marković *et al.*, 2008; Vasiliniuc *et al.*, 2011). In the Danube regions, this has led to efforts to establish a unified long-term chronostratigraphic LPS model (Marković *et al.*, 2015).

LPS preserving evidence of short-term pedogenesis (i.e. embryonic soils) within glacial loess units have been long studied in Western European loess (Antoine *et al.*, 2001, 2003; Haesaerts *et al.*, 2016; Meszner *et al.*, 2013). Their development and paedogenetic intensity have been linked to millennial-scale variability and availability of moist, oceanic air from the North Atlantic (Antoine *et al.*, 2001; Rousseau *et al.*, 2017a; Terhorst *et al.*, 2015). In contrast, a lack of such embryonic soils in the Danube loess has been associated with continental climates, too dry to sustain short-term pedogenesis (Marković *et al.*, 2015). However, there are a growing number

of studies in Central Europe that report complex LPS sequences preserving very thin, poorly developed, soils and soil-like horizons in Austria (Terhorst *et al.*, 2014, 2015), Czech Republic (Antoine *et al.*, 2013; Hošek *et al.*, 2015), Poland (Jary and Ciszek, 2013) and Ukraine (Rousseau *et al.*, 2011; Veres *et al.*, 2018). This could further indicate strong regional imprints on the broader orbital-scale records, either resulting from regional climatic complexities, or from strong geomorphological influences potentially providing more “local” records of the past. If such sequences recording regional and local drivers of loess-soil development are more widespread across Central Europe, especially along the Danube where the “typical loess sequence” view has been adopted, there would be major implications for loess development models that imply orbital controls and interregional record synchronicity.

A robust, absolute chronology is a critical underpinning for investigating and exploring links and variability between loess sites, and other paleoclimate archives. Despite recent progress in loess radiocarbon dating (Moine *et al.*, 2017; Újvári *et al.*, 2014a), the limited span and preservation of datable remains limit the application of this method to last ~50ka.

Optically stimulated luminescence (OSL) dating has become the chronological approach of choice within loess research as the method provides an estimate of the time of deposition of sediment, and can provide chronologies for the whole glacial-interglacial cycle. This includes work in Bulgaria (Lomax *et al.*, 2018), Croatia (Wacha and Frechen, 2011), Hungary (Novothy *et al.*, 2002, 2011; Újvári *et al.*, 2014a), Serbia (Murray *et al.*, 2014; Perić *et al.*, 2019; Stevens *et al.*, 2011), and Romania (Constantin *et al.*, 2014; Fitzsimmons and Hambach, 2014; Vasiliniuc *et al.*, 2011). However, there are studies where the dating is of a relatively low resolution (Bösken *et al.*, 2019; Marković *et al.*, 2014), or lacks an absolute chronology, relying instead on ‘wiggle-matching’ based on soil horizons, magnetic susceptibility (Marković *et al.*, 2008, 2012) or grain size (Antoine *et al.*, 2009a). These approaches inevitably make assumptions regarding factors

such as the continuity of the deposition (Stevens *et al.*, 2008, 2018), or magnetic susceptibility shifts as an indicator of geochronological change (Constantin *et al.*, 2019).



Figure 5.1 Site location (black square) within the wider Danube loess context. Other loess (red circles), cave (pink) and tephra source (green) sites discussed in the text are marked. (DEM Source: ©JAXA).

Most studies characterising the provenance of loess along the Danube have relied on bulk geochemical analyses (Buggle *et al.*, 2008; Schatz *et al.*, 2015; Újvári *et al.*, 2008, 2014b) that may provide incomplete or limited information about loess provenance (Stevens *et al.*, 2010). A significant body of work carried out using single-grain approaches on the Chinese Loess Plateau has transformed understanding of the provenance of loess deposits (e.g. Bird *et al.*, 2015; Fenn *et al.*, 2018; Licht *et al.*, 2016; Nie *et al.*, 2015). To date, only a handful of sites along the Danube, such as Mende, Paks, Basaharc, Zmajevac (Újvári *et al.*, 2012), Krems, Wels, and Stratzing (Újvári *et al.*, 2013; Újvári and Klötzli, 2015), have used single-grain provenance methods (Figure

5.1). While none of these studies were carried out at high resolution, they are a first step in gaining a better understanding of loess provenance in Central Europe.

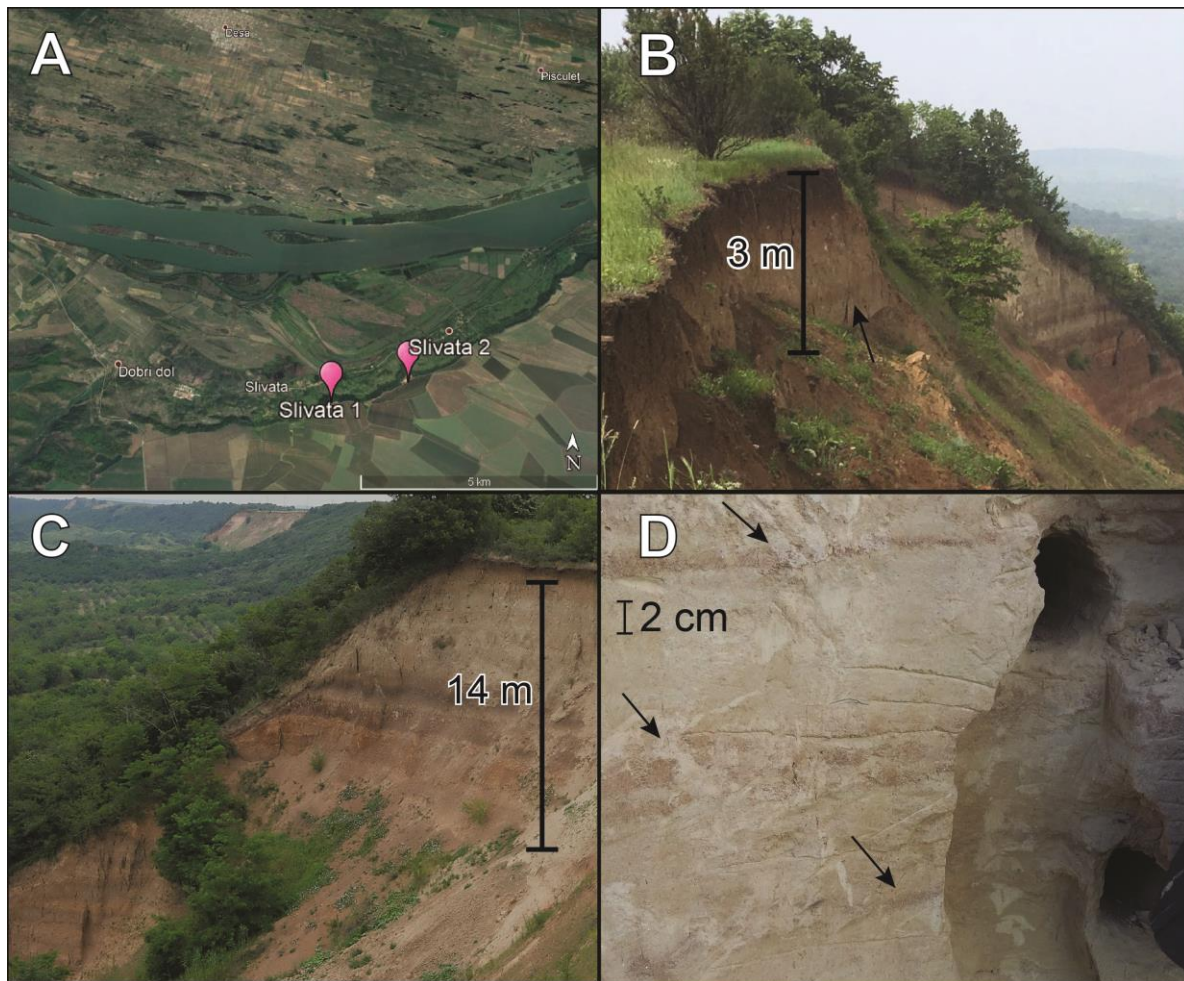


Figure 5.2 A) Area map as showing the relative locations of the two Slivata profiles (Source: ©GoogleEarth); B) Slivata 1 loess-palaeosol profile. A faint brown horizon (marked by the black arrow) towards the bottom of the marked 3m part of the section is the Unit IV; C) Slivata loess-palaeosol 2 profile. A number of palaeosols are visible extending to the bottom of the section. Slivata 1 exposure is visible in the background; D) Thin bands described at the Slivata 2 profile (see Figure 5.3).

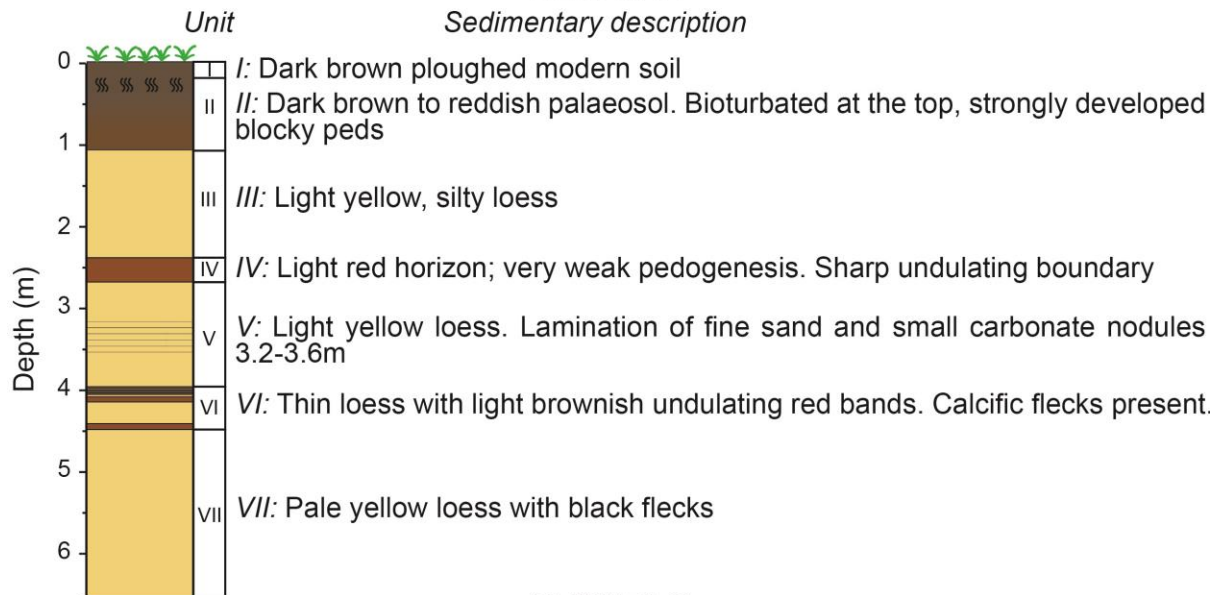
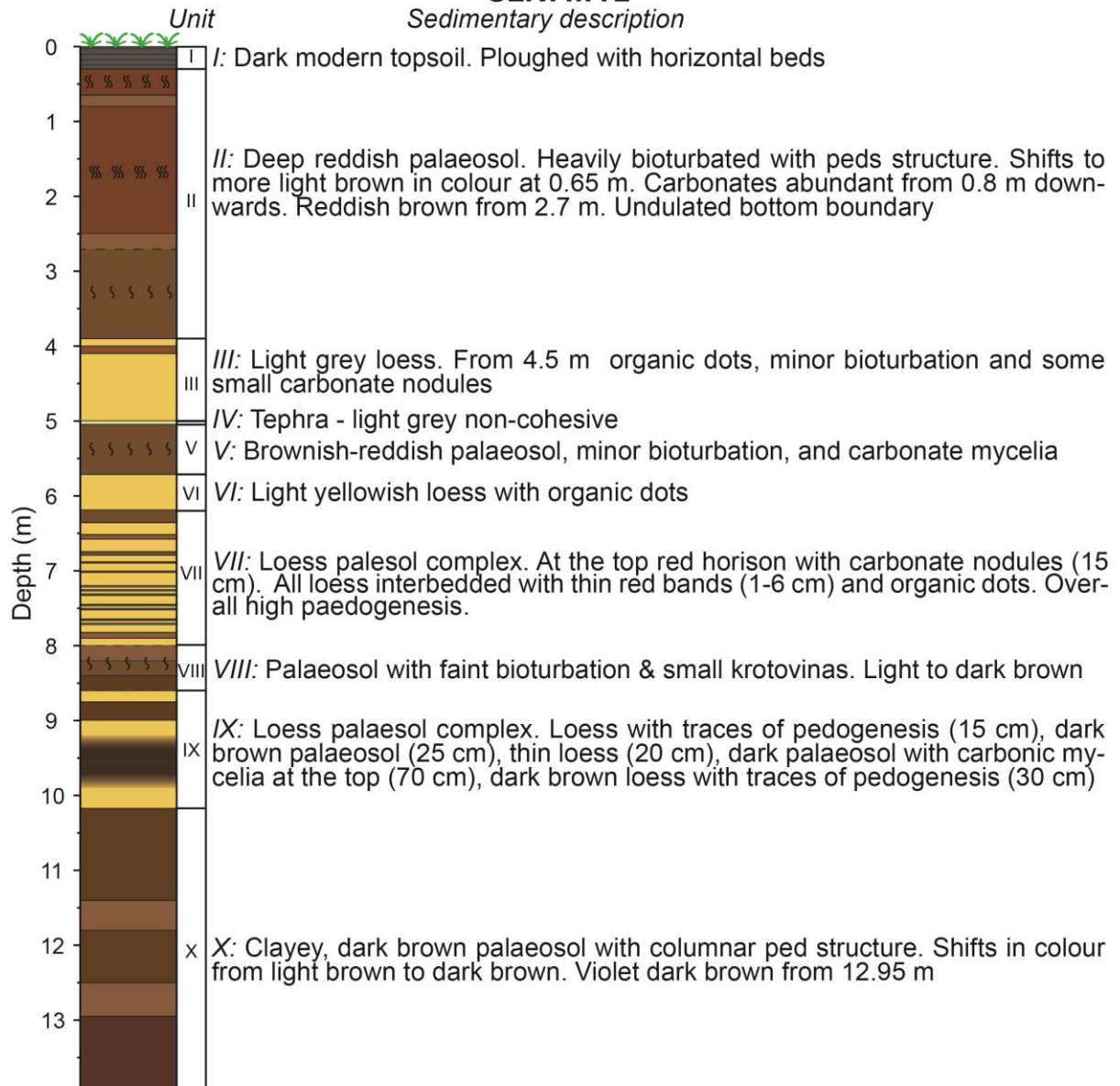
This study provides a detailed multi-proxy investigation of two LPS near Slivata village, northern Bulgaria (Figure 5.1). These sites appear stratigraphically distinctive from many late Quaternary LPS in the Lower Danube (Balescu *et al.*, 2010; Fitzsimmons and Hambach, 2014; Lomax *et al.*,

2018; Zeeden *et al.*, 2018b) or the Carpathian Basin (e.g. Fuchs *et al.*, 2008; Stevens *et al.*, 2011; Újvári *et al.*, 2014a). We combine results of single-grain detrital zircon U-Pb dating with sedimentological analyses supported by 17 luminescence ages and tephrochronology to help understand and reconcile the complex sedimentary histories of both sites.

5.2. Study area and site description

In this study two LPSs, ~2km apart, were investigated: Slivata 1 (43°46'0.91"N, 23°04'48.49"E) and Slivata 2 (43°45'45.44"N, 23°03'29.55"E) exposed in the southern flank of the Danube valley, 25 m above the alluvial floodplain, in relatively close proximity to the Carpathian and Balkan Mountains (Figure 5.1). The exposures are ~3km from the modern Danube channel and between the confluences of the Lom and Skomlya rivers with the Danube. The natural exposures reveal over 15 m of loess and loess like deposits (Figure 5.2 and Figure 5.3), underlain by a complex sequence of welded palaeosols. Loess sequences along the Lower Danube rest on Pleistocene to Pliocene river terraces (Evlogiev, 2007). This is also the case for the Slivata sequence, which is thought to rest on the on the fifth river terrace (T5; Avramov *et al.*, 2006). While development of T0 alluvial plain is linked to modern day processes and T1 to Holocene, the exact age of the T5 terrace is not known. The sections were logged in detail in the field prior to sampling for dating and sedimentary analyses.

Figure 5.3 Schematic stratigraphy for both Slivata loess-palaeosol profiles including sedimentological descriptions based on field observations.

SLIVATA 1**SLIVATA 2**

5.3. Methods and materials

5.3.1. Sample collection

Section details, sedimentary descriptions and age sampling locations are shown in Figures 2 and 3. For sedimentological analyses, 527 samples were collected contiguously at 2cm resolution; at Slivata 1 that represents the top 6m of the profile and at Slivata 2 the middle ~4.5m (Figure 5.3). For luminescence dating 17 samples were collected, ~50cm apart by hammering opaque, light-tight plastic tubes into the freshly cleaned profiles. Additionally, at the depth of each luminescence sample, 1-2kg of sediment was collected for provenance analysis. Finally, a sample was collected from the visible tephra horizon at 5m at the Slivata 2 for geochemical analysis.

5.3.2. Sedimentological analysis

Following overnight sample drying and homogenisation, grain-size analyses were carried out using a Malvern Mastersizer Hydro 2000MU laser diffraction particle size analyser. Chemical treatment of samples prior to analysis proved to be unnecessary (Figure S.1) and therefore samples were measured without pre-treatment.

Magnetic susceptibility (χ) measurements were made to investigate the strength of pedogenesis using a Bartington MS2 Magnetic Susceptibility System with a MS2B dual frequency sensor. Following the established protocol (Buggle *et al.*, 2014; Gocke *et al.*, 2014), prior to analysis samples were oven dried (max. 40°C), gently disaggregated, and packed into 10cm³ plastic cylindrical containers. Results are presented as low frequency mass-specific magnetic susceptibility (χ_{lf} in m³/kg).

Frequency-dependent magnetic susceptibility (X_{FD}) provides an indication of the changes in concentration of ultra-fine superparamagnetic material, that is pedogenic in origin (Buggle *et al.*, 2014). To calculate X_{FD} , measurements were conducted at low and high frequencies, 0.465kHz and 4.65kHz respectively. The X_{FD} was calculated as:

$$\chi_{FD}(\%) = (\chi_{lf} - \chi_{hf})/\chi_{lf}$$

5.3.3. Tephra

5.3.3.1. Sample preparation

A standard non-destructive tephra extraction method (Blockley *et al.*, 2005) was followed to concentrate tephra glass shards. Tephra sample was treated with 7 % HCl to remove carbonates, wet sieved (>25µm), and density separated (1.95-2.55gcm⁻³). Finally, to prepare them for electron microprobe analysis, isolated shards were mounted on epoxy resin stubs, and polished to expose their surfaces ready for shard-specific compositional analysis.

5.3.3.2. Geochemical analysis

To determine concentrations of major and minor element oxides within glass shards, samples were analysed using a Cameca SX100 wavelength dispersive electron microprobe analyser (WDS-EPMA) in the Department of Earth Sciences, University of Cambridge. A 10µm diameter defocused beam spot operating at 15kV and 6nA was used. Counts were for sodium were collected over 10 second acquisitions, chlorine and phosphorus for 60 seconds and all other elements for 30 seconds. Secondary standards including a range of MPI-DING (Jochum *et al.*, 2006) fused volcanic glasses were periodically measured to monitor analytical precision and accuracy.

Table 5.1. Mean values for major and minor element oxide glass shard composition (normalised to 100%) for glass shards from Slivata. Please see Table S1 for details of individual shard analysis and Table S2 for raw, unnormalized data.

SLV_T5	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
Mean	72.62	0.46	14.29	3.13	0.12	0.42	1.72	4.09	3.08	0.08	100
2σ	0.51	0.03	0.33	0.20	0.08	0.03	0.09	0.45	0.17	0.06	

Data reduction involved the removal of three analyses that erroneously targeted non-tephra grains, and three individual glass shard analyses with element oxide analytical totals below 94 weight %. The remaining compositional data (n=43) were normalised to anhydrous basis for comparison to reference datasets (Table 5.1, Figure 5.4).

5.3.4. Luminescence dating

Samples for luminescence dating were opened and prepared under subdued orange light conditions at the Oxford Luminescence Dating Laboratory. Sediment was treated with HCl and H₂O₂ to remove carbonate and organic matter. The 4-11µm and 63-90µm fractions were isolated through a combination of sieving and settling. The coarse-grained potassium feldspar was obtained through density separation, while quartz enriched fine-grained sediment was treated with H₂SiF₆ to remove non-quartz minerals and remove the alpha-irradiated outer layer. 4-11µm quartz grains were dispensed onto the surface of 9 aluminium discs, whereas for 63-90µm K-feldspar small aliquots (2mm in diameter) were used.

All measurements were carried out using Risø TL/OSL luminescence readers fitted with a calibrated ⁹⁰Sr/⁹⁰Y beta source and a bi-alkali photomultiplier tube. Quartz grains were stimulated with blue-light emitting diodes (470nm) and the signal was measured in a UV detection window through 7.5mm U-340 glass filters (Bøtter-Jensen *et al.*, 2000). K-feldspars were stimulated with infra-red emitting diodes (870nm), and the signal was detected in the blue-violet region through a combination of Schott BG39/Corning 7-59 filters. The single aliquot regenerative (SAR) dose protocol (Murray and Wintle, 2000; Wintle and Murray, 2006) was used for equivalent dose determinations. Full details of the measurement conditions and analysis for quartz and feldspar protocol determination (Figures S.2, S.3, and S.4) are provided in supporting information. Prior to final D_e calculation, all luminescence signals were screened using a standard rejection criteria, i.e. signal recuperation (<5%), recycling ratio (Murray and Wintle, 2000), and in the case of quartz OSL IR depletion ratios (Duller, 2003) which were set

at $1\pm 10\%$. Given the low overdispersion (between 0% and 9.9%) of dose distributions, D_e s were calculated using the central age model (CAM; Galbraith *et al.*, 1999).

Concentrations of uranium, thorium, potassium and rubidium were measured by inductively coupled plasma mass spectrometry at British Geological Survey, Keyworth (BGS) to determine environmental dose rates. Radionuclide concentrations were converted to infinite-matrix dose rates using the conversion factors of Guérin *et al.* (2011) and a moisture content of $15\pm 5\%$, which is typically used for loess sediments (Schatz *et al.*, 2012; Stevens *et al.*, 2011; Újvári *et al.*, 2014a). Dose rate calculation was carried out using the DRAC (v1.2) software (Durcan *et al.*, 2015).

5.3.4.1. Age-depth model

To better visualise the age distributions, age-depth models for both Slivata profiles were developed based on the luminescence ages and further constrained through tephra results. Although some age-depth modelling software can incorporate luminescence data, e.g. Bacon (Blaauw and Christeny, 2011) or OxCal (Bronk Ramsey, 1995), they were created for radiocarbon age calibration and modelling, and therefore do not capture fully the complexities of luminescence age errors.

The recently developed Zeeden *et al.* (2018a) method uses a composite of an inverse modelling and a Bayesian age-depth model to refine luminescence ages. It creates separate probability density functions for both types of systematic and random uncertainties, but utilises only the random uncertainty to recalculate the uncertainties. All the luminescence ages were modelled using this approach (Appendix K). All ages subsequently mentioned in the text refer to the modelled results (Figures 5.5 and 5.7).

Table 5.2 Radionuclide concentrations, dose rates, D_e values and final luminescence ages for the 4-11 μ m quartz and 63-90 μ m K-feldspars. Alpha efficiency (0.04 ± 0.004 for 4-11 μ m quartz (Rees-Jones, 1995), and 0.15 ± 0.05 for coarse K-feldspars (Balescu and Lamothe, 1994)), grain size attenuation (alpha (Brennan *et al.*, 1991) and beta (Mejdahl, 1979)), and internal K concentration of $12.5 \pm 0.5\%$ (Huntley and Baril, 1997) used for calculations of external dose rates. All calculations were made prior to rounding. Modelled ages were calculated using Zeeden *et al.* (2018a) script and are used in the discussion. *m–measured, a–accepted, **OD-Overdispersion

Sample	Depth (m)	Mineral	Aliquots (m/a)*	U (ppm $\pm 1\sigma$)	Th (ppm $\pm 1\sigma$)	K (% $\pm 1\sigma$)	Cosmic (Gy ka ⁻¹ $\pm 1\sigma$)	Total dose rate (Gy/ka)	OD (%)**	D_e (Gy)	Age (ka)	Modelled age (ka)
BUL17/1/1	1.00	Quartz	15/15	1.45 ± 0.15	8.94 ± 0.89	1.48 ± 0.15	0.19 ± 0.02	2.70 ± 0.18	5.4	38.06 ± 0.68	14.11 ± 1.00	14.11 ± 1.07
BUL17/1/2	1.65	Quartz	15/15	1.48 ± 0.15	8.19 ± 0.82	1.20 ± 0.12	0.17 ± 0.02	2.37 ± 0.16	3.2	46.36 ± 0.60	19.53 ± 1.36	18.88 ± 1.05
BUL17/1/3	2.35	Quartz	15/15	1.68 ± 0.17	8.63 ± 0.86	1.41 ± 0.14	0.16 ± 0.02	2.65 ± 0.18	6.6	51.20 ± 1.10	19.32 ± 1.38	19.57 ± 1.07
BUL17/1/5	3.10	Quartz	15/15	1.58 ± 0.16	8.62 ± 0.86	1.40 ± 0.14	0.15 ± 0.02	2.60 ± 0.18	2.8	53.40 ± 0.90	20.57 ± 1.45	20.53 ± 1.06
BUL17/1/7	3.90	Quartz	15/15	1.73 ± 0.17	8.82 ± 0.88	1.22 ± 0.12	0.13 ± 0.01	2.48 ± 0.17	9.9	54.00 ± 1.80	21.80 ± 1.68	21.40 ± 1.08
BUL17/1/9	4.55	Quartz	15/15	1.76 ± 0.18	8.86 ± 0.89	1.28 ± 0.12	0.12 ± 0.01	2.53 ± 0.18	0.0	56.30 ± 0.90	22.22 ± 1.60	22.04 ± 1.05
BUL17/1/11	5.55	Quartz	15/15	1.83 ± 0.18	9.13 ± 0.91	1.17 ± 0.12	0.11 ± 0.01	2.47 ± 0.18	7.3	55.77 ± 0.87	22.61 ± 1.65	22.66 ± 1.21
BUL17/1/12	6.00	Quartz	15/14	1.68 ± 0.17	7.92 ± 0.79	1.36 ± 0.14	0.11 ± 0.01	2.48 ± 0.17	6.0	54.87 ± 1.28	22.09 ± 1.63	23.30 ± 1.50
BUL17/2/12	6.36	Quartz	14/15	1.81 ± 0.18	8.40 ± 0.84	1.22 ± 0.12	0.10 ± 0.01	2.44 ± 0.17	4.6	72.15 ± 3.93	30.85 ± 2.26	30.17 ± 1.62
BUL17/2/11	6.94	Quartz	15/15	1.64 ± 0.16	8.31 ± 0.83	1.36 ± 0.14	0.10 ± 0.01	2.50 ± 0.18	6.4	80.40 ± 1.90	32.18 ± 2.39	31.58 ± 1.58
BUL17/2/9	7.40	Quartz	15/15	1.75 ± 0.18	8.07 ± 0.80	1.39 ± 0.14	0.09 ± 0.01	2.53 ± 0.18	0.0	85.00 ± 1.30	33.56 ± 2.40	32.43 ± 1.64
BUL17/2/7	8.00	Quartz	15/15	1.88 ± 0.19	9.02 ± 0.90	1.45 ± 0.14	0.09 ± 0.01	2.70 ± 0.19	0.0	86.70 ± 1.40	32.11 ± 2.34	33.10 ± 1.77
BUL17/2/6	8.50	Quartz	15/15	1.93 ± 0.19	9.41 ± 0.94	1.61 ± 0.16	0.08 ± 0.01	2.89 ± 0.20	0.0	94.35 ± 2.07	32.67 ± 2.40	34.20 ± 2.31
BUL17/2/5	9.00	Quartz	15/15	2.01 ± 0.20	9.89 ± 0.99	1.62 ± 0.16	0.08 ± 0.01	2.96 ± 0.21	7.3	111.79 ± 3.14	37.80 ± 2.86	37.91 ± 3.03
BUL17/2/3	10.0	Quartz	15/13	1.97 ± 0.20	9.48 ± 0.95	1.49 ± 0.15	0.07 ± 0.01	2.79 ± 0.20	0.0	143.68 ± 5.86	51.54 ± 4.22	49.73 ± 3.56
BUL17/2/2	10.5	Quartz	17/17	1.86 ± 0.19	10.12 ± 1.01	1.72 ± 0.17	0.07 ± 0.01	3.22 ± 0.23	6.7	153.12 ± 3.69	50.83 ± 3.78	52.29 ± 4.00
BUL17/2/1	13.7	Feldspar	15/15	1.78 ± 0.18	9.38 ± 0.94	1.43 ± 0.14	0.05 ± 0.01	2.65 ± 0.19	2.5	271.57 ± 4.48	95.53 ± 6.00	95.55 ± 6.29

5.3.5. Provenance

Zircon-enriched sub-samples were separated through a combination of wet separation using a shaking table, heavy liquid (di-iodomethane; 3.3gcm^{-3}) and magnetic separation. They were mounted on epoxy disks and polished to reveal the centres. Prior to U-Pb analysis, each grain was imaged using cathodoluminescence (CL) on a Quanta FEI scanning electron microscope to assess the positions of cores or any rims. U-Pb in detrital zircons was analysed with a $20\mu\text{m}$ laser spot in Nu Plasma HR multi-collector mass spectrometer (MC-ICP-MS) with one of three New Wave laser systems at the Geochronology and Tracers Facility at the British Geological Survey.

To correct for instrument mass bias and depth-dependent inter-element fractionation of U, Pb, and Th, three standards were measured cyclically as a reference material; $337.13\pm0.37\text{Ma}$ Plešovice zircon (Sláma *et al.*, 2008); $1065.4\pm0.3\text{Ma}$ 91500 (Wiedenbeck *et al.*, 1995); and GJ-1 ($^{206}\text{Pb}/^{238}\text{U}$ $602.3\pm1\text{Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}$ $609.2\pm0.7\text{Ma}$ (in-house TIMS, unpublished)). $^{206}\text{Pb}/^{238}\text{U}$ ages were used for zircon grains $<1.2\text{Ga}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages were used for grains $>1.2\text{Ga}$. Data was screened according to the degree of discordance of the $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages for each grain; for ages $<1.2\text{Ga}$, data $>\pm5\%$ discordant was discarded; for ages $>1.2\text{Ga}$, data $>\pm10\%$ discordant was discarded. Raw data including element concentrations, ratios, and ages can be found in the supplementary data (Appendix I).

To statistically analyse provenance results two approaches were used: Kernel Density Estimation (KDEs), that provides visual assessment of U-Pb age distributions (Andersen *et al.*, 2018; Vermeesch, 2012), and Multi-Dimensional Scaling (MDS; Vermeesch, 2013), that investigates the similarity between large numbers of datasets, allowing a comparison. MDS is based on Kolmogorov-Smirnov (KS) statistics, which outputs a two-dimensional

diagram where similarity/dissimilarity is represented as a relatively short/larger distance between samples. In this paper the “non-metric” algorithm was used.

5.4. Results

5.4.1. Identification of tephra

Results of the geochemical analysis of individual glass shards ($n=46$) from the tephra sample found in Slivata 2 are presented in Table 5.1, with bi-plots of selected major elements presented in Figure 5.4. The geochemical composition of analysed shards from Slivata 2 shows a homogenous rhyolitic affinity (high SiO_2 content 72.65 ± 0.55 wt%). Further the composition is characterised by relatively high CaO and MgO contents, of 1.73 ± 0.09 wt% and 0.43 ± 0.03 wt% respectively. The consistent geochemical clustering (Figure 5.4), supported by the chronostratigraphic position at Slivata 2, indicates that the tephra layer is correlated with the Cape Riva (Y2) tephra, erupted from the Santorini volcanic centre (Druitt, 1985; Vespa *et al.*, 2006). The most up-to-date and precise age estimate, based on modelled radiocarbon ages, places the date of the Cape Riva eruption at 22,523–21,308 cal BP (Lee *et al.*, 2013). While ash correlated to the Cape Riva/Y-2 eruption has been reported widely in marine deposits (Kwiecien *et al.*, 2008; Satow *et al.*, 2015; Wulf *et al.*, 2002), in the terrestrial realm it has only been reported as far as mainland NE Greece (Müller *et al.*, 2011; Seymour *et al.*, 2004). Therefore, the discovery of tephra from the Cape Riva/Y-2 eruption tephra in Northern Bulgarian loess extends the know dispersal area for the fine ash from this eruption into a continental setting for the first time. Furthermore, the Cape Riva/Y-2 provides a potential chronostratigraphic marker for loess deposits in Central and Eastern Europe during the LGM.

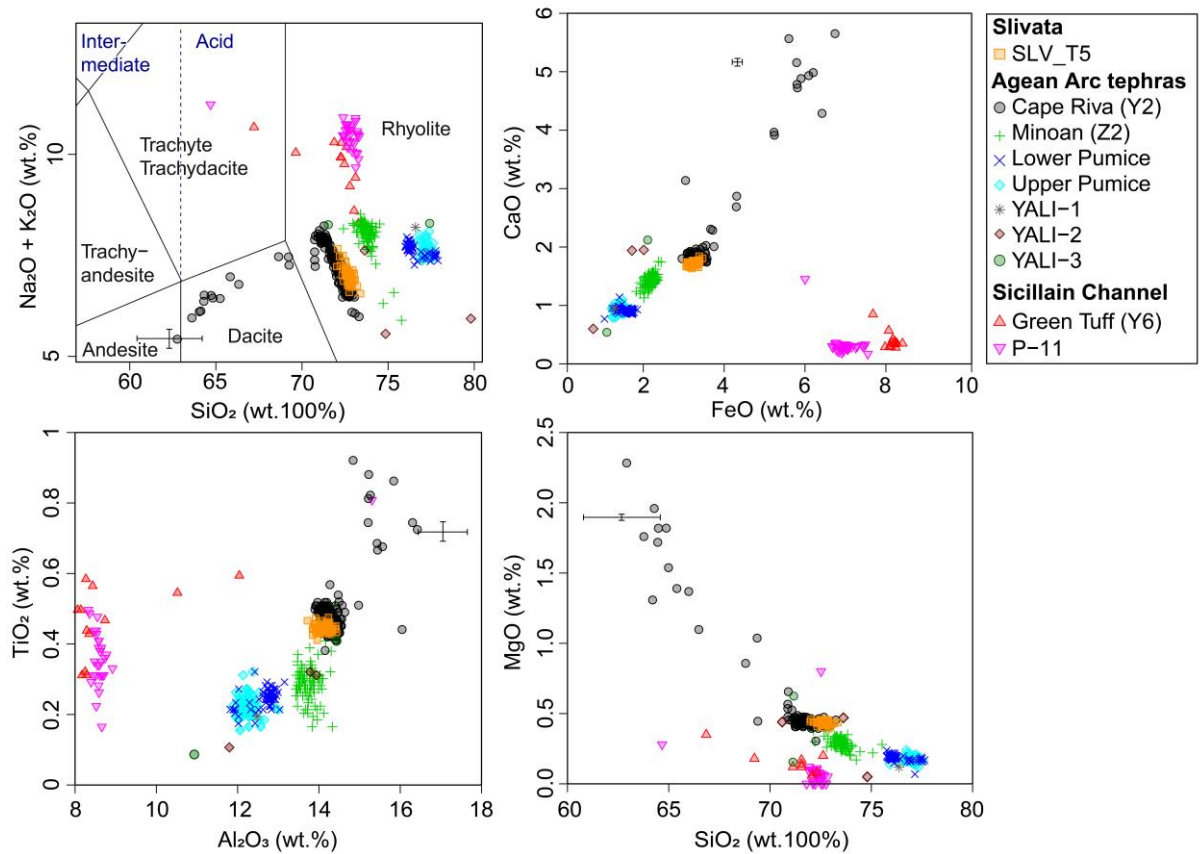


Figure 5.4 Geochemical bi-plots of the major and minor element oxide data from Slivata 2 (orange), plotted with known rhyolitic eruptions from volcanic sources in Mediterranean Region. Reference tephras for Aegean Arc (Cape Riva (Y2): Kwiecien et al., 2008; Margari et al., 2007; Tomlinson et al., 2015; Wulf et al., 2002; Minoan (Z2): Eastwood et al., 1999; Kwiecien et al., 2008; Tomlinson et al., 2015; Nisyros Upper and Lower Pumice: Karkanis et al., 2015; Tomlinson et al., 2015; YALI: Federman and Carey, 1980; Hardiman, 2008; Vinci, 1985) and Sicilian Channel (Green Tuff (Y6): Vogel et al., 2010; P-II: (Karkanis et al., 2015; Lézine et al., 2010; Paterne et al., 2008). Error bars show 2 standard deviations of repeat analysis of the StHs6/80-G MPI-DING standard glass.

5.4.2. Slivata 1

Figure 5.5 provides age, magnetic susceptibility and sedimentary data for Slivata 1. Ages show that the section spans from 23.30 ± 1.50 ka at 6m depth, to 14.11 ± 1.07 ka just above the

transition to the Holocene topsoil. The accumulation rates based on the OSL data show significant variability regardless of whether minimum or mean accumulation rates are calculated (Figure 5.6). The highest sediment accumulation rate occurred between 22.66 ± 1.21 and 22.04 ± 1.05 ka (mean = 161 cm ka^{-1} ; minimum = 34 cm ka^{-1}). This peak is part of a general accumulation rate rise that continued until 18.88 ± 1.05 ka (mean = 92 cm ka^{-1} , min = 55 cm ka^{-1}).

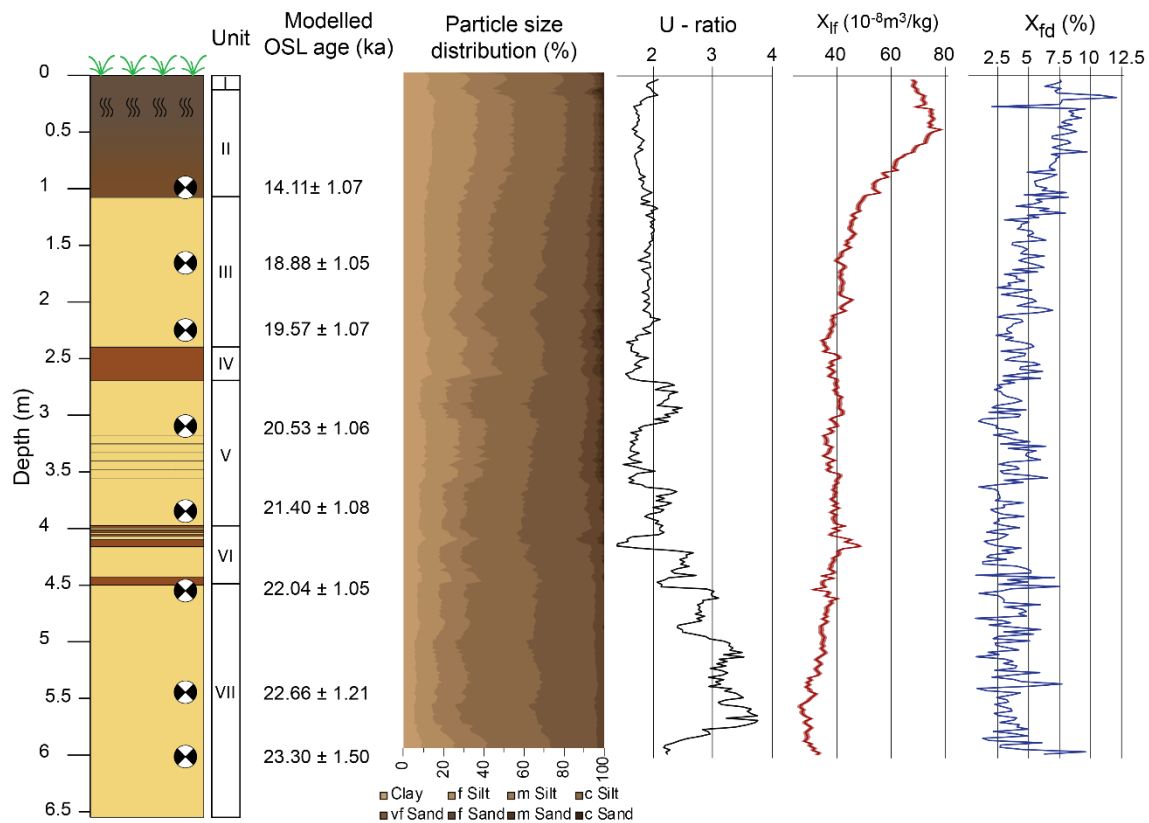


Figure 5.5 Stratigraphic log of Slivata I sedimentary units (Figure 5.3) and modelled OSL ages (Zeeden *et al.*, 2018a) and particle-size distribution. U-ratio represents the ratio of medium and coarse silt (16-44 μm) to very fine and fine silt (5.5-16 μm). Magnetic susceptibility is presented as low-frequency (X_{lf}) and frequency dependant (X_{fd}) values.

There is a general particle size reduction from the bottom of the section upwards (Figure 5.5), in particular there is a decrease in the proportion of very fine and fine sands, from ~30% to less than 20% combined. Coarse silt is the most abundant grain size fraction,

closely followed by very fine sand in Units VI and VII and fine silt in Unit III. The U-ratio values show oscillations with almost step like changes below 2.5m, whereas in the top 2.5 metres it is rather stable with values around 2.

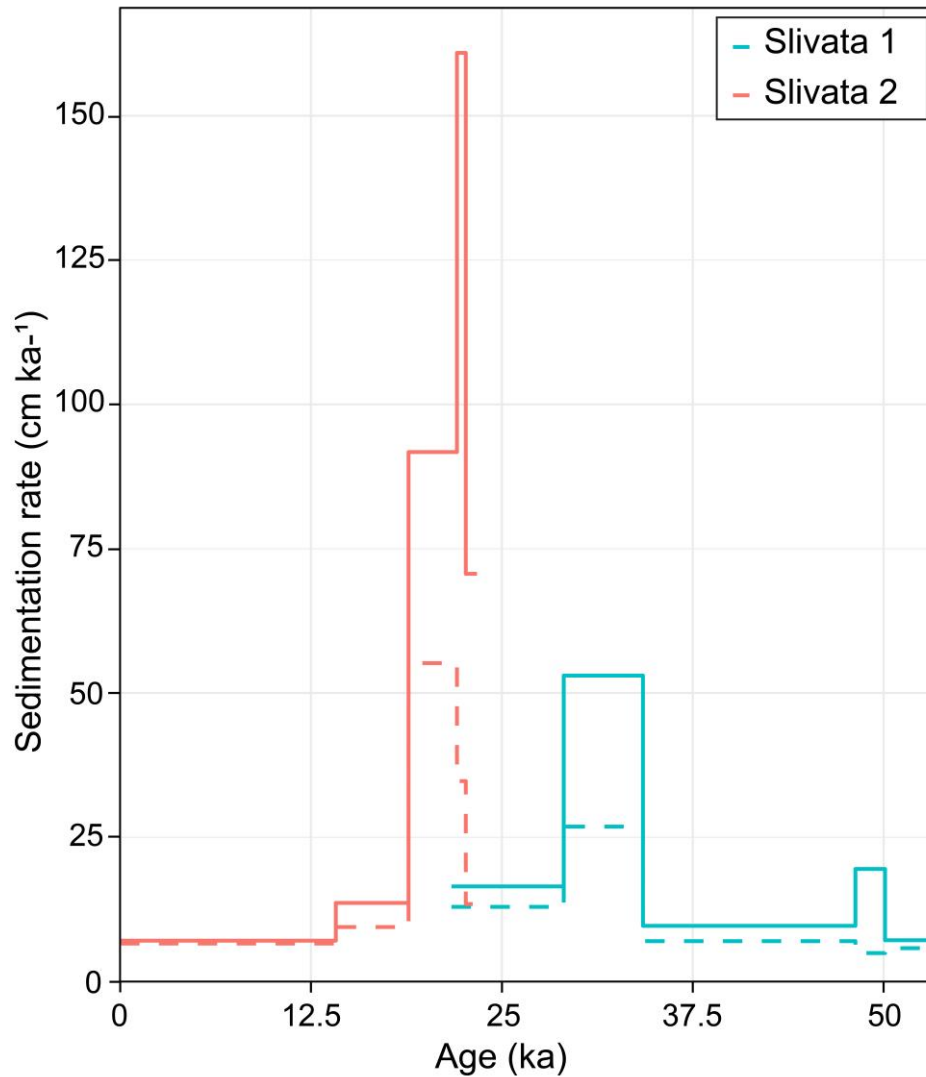


Figure 5.6 Sedimentation rates (cm ka^{-1}) for both Slivata profiles presented as mean (solid line) and minimum (dashed line) values based on the modelled ages.

The highest X_{lf} values (Figure 5.5) were detected in the soil, and the lowest in the loess below 5m depth and values generally decrease with depth. After an initial period of relatively enhanced and stable X_{lf} in Unit I, the values drop quite rapidly over Unit II/III, from which point they gradually decreases down section. Additionally, three peaks of

relatively enhanced X_{lf} at ~2m, 2.5m, and 4m can be noted. The frequency-dependent (X_{FD}) record is variable, mostly oscillating between 2-5% up to the transition to the palaeosol (Unit II), followed by an increase towards the top of the sequence.

5.4.3. Slivata 2

The results of the sedimentological analyses and chronology for the sampled section at Slivata 2 are presented in Figure 5.7. Additional samples were collected in the field that provide the uppermost and the lowermost chronological control points: the tephra horizon (Unit IV) dated to 21.92 ± 0.61 ka cal BP (Lee *et al.*, 2013); and the luminescence age 95.55 ± 6.29 ka (Unit X), respectively. However, the sedimentological data was collected between Units IV and X and covers the period between 30.17 ± 1.62 ka and 52.29 ± 4.00 ka. The highest net accumulation rates are observed between 30.17 ± 1.62 ka and 34.20 ± 2.31 ka (Unit VII), where they reach $27\text{-}53 \text{ cmka}^{-1}$ (Figure 5.6).

The particle size distribution is highly variable throughout the Slivata 2 profile, in particular between 6.7m and 7.8m (Figure 5.7). Although the range of values in the U-ratio is small, the shifts are abrupt. Particularly striking are the grain size changes in Unit VII, with shifts in values as high as 1.25 between neighbouring samples. There is a slight coarsening trend from the bottom upwards as the clay and fine silts are replaced by coarse silt and very fine sand.

At Slivata 2, X_{lf} broadly increases with depth. The values rise slightly in Unit VII, but become very irregular with some of the largest peaks, indicating ferrimagnetic mineral enhancement, recorded in this part, but there seem to be no correlation between X_{lf} and X_{FD} . X_{FD} is highly variable, decreasing over time in three step-like shifts from Unit X to Unit IX, in the loess-palaeosol 10.15-9m, and 9-7.7m. The fourth shift, through the top of Unit VIII has a more gradual trend.

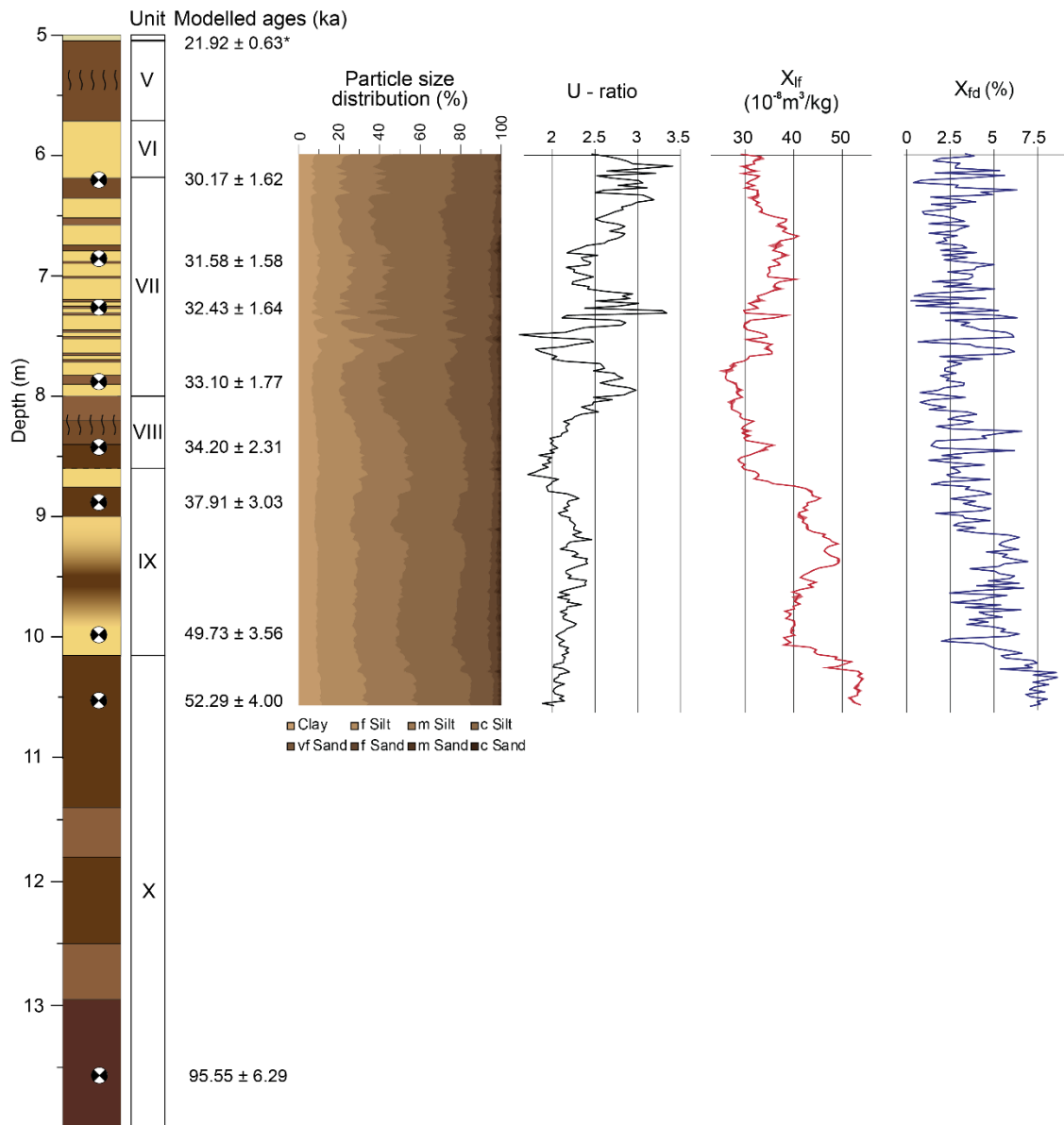


Figure 5.7 Stratigraphic log of Slivata 2, sedimentary units (Figure 5.3) and modelled OSL ages (Zeeden *et al.*, 2018a) and particle-size distribution. U-ratio represents the ratio of medium and coarse silt (16-44 μm) to very fine and fine silt (5.5-16 μm). Magnetic susceptibility is presented as low-frequency (X_{lf}) and frequency dependant (X_{fd}) values. *- denotes age based on tephra sample.

5.4.4. U-Pb results

Figure 5.8 shows that the majority of the zircon U-Pb ages at Slivata fall in the 200-800Ma bracket. However, additional groupings, albeit much smaller, of Precambrian ages can be

seen. Most samples also contain very young (<100Ma) zircon grains. For most samples, three distinct populations are observed at ~300Ma, ~450Ma, and ~650Ma. Interestingly, whilst the largest population is seen at ~450Ma, in samples BUL17/1/3 and BUL17/1/5 this Ordovician population is subordinate. Further, the Carboniferous population (~300Ma) does not seem to contribute greatly to the age distribution in sample BUL17/1/11.

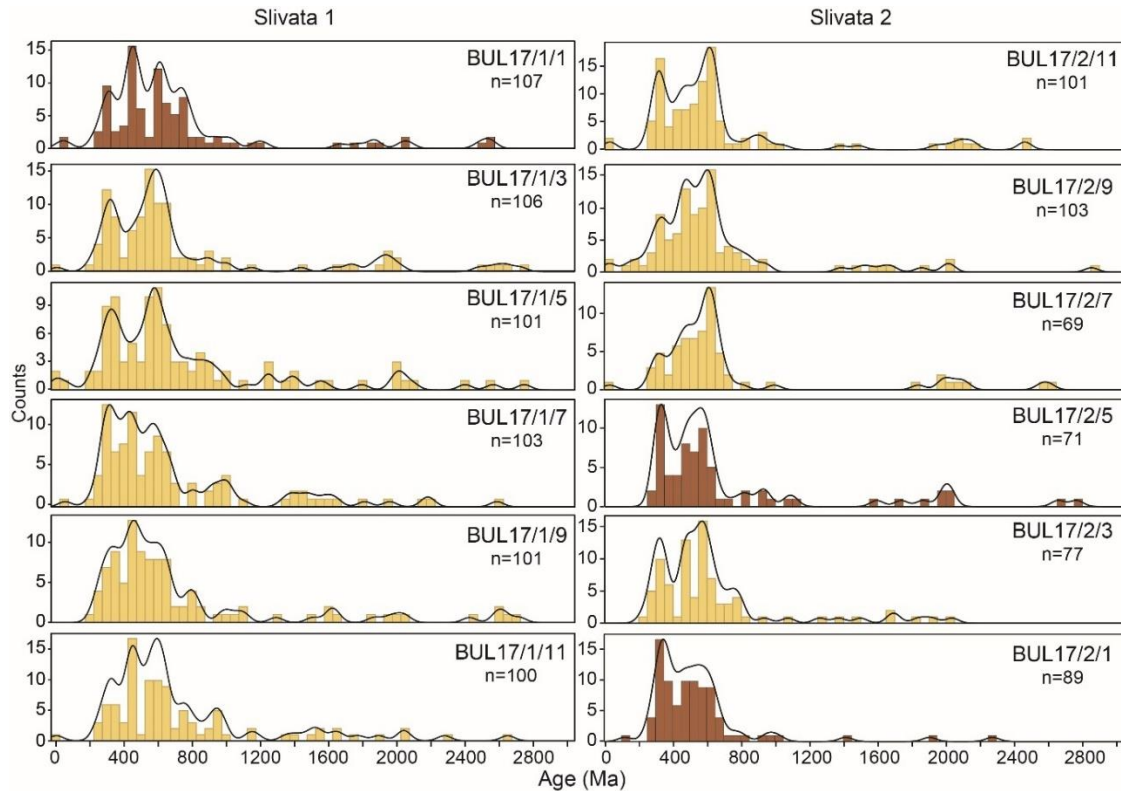


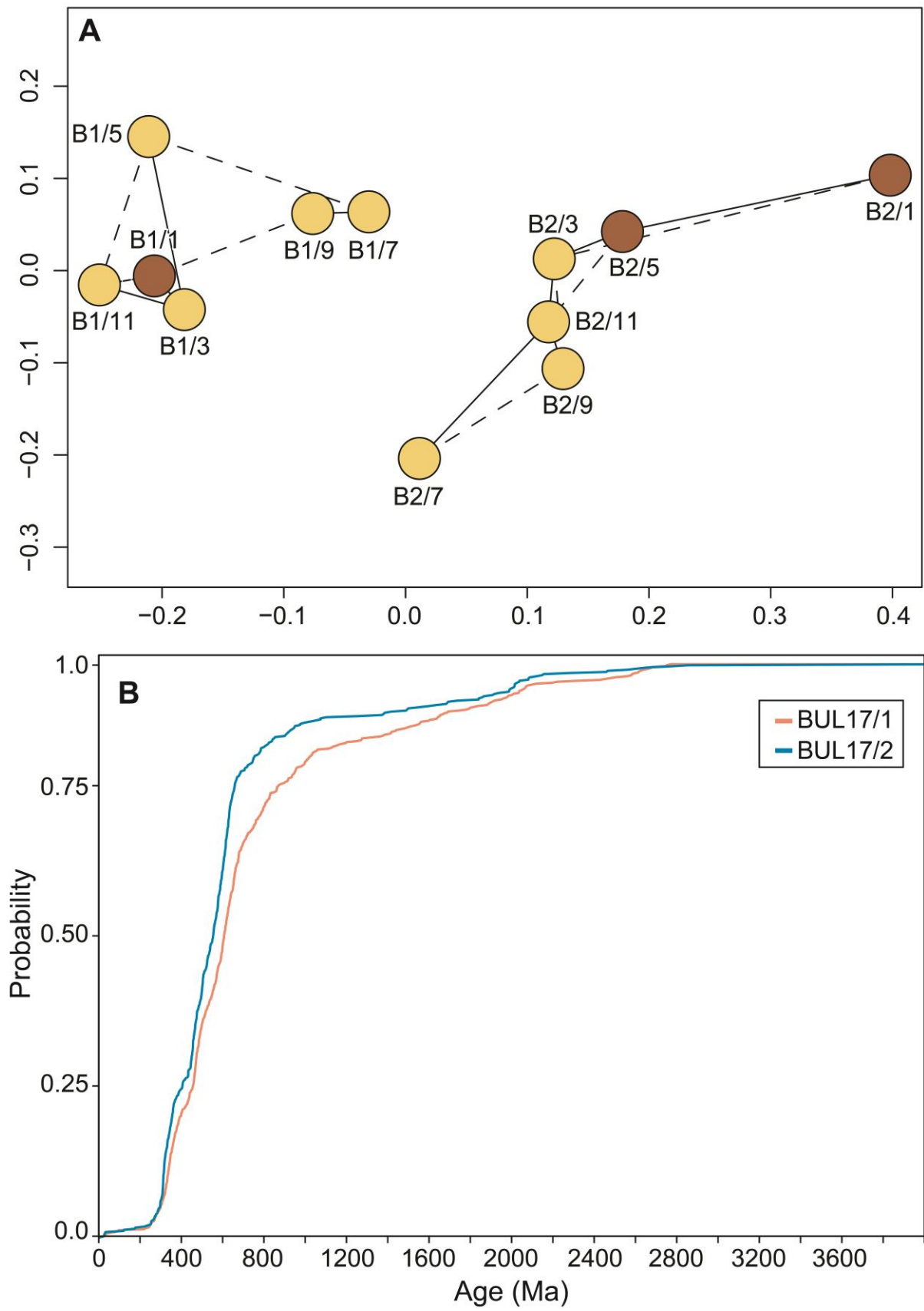
Figure 5.8 Zircon U-Pb Kernel Density Estimator (KDE) diagram for loess (beige) palaeosol (brown) units from both Slivata profiles. Samples are presented in stratigraphic order and colours denote loess vs palaeosol samples. Based on 30 bandwidth.

KDEs for Slivata 2 also show that the majority of ages obtained are of Mesozoic-Palaeozoic age. Although there is also an indication of three distinct peaks in the distributions, this is not as apparent as in Slivata 1, however this could be an artefact of the smaller number of grains analysed. For the top three samples the largest population is observed at ~650Ma, however grains of that age are not as abundant in samples BUL17/2/1, BUL17/2/3, and BUL17/2/5, where an additional population at ~550Ma is observed. In all samples the

~350Ma population observed is one of the more dominant, apart from samples BULI7/2/7 and BULI7/2/9. In the case of the former this is possibly due to a smaller number of grains analysed, but this is not the case for the latter. The proportion of grains forming the ~450Ma population is variable between samples. While the contributions of grains of that age are obvious in samples BULI7/2/3, BULI7/2/5, and BULI7/2/9, in the other three samples they are not. Finally, very young grains (<100Ma) are only observed in the top three samples.

To statistically investigate the differences in distribution between the individual samples, U-Pb zircon ages were plotted using an MDS map (Figure 5.9 A). It is rather striking that the two sites plot in two distinct clusters, that do not overlap with each other. For the next step individual samples were combined into datasets representing both profiles, Slivata 1 and Slivata 2, (Figure 5.9 B) and plotted as a frequency distribution. This shows that the two curves do not overlap. Further, the initial separation of the two distributions occurs at ~300Ma, but it's the general lack of grains of 600Ma> at Slivata 1 that is driving the difference.

Figure 5.9 A) Multi-dimensional scaling (MDS) map for data in Figure 5.7, showing individual samples from both Slivata profiles. Full lines connect the two most similar samples, whereas dotted lines show the second closest data matches. For clarity, sample codes for samples are shortened (e.g., BULI7/1/1 is B1/1). B) Age distributions presented as a cumulative percentage with individual samples from Slivata 1 and Slivata 2 combined.



5.5. Discussion

5.5.1. Chronology assessment

The interpretation of the complex stratigraphic and sedimentary records preserved within the LPS at Slivata requires a careful consideration of chronological reliability. First, samples were collected predominantly from aeolian deposits and the field investigation (Figure 5.3) revealed no signs of sediment displacement as a result of e.g. solifluction or cryoturbation. Further, areas affected by bioturbation were avoided. Therefore, it is likely that the dated aeolian material was bleached during transport and results reliably constrain the age of burial.

The luminescence signals (Appendix K) indicate rapidly decaying signals in quartz, dominated by a strong fast component. The signal from the feldspar pIRIR protocol does not fade above the accepted measurement detection levels (section 3.6.6.5). These intrinsic luminescence signal characteristics indicate stability of the luminescence signal.

5.5.2. Provenance overview

The U-Pb zircon dating results presented here are the first attempt at utilising provenance data to support an interpretation of a complex Quaternary stratigraphic and sedimentary record. The provenance component requires further investigation, in relation to the source(s) of the material, to be able to provide definitive answers. Nonetheless Figures 5.8 and 9A indicate that there is a general lack of variability in age distributions within each site. This is particularly evident from the MDS where each site plots as a separate cluster.

Further there is a consistent difference between both loess-palaeosol profiles, seen in the zircon age distributions (KDEs), MDS and cumulative percentages (Figure 5.9). With Slivata 2 comprising more grains <600 Ma, whereas Slivata 1 has more Neoproterozoic and

Mesoproterozoic grains, this could be driven by some episodic contributions from older rocks to Slivata 1.

5.5.3. Environmental interpretation

5.5.3.1. Slivata 2

The bottom unit (X) at Slivata 2 is part of a thick, welded pedocomplex (Figures 5.1 and 5.8) thought to be corresponding to regionally-defined palaeosols SI-S4 (Avramov *et al.*, 2006). The age from the bottom of this unit indicate that sediment deposition commenced at 95.55 ± 6.29 ka and concluded shortly after 52.29 ± 4.0 ka. These ages suggest that loess deposition either did not occur at this site at the onset of the glacial period (equivalent to the MIS 4 stage) or is not preserved. While considerably thin, other loess sites across the region e.g. Costineşti (Constantin *et al.*, 2014) or Semlac (Zeeden *et al.*, 2016), usually record loess units during this period. However, further detailed sedimentological and chronological investigation is required to determine whether loess deposition did not occur during this period or if it was eroded.

Units IX and VIII represent the onset of loess deposition, punctuated by three dark brown palaeosol like layers. The age from near the bottom of Unit IX places the beginning of loess deposition at 49.73 ± 3.56 ka that persisted until shortly after 33.10 ± 1.77 ka. During this time there is only a slight increase in sediment accumulation rates indicating that the environment was still relatively stable and/or that the sediment delivery from the immediate source (Danubian floodplains) was still low.

Despite the relatively variable X_{FD} signal, a step changes can be identified from Unit X to Unit IX and from the middle of unit IX to the start of unit VII. This is interpreted as representing a rapid shift towards more arid conditions, at $\sim 49.73 \pm 3.56$ ka and again at 37.91 ± 3.03 ka. The later change is in broad agreement with magnetic susceptibility results

from Vlasca and Urluia (Obreht *et al.*, 2017). However, these sites show a continuous decrease in X_{FD} and U-ratio, whereas Slivata's shifts are only seen in magnetic properties and are more abrupt (Units X and IX; Figure 5.7). A similar dissimilarity between records from the Lower Danube and records from the Carpathian Basin has been explained by progressive continentalisation in response to changes in atmospheric circulation patterns and moisture sources (Obreht *et al.*, 2017).

The most striking feature of the Slivata 2 loess-palaeosol sequence is unit VII (Figures 5.2 and 8). This loess-palaeosol complex comprises 13 thin reddish-brown bands. The samples collected at the bottom and top of this unit provide ages of 33.10 ± 1.77 ka and 30.17 ± 1.62 ka respectively, indicating that this complex was deposited relatively rapidly ($27\text{--}53 \text{ cm ka}^{-1}$; Figure 5.6). The U-ratio and particle size distribution reveal dramatic shifts (Figure 5.7), especially in the lower portion of this unit. This variability is also seen in magnetic susceptibility (X_{FD}), although it shows a gradual decreasing trend throughout the unit. When analysed together however, the results from the stratigraphy, magnetic susceptibility and grain size do not always match. In a few cases the red bands, while showing slightly higher clay content, do not correspond to higher magnetic susceptibility values, and vice versa.

Although thin and weakly developed incipient soils are common in Western European loess profiles (e.g. Antoine *et al.*, 2009b; Lehmkuhl *et al.*, 2016) they have rarely been reported from Central European loess sequences. An investigation from Stayky in Ukraine (Rousseau *et al.*, 2011) is a notable exception, with eleven similar soil-like horizons being reported from within a loess unit. As with Slivata, the particle size shifts abruptly within the sequence, and field magnetic susceptibility results did not always align with the stratigraphy (Rousseau *et al.*, 2011). At Stayky these features have been interpreted as embryonic soils, based on sedimentological and pollen analyses, and linked with North

Atlantic climate influences (Rousseau *et al.*, 2011) and changes to the hydrological cycle (Veres *et al.*, 2018). Despite a relatively high chronological resolution for the soil features at Slivata 2, the inherent uncertainty of luminescence ages precluded any definitive connection between them and short lived climatic and/ hydrological shifts.

Although some of these features at Slivata could represent *in-situ* pedogenesis, from a chronological point of view the paedogenetic ‘events’ would have had to occur on average every ~300-580 years. It is proposed here that that these horizons do represent soils, but in the form of colluvial soil material eroded from upslope from loess sequences and redeposited during primary loess deposition, disrupting the stratigraphy. In fact, colluvial soils are not an uncommon feature in the loess landscape due to the erodibility of the material (Wolf and Faust, 2013). The dramatic shifts in the U-ratio further point to aggregates of soil material, which would be likely to retain higher magnetic susceptibility values. The development of these soils, colluvial in origin, would be closely tied to climatic conditions, local topography, and geomorphology (Lehmkuhl *et al.*, 2016). The ubiquitous gullies and incised valleys in the vicinity of Slivata further indicate a dynamic landscape.

Increased rainfall could be a trigger for soil erosion and slope wash. Paleoenvironmental reconstructions from the Ascunsă Cave show abrupt changes in $\delta^{18}\text{O}$ signal after ~35ka, indicating large fluctuations in regional hydrologic conditions (Staubwasser *et al.*, 2018). However, analysis of core samples from the Black Sea (Wegwerth *et al.*, 2015, 2016) and other loess sites (Obrecht *et al.*, 2017) suggests that the period after ~34 ka was characterised by more progressive continentalization and prolonged severe winters. In addition, there is also an indication of stronger seasonality, which could lead to periodical ice melting (Rostek and Bard, 2013; Wegwerth *et al.*, 2016), combined with decreased boreal vegetation cover (Connor *et al.*, 2013) which would also lead to increased soil erosion. Given Slivata’s closer proximity to mountainous regions than other Lower Danube

sites the re-distribution of material from higher ground is likely. The genesis of unit VII cannot be resolved without further investigation using e.g. micromorphology, which could help to determine if pedogenic processes (e.g. clay coating, or biological activity) took place within sediment.

5.5.3.2. *Slivata 1*

The investigated part of the Slivata 1 loess-palaeosol profile (Figure 5.5), preserves a record of the last ~23ka, and corresponds with the LGM in Eastern Europe (Feurdean *et al.*, 2014). Units VII, V and III comprise loess deposited between 23.30 ± 1.50 ka and 14.11 ± 1.07 ka, interrupted for brief periods by palaeosol like features (Units VI and IV). The dominance of silt-size sediment, low magnetic susceptibility values (Figure 5.5), and highest accumulation rates (Figure 5.6) across both sites, indicate primary loess deposition. This loess deposition could be linked to a multiple glacial advance during the LGM, experienced at 25-23ka and at 16-18ka in the Balkan Mountains (Kuhleemann *et al.*, 2013) and ~21ka, ~19.5ka, and ~16.3ka in the South Carpathians (Ruszkiczay-Rüdiger *et al.*, 2016). While another re-advances, at ~15.2ka, and ~13.5ka, was suggested for the South Carpathians (Ruszkiczay-Rüdiger *et al.*, 2016), it is likely it is absent from Slivata 1 record due to relatively small nature of the re-advances (seen only above c. 1900m).

Slivata 1 also preserves a number of thin, brown, palaeosol-like bands separated by loess (Figure 5.3 and 5.5). Units VI and IV are both constrained by luminescence ages, placing their development between 22.04 ± 1.05 ka and 21.40 ± 1.08 ka, and 20.53 ± 1.06 ka and 19.57 ± 1.07 ka, respectively. In both cases although there is an increase in the proportion of clay and fine silt, as in the case of Slivata 2, the stratigraphic bands do not always match with changes in grain size or magnetic susceptibility. The conflicting sedimentological proxy data from both units precludes a definitive interpretation of these features as palaeosols, without further investigation. Rather it is more likely that these features, as

with Slivata 2, represent colluvial redeposition of soil material. Additionally, in both cases there is simultaneous coarsening of the sediment which could suggest mixing in of other material during slope wash or aeolian additions of sediment from Danube's alluvium or fluvial dunes.

The final Unit (II), defined by a luminescence age of 14.11 ± 1.07 ka from just above the boundary, marks a pre-Holocene period of environmental stability with favourable conditions for pedogenesis. The age could reflect the timing of sediment deposition, into which soil has later developed. The luminescence research of Constantin *et al.* (2018) on Ukrainian, Serbian and Romanian loess showed that the sedimentary boundary or magnetic threshold may not provide precise chronological markers for the onset of the Holocene. On the other hand, it is possible that, despite the continued sediment delivery to the site, conditions during the Late Glacial were already favourable for vegetation to establish and soil processes to begin. Chironomid records from the South Carpathians indicate a rapid summer temperature rise around $\sim 14,700$ cal BP, followed by a weakly expressed Younger Dryas cooling (Tóth *et al.*, 2012), with the absence of a YD glacial re-advance in the South Carpathians (Ruszkiczay-Rüdiger *et al.*, 2016). With the absence of loess post ~ 14 ka it is possible preserves a record of earlier warming from 14.11 ± 1.07 ka, ahead of the Holocene.

5.5.3.3. *Sediment production and transport*

The environmental reconstruction points to a very dynamic system with plenty of available sediment for deposition during the LGM and deglaciation. The proximity to the floodplains of the Danube river, the South Carpathians and the Balkan Mountains (Figure 5.1), likely drove sediment production and delivery to the site.

Slivata appears to fit the sediment production and transport model proposed by Smalley *et al.* (2009). Sediment produced by glacial erosion in the nearby mountainous regions

was delivered to more distant locations by fluvial transport, in this case in the Danube system, redistributed on the floodplains as alluvium and finally transported by aeolian processes and deposited as loess. This is particularly evident from increased sedimentation rates ($92\text{--}161\text{ cm ka}^{-1}$; Figure 5.6) that coincide with glacial re-advance (Ruszkiczay-Rüdiger *et al.*, 2016). Further, the relatively mixed composition of particle sizes in the loess units indicates the key role of the Danube's alluvial plains as an immediate source of material. This is evidenced by the significant components of medium and coarse sand, which are not available for long distance aeolian transport but are predominantly subject to movement via saltation (Nickling and McKenna Neuman, 2009).

Support for the upslope soil erosion and colluvial delivery mechanism for the redeposited soil sediment comes from a combination of sediment accumulation rates and provenance data. Figure 5.6 indicates that at Slivata 2, the highest net sediment accumulation rates are seen in Unit VII. Figures 5.8 and 5.9 show that while similar for the most part, there seems to be a variability between Slivata 1 and Slivata 2. We suggest that episodic inputs from locally derived geologies, in the form of the in-washed upslope soil could explain the variability in provenance between two profiles located so closely to each other.

5.5.3.4. *Inter-site variability*

Although the investigated sections of Slivata do not have a great chronological overlap, Figure 5.3 shows that there are marked differences between the stratigraphy of both sites. Especially, the thickness of the soil at the top of Slivata 2 (not investigated in detail as a part of this study), which without further chronological work should not be assigned entirely to the Holocene. The chronological results from Unit II at Slivata 1, supported by the research of Constantin *et al.* (2018), show that the stratigraphic boundaries do not equate with precise age determinations for regionally and globally defined climato-stratigraphic units (e.g. the LGM, the Younger Dryas). Further, based on the presence of

the ~22 ka cal BP Cape Riva (Y-2) tephra horizon in Slivata 2, Units VI and V at Slivata 2 must correspond in some part with Units V, VI and VII at Slivata 1 – yet they record distinctly different sedimentary sequences. This stratigraphic variability cannot be explained by climatic influences as the sites are less than 2km apart; rather, it highlights the importance of local factors such as geomorphology or palaeotopography in sediment preservation.

Further, an inspection of regional LPS stratigraphy, proxies and chronologies indicates that when scaled up the differences in response seen at Slivata 1 and 2 persist between sections of the Lower Danube. The nearby loess-palaeosol site at Harletz (Lomax *et al.*, 2018) shows a 2m thick last interglacial palaeosol which is only about half as thick as the palaeosol seen at Slivata 2 (Figure 5.7). On the other hand, the Harletz luminescence chronology suggests a similar prolonged timing of palaeosol development (82 ± 7 ka to 62 ± 5 ka), contrasting other sites in the Lower Danube that indicate loess accumulation from ~90ka (Timar-Gabor *et al.*, 2011; Timar *et al.*, 2010; Vasiliniuc *et al.*, 2011). The thickness of the LGM loess at Slivata is also higher (over 5m) than at sites further downstream, e.g. Harletz (Lomax *et al.*, 2018), Mostiștea (Vasiliniuc *et al.*, 2011), Vlasca and Urluia (Obreht *et al.*, 2017). This could be driven by higher preservation potential and/or higher availability of sediment.

The magnetic properties of Slivata 2 and sites in Dobrogea (Obreht *et al.*, 2017) both show a decreasing trend over last ~50ka, indicating that they are both responding to progressive increase in continental influence. However, they do so in different manners. Whilst the latter changes gradually over time, the former shifts in a step like manner reaching temporary periods of stable magnetic signal and therefore periodically increasing aridity. This should not be surprising as they are separated by over 500km and might have other

proximal influences overprinted; i.e. Black Sea (Dobrogea) and Carpathian and Balkan Mountains (Slivata).

This study highlights the risks of correlating loess sites based only on stratigraphy, grain size, magnetic susceptibility records or a fragmented chronology. The observed regional differences raise questions as to how representative a single site is of a region and whether these arbitrary connections between sites should be made without robust and independently-derived absolute chronologies that have been verified using multi-chronometer approaches.

5.5.3.5. *Scaling of climatic influences*

There is currently a drive to report on, and compare, loess sites with Greenland records (e.g. Meyer-Heintze *et al.*, 2018; Moine *et al.*, 2017; Zeeden *et al.*, 2018c). Loess-palaeosol sequences in general provide a record of glacials and interglacials (i.e. global large-scale changes). However, should there be a pursuit for identification of a response to short-lived continental-global scale climatic episodes represented in Greenland in LPS proxies that do not directly respond to the same climate forcing, e.g. grain size?

The thin palaeosols developed during the LGM (22.04 ± 1.07 - 21.40 ± 1.08 ka and 20.53 ± 1.06 - 19.57 ± 1.07 ka; Figure 5.5) are not specific only to Slivata. A high number of palaeosol like features in loess were also reported in Stayky (Ukraine) where they developed between 25.0 ± 2.1 ka and 16.3 ± 1.3 ka (Veres *et al.*, 2018) and were interpreted as embryonic soils. These features have been previously thought to be driven by changes in the North Atlantic climate system (Rousseau *et al.*, 2011), as represented in the Greenland ice core records. However, a high resolution chronology presented by Veres *et al.* (2018) showed a lack of coincidence with Greenland ice core $\delta^{18}\text{O}$ isotope records, which do not record sufficient variability for the period of 19.57 ± 1.07 ka to 22.04 ± 1.05 ka (Blockley *et al.*, 2012). Additionally, recent high-resolution radiocarbon dating of Nussloch LGM loess was also

unable to tie all pedogenic horizons to Greenland records (Moine *et al.*, 2017), showing that there might be other factors that influence development of these features.

Firstly, this should not be surprising as the Greenland isotopic record provides primarily a picture of temperature and water source changes in Greenland. While often seen as the record of global climatic change, it does not necessarily correspond with signals of regional or local climatic and environmental change at distant sites. The loess-palaeosol records from Slivata, Nussloch, and Stayky suggest that although global climatic changes (i.e. glacial-interglacial) are preserved in the sediment stratigraphy, evidence of changes in regional and local conditions can be imprinted onto “the main” loess units. This shows that these terrestrial archives respond in much more complex ways than it is often assumed, especially as such striking sedimentological differences between two loess-palaeosol profiles are seen at such short distances. Secondly, these three records indicate that LGM climate was not as uniform across the continent as has been assumed, with the classic interpretation of “cold and dry” being an oversimplification. Therefore, sites such as Slivata show that loess deposits can provide much more paleoenvironmental information than just ties to global atmospheric or marine records.

5.6. Conclusion

This study provides the results of a high-resolution particle size and magnetic susceptibility investigation supported by 18 OSL and pIRIR ages for two loess profiles at Slivata, Bulgaria. The chronological framework is further supported by a tephra layer, correlated to Cape Riva (Y-2) tephra. It has implications for both the loess and tephra communities, as this is the most northerly terrestrial detection of Cape-Riva tephra. Further, this discovery provides a new tephrostratigraphic marker for loess sites and other Mediterranean palaeoclimatic archives during the LGM.

The combination of the tephra marker and luminescence dating has provided a robust basis for connecting both sites and developing an age depth model. While the chronology encapsulates almost the whole glacial-interglacial cycle, the primary focus of the sedimentological work covers the last ~52ka. Our results show that despite the short distance between the two profiles there are some discrepancies between the stratigraphic records. Further, Slivata preserves thin soil like features, similar to the ones previously described at Stayky (Veres *et al.*, 2018) and Nussloch (Moine *et al.*, 2017). While their origin is still debated, we interpret these features as in-washed soil sediment, rather than pedogenic features, based on their timing of deposition, sedimentation rates and provenance signatures. We further suggest that while the signal of big global climatic shifts is preserved in loess, it is the local rainfall events, palaeotopography, geomorphology, and hydrological configuration that provide a more likely explanation for the variability seen within individual loess units rather than tele-connections with distant Greenland. Finally, while the thin soil like features require further investigation to determine their origin, their deposition during the periods of loess accumulation suggests that these periods are much more complex than “cold and dry”.

SUMMARY: Paper 2

Chapter 5 addresses **Objective 1** for site two, i.e. it produces a chronology and reconstructs the palaeoenvironmental history of the site, by applying particle size, magnetic susceptibility, luminescence dating, tephra and provenance techniques.

In Central and Eastern Europe loess-palaeosol sequences are considered relatively straightforward sedimentary sequences, with glacials represented by loess deposits and interglacials preserved as one or two palaeosols. Paper 2 presents a record from two nearby loess sites in (Slivata) North Bulgaria that preserve thin soil like features, similar to the ones previously described outside the Carpathian Basin e.g. Stayky (Veres *et al.*, 2018) and Nussloch (Moine *et al.*, 2017). Based on the multi-proxy investigation, supported by an absolute chronology and provenance, this paper identifies these features as colluvial deposits rather than pedogenetic features. It also suggests that while the signal of large climatic changes is represented in loess sequences, it is the local and regional influences which are preserved within individual loess units, rather than the tele-connection with distant archives of global change.

This paper also presents the results of a geochemical analysis of a tephra layer discovered at Slivata, which is confidently correlated to Cape Riva (Y-2) tephra. This is the most northerly terrestrial discovery of the Cape-Riva tephra, which has implications both for the loess and tephra communities, providing a new tephrostratigraphic marker for loess sites and other Mediterranean palaeoclimatic archives during the LGM.

Finally, this is a first of its kind analysis that combines a multi-proxy investigation with high resolution luminescence chronology, tephra, and provenance approaches, to interpret complex stratigraphic and sedimentary loess-palaeosol records.

Chapter 6: Paper 3

Re-analysis of late Quaternary dust mass accumulation rates in Serbia using new luminescence chronology for loess-palaeosol sequence at Surduk

Paper 3: Fenn, Kaja, Durcan, Julie A., Thomas, David S.G., Millar, Ian L., Marković, Slobodan .B.

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Abstract

Despite numerous palaeoenvironmental investigations of loess-palaeosol sequences across the Carpathian Basin, well dated high-resolution records are scarce. This paper presents a new high-resolution chronology for the loess-palaeosol sequence at Surduk (Serbia), based on optically stimulated luminescence (quartz) and post-infrared infrared stimulated luminescence (polymineral) dating. The presented record spans 53-19 ka, with primary loess deposition occurring after 52 ± 2 ka, and differs from previously published chronologies that relied on less precise and now superseded dating protocols. Based on the new chronology, mass accumulation rates (MARs) for Surduk were constructed and compared with sites in the Carpathian Basin. The results demonstrate that accumulation periods are not consistent in timing or rates, across this area. The high-resolution dating strategy identifies a disturbance in sediment deposition that occurred after 45 ± 2 ka and implies that site contains a hiatus. Finally, we show samples that failed routine dose recovery and preheat plateau tests, and had low fast ratios. Supported by bulk sample geochemical analysis it is proposed that a potential abrupt source shift, during the Last Glacial Maximum, may be the cause of the anomalous luminescence behaviour.

Loess-palaeosol deposits in the Carpathian Basin preserve some of the longest, most complete terrestrial records of Quaternary climate change in central Europe (Fitzsimmons *et al.*, 2012; Marković *et al.*, 2012, 2015). Palaeoenvironmental interpretations of these sedimentary deposits are most valuable when supported by detailed chronologies. Recent advances in radiocarbon dating of loess, utilising earthworm granules (Moine *et al.*, 2017) and mollusc shells (Újvári *et al.*, 2014a, 2017), are contributing to very high resolution interpretations of the records. However, the absence of suitable material for radiocarbon dating at some locations, and an upper radiocarbon dating limit of ~50 ka, still present significant limitations to chronology generation. Further, radiocarbon dating provides ages for system closure, i.e. when the exchange of carbon with the environment ceased, which in most cases was when the organism died (Ramsey, 2008), rather than an age for the sediment deposition. Therefore, luminescence dating which directly dates the burial of sediment grains, is often the most suitable geochronological approach in loess research.

Due to a better understanding of electron transfer within the crystal lattice (e.g. Aitken 1985, 1998; Preusser *et al.* 2008), and athermal stability (Murray and Wintle, 1999; Wintle, 1973), optically stimulated luminescence (OSL) dating of quartz is usually favoured over the infrared stimulated luminescence (IRSL) of feldspars. However, the use of IRSL signals from feldspars offers an opportunity to date much older material (<500 ka; Thomsen *et al.* 2011), as quartz reaches saturation at 100-200 Gy (Timar-Gabor *et al.*, 2015; Wintle and Murray, 2006). With the dose rates for quartz varying between ~2.5 and ~4 Gy ka⁻¹ in the European loess context (e.g. Schmidt *et al.* 2010; Stevens *et al.* 2011; Fuchs *et al.* 2013; Újvári *et al.* 2014; Perić *et al.* 2019), this provides an upper dating limit approximately of 70 ka when using quartz OSL signals. Attempts to utilise more stable feldspar signals has seen the development of protocols, such as the post-infrared IRSL (pIRIR) protocol (Buylaert *et al.*, 2011; Thomsen *et al.*, 2008), which accesses more stable signals in comparison to lower temperature IRSL signals, and often bypasses the need for

a fading correction (Huntley and Lamothe, 2001; Kars *et al.*, 2008; Li and Li, 2008; Morthekai *et al.*, 2008).

Feldspar and polymineral based luminescence chronologies have been generated for numerous sites across the Carpathian Basin including in Serbia, Hungary, and Croatia. However, in many locations, such as Albertirsa (Novothny *et al.*, 2002), Erdut (Galović *et al.*, 2009), Surduk (Fuchs *et al.*, 2008), Paks (Frechen *et al.*, 1997), or Süttő (Novothny *et al.*, 2009), the chronology was determined from IRSL signals which had not been corrected for fading. Recently study used non-fading pIRIR signals rather than IR₅₀ signals to re-evaluate chronology at Paks (Thiel *et al.*, 2014). They showed that IR₅₀ signals fade by approximately 3%/decade, suggesting the need for many of previously investigated sites to be revisited.

High resolution, absolute ages provide a basis for a mass accumulation rate (MAR) estimations (Kohfeld and Harrison, 2003). MARs can provide an additional proxy for the past environmental change at site (Újvári *et al.*, 2017), as they “normalise” the magnitude and rate of the changes. This not only allows the opportunity to investigate and correlate change between different loess sites, but also other dust record archives (Frechen *et al.*, 2003; Perić *et al.*, 2019; Pigati *et al.*, 2013; Újvári *et al.*, 2010a). These datasets also feed into global palaeo-dust cycle models, providing information on the global and regional dust fluxes, and interactions between atmosphere and dust (Albani *et al.*, 2015; Mahowald *et al.*, 2006; Muhs, 2013).

We present a new luminescence chronology for the loess-palaeosol profile at Surduk, Serbia. A published chronology from a profile ~2 km from our site (Fuchs *et al.*, 2008) relied on ten OSL ages determined using an uncorrected IR₅₀ signal obtained using an older, multi aliquot additive-dose measurement protocol (MAAD). Subsequently, research by Antoine *et al.* (2009) supplemented the original chronology with radiocarbon ages and showed that the luminescence chronology was likely underestimating the burial age due to the use of the uncorrected IRSL signal. Here we present a new chronology based on thirteen quartz OSL and ten polymineral

PIRIR₂₂₀ ages. Based on this new chronology, MARs are calculated and discussed in the context of regional and global dust records.

6.1. Regional setting and site description

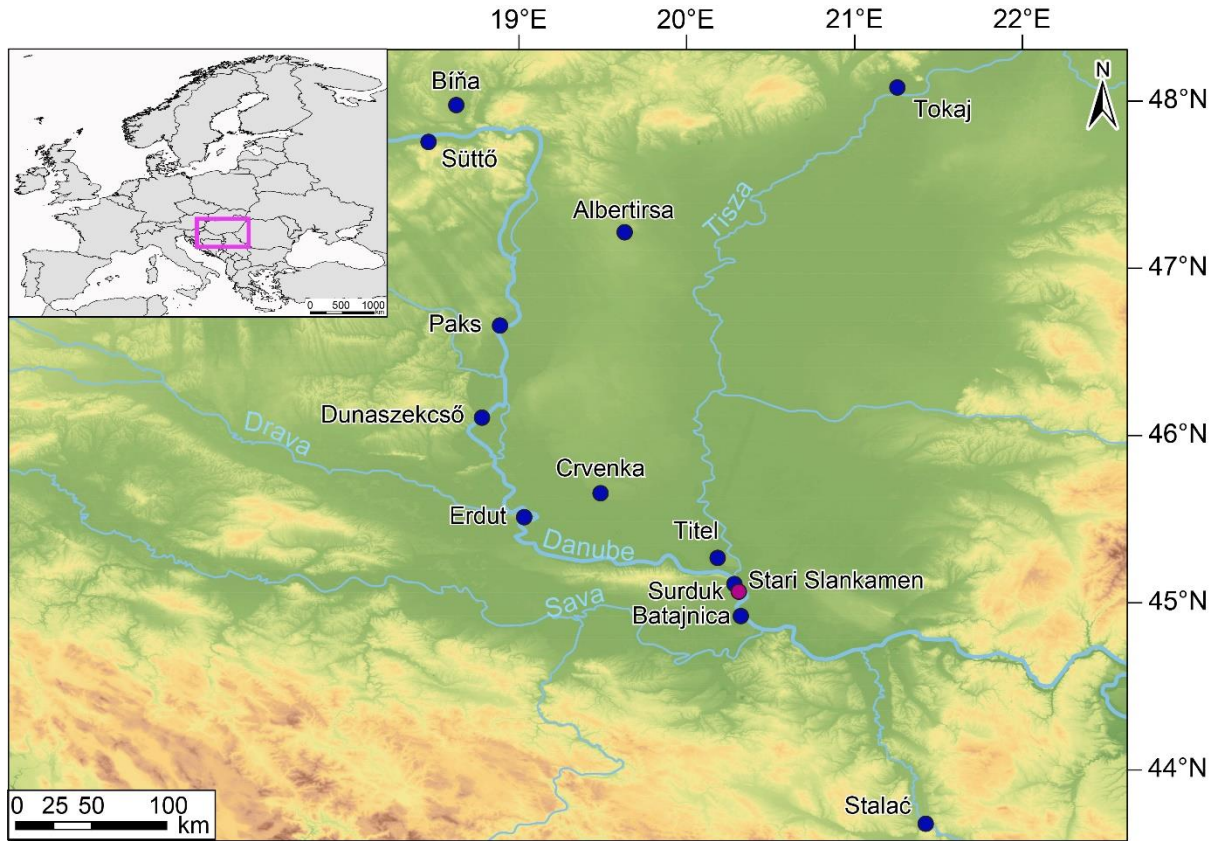


Figure 6.1 Map of the study region, study site (Surduk) and other sites discussed in the text (DEM Source: ©JAXA).

Surduk is part of a long stretch of thick loess deposits along the western bank of the Danube in Serbia, with a number of other sites such as Batajnica (Marković *et al.*, 2009), and Stari Slankamen (Marković *et al.*, 2011) previously investigated. The site (45°4'50.24"N, 20°18'50.12"E; 107 m a.s.l.) is situated 2 km northwest from a previously studied profile at Surduk, which was investigated for particle size, magnetic susceptibility, total organic carbon, carbonate content, and carbon isotopes (Antoine *et al.*, 2009a; Fuchs *et al.*, 2008; Hatté *et al.*, 2013). Due to access constraints the original site, referred to here as Surduk 1, could not be investigated. The new location analysed here is referred to as Surduk 2.

Surduk 2 is located 7 km downstream of the Danube's confluence with the Tisza River and ~20 km from the Titel Loess Plateau (Figure 6.1). The selected loess-palaeosol exposure is located in a gully along a road cutting 200 m from the main river channel. Figure 6.2 shows a simplified sedimentary succession and sample positions in the investigated Surduk 2 profile. The profile was sampled as two sub-profiles, A and B (Figure 6.2), 10 m apart. While fieldwork aimed to ensure the two profiles overlapped, we subsequently suspect that there is a gap of up to 1.5 m between the profiles.

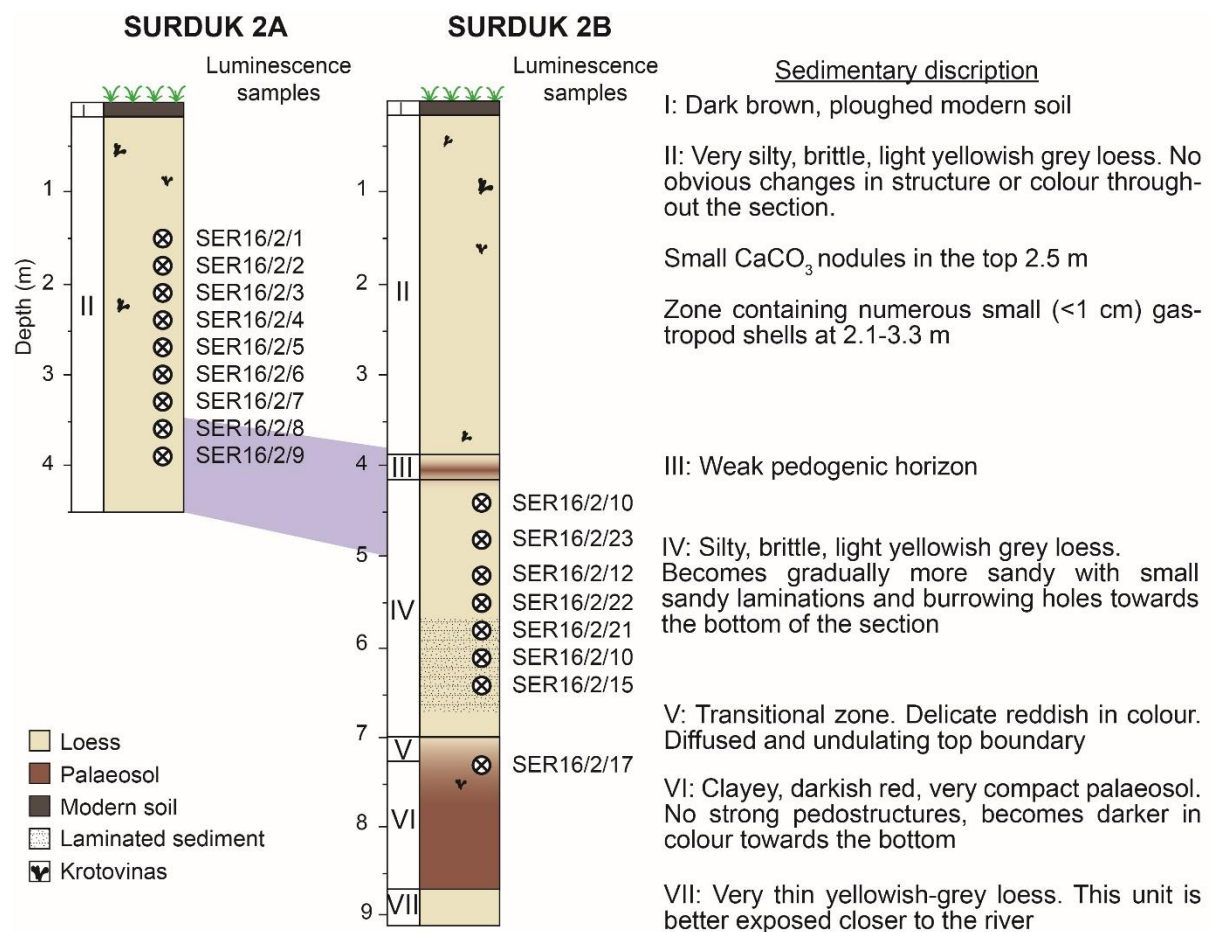


Figure 6.2 Stratigraphic logs for Surduk A and B, and sedimentary description for the profile. The blue shading indicates the expected age overlap on the basis of visual correlation in the field.

6.2. Luminescence dating

6.2.1. Sampling, preparation, measurement

Surduk 2 was sampled for luminescence dating using opaque light tight plastic tubes, hammered into the cleaned loess-palaeosol profile. Seventeen samples were collected at a 30 cm resolution throughout the profile, access permitting. All samples were prepared and analysed at the Oxford Luminescence Dating Laboratory, University of Oxford, under subdued orange-light conditions. To avoid light contamination, sediment from both ends of the sampling tubes was removed and used for particle size and dose rate analysis. All sediment was treated with 32% HCl (~2 h) and 30% H₂O₂ (up to two weeks), to remove carbonates and organic matter, respectively. Sieving and settling was used to isolate 4-11 µm grain sizes, which were divided into two fractions; polymineral and quartz. To prepare the quartz enriched fine grained fraction, samples were additionally treated with H₂SiF₆ (up to two weeks) to remove non-quartz minerals, followed by a brief 32% HCl (~2 h) immersion to dissolve any potential fluorite precipitates. In both polymineral and quartz cases, sediment was dispensed onto the surface of 9.7 mm aluminium discs.

Luminescence measurements were made using Risø TL/OSL readers fitted with a calibrated ⁹⁰Sr/⁹⁰Y beta source and a bi-alkali photomultiplier tube. For all quartz analyses, OSL signals were measured in a UV detection window through 7.5 mm U-340 glass filters (Bøtter-Jensen *et al.*, 2000) by stimulating with blue-light emitting diodes (470 nm). In the case of polymineral aliquots, IRSL signals were detected in the blue-violet region of the electromagnetic spectrum through a combination of Schott BG39/Corning 7-59 filters by stimulation with infra-red light emitting diodes (870 nm).

6.2.2. Dosimetry

Light-exposed sediment from the sampling tubes was dried, homogenised, and used to determine radionuclide concentrations for all samples. Concentrations of uranium, thorium, potassium and rubidium were determined by inductively coupled plasma mass spectrometry (ICP-MS) at the British Geological Survey, Keyworth, and converted to infinite-matrix dose rates using the conversion factors of Guérin *et al.* (2011). These dose rates were adjusted for alpha efficiency using a -values of 0.04 ± 0.04 for quartz and 0.11 ± 0.02 for polymineral fractions (Kreutzer *et al.*, 2014), grain size attenuation for alpha dose rates by Brennan *et al.* (1991) and Mejdahl (1979) for beta dose rates, and a typical loess moisture content of $15 \pm 5\%$ (e.g. Stevens *et al.* 2011; Schatz *et al.* 2012; Újvári *et al.* 2014). Geographic location, sediment thickness, and altitude were used to calculate the cosmic dose rate (Prescott and Hutton, 1994). All dose rates were calculated using the DRAC (v1.2) software (Durcan *et al.*, 2015).

6.2.3. OSL measurements

All of the tests and equivalent doses (D_e s) for quartz aliquots were determined using the single aliquot regenerative dose (SAR) protocol (Murray and Wintle, 2000; Wintle and Murray, 2006). In all cases luminescence was measured at 125 °C for 40 seconds following a preheat, while a 160 °C cut-heat was applied for the test dose. D_e s were determined by integrating the first 0.5 seconds of stimulation and by subtracting the background calculated from the last 20 seconds of stimulation. Depending on the fit, an exponential or an exponential plus linear function was used to fit the dose response curves.

6.2.3.1. Preheat plateau

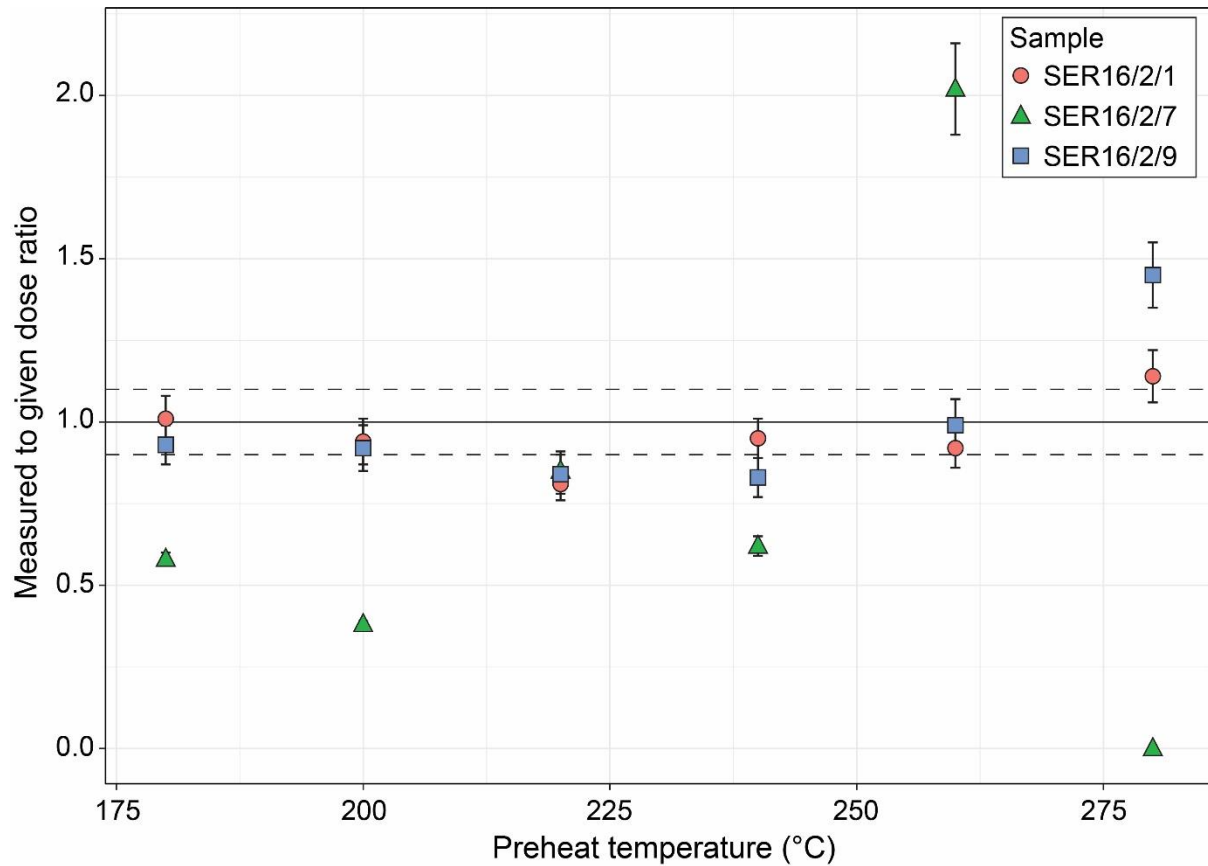


Figure 6.3. Preheat plateau for quartz samples SER16/2/1, SER16/2/7 and SER16/2/9. Each point represents an average of three aliquots at each temperature. Dotted lines mark $\pm 10\%$ from unity.

To determine the most appropriate temperature conditions for the quartz SAR protocol, a preheat plateau test for samples SER16/2/1, SER16/2/7 and SER16/2/9 was conducted. Aliquots were bleached twice for 1000 seconds with blue light stimulation at 50 °C with 10000 seconds pause in-between, before administering a dose approximating a natural one; ~65 Gy, ~149 Gy and ~119 Gy, respectively. Three aliquots for each of the six tested temperatures were measured using the SAR protocol described above. Figure 6.3 shows the results of the quartz preheat plateau. Samples SER16/2/1 and SER16/2/9 show a similar pattern with a drop in the ability to recover the given dose at intermediate temperatures. While a number of temperatures appear

suitable, further dose recovery tests at 200 °C and at 260 °C showed that the latter recovers the dose more accurately. On that basis a 260 °C preheat temperature was selected for all further tests and D_e determination. In contrast, sample SER16/2/7 performed poorly across the preheat temperature range (Figure 6.3) and did not recover the administered dose. Additionally, initial D_e tests showed that all measured discs failed the recycling ratio, suggesting D_e determination using the SAR protocol is not appropriate for this sample. Therefore, no further measurements using the quartz OSL signal were made for this sample.

6.2.3.2. Dose recovery

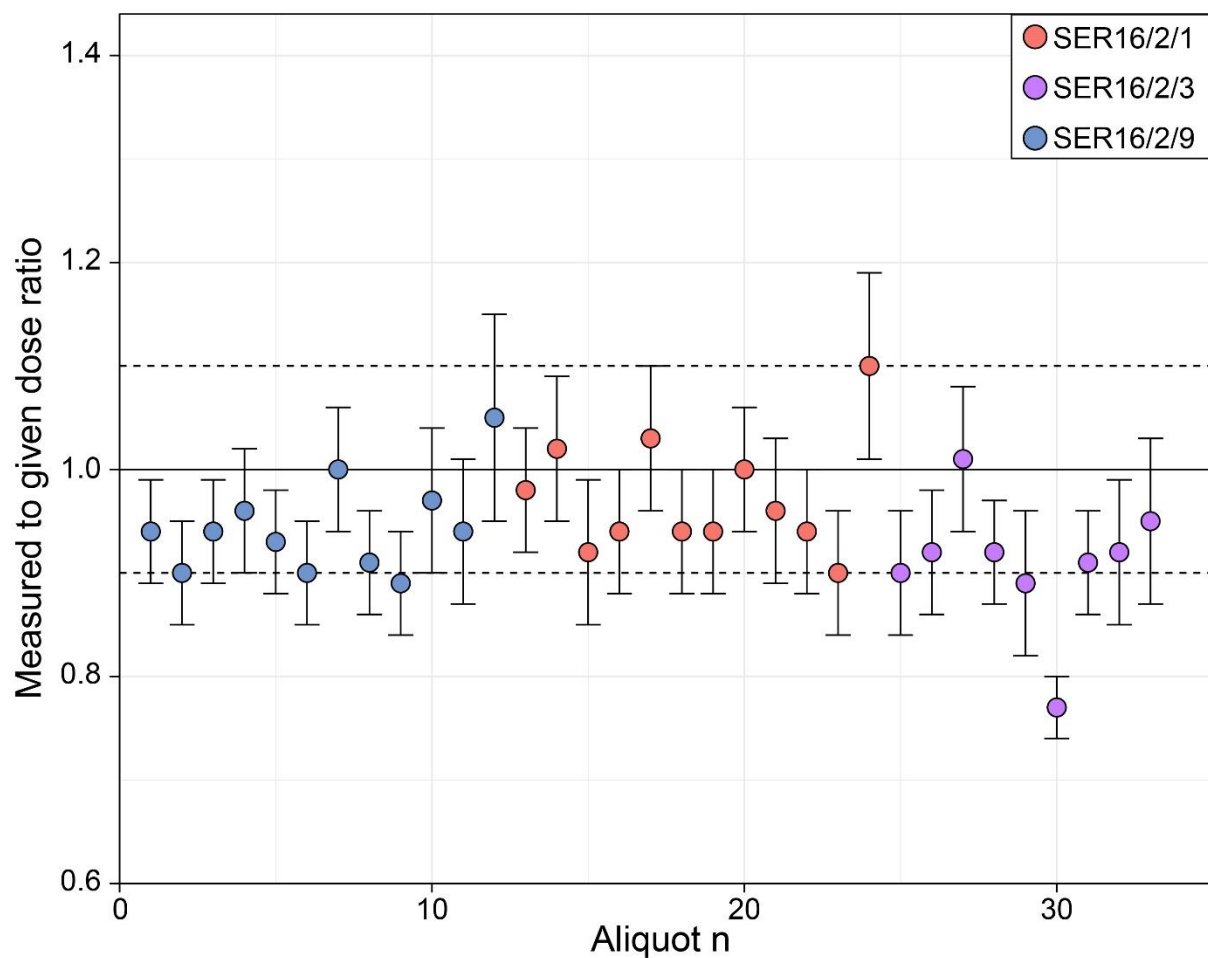


Figure 6.4. Quartz dose recovery for samples SER16/2/1, SER16/2/2, and SER16/2/9. Dotted lines mark $\pm 10\%$ from unity.

To examine the suitability of the selected preheat temperature, and therefore the SAR protocol's ability to recover a laboratory administered dose, dose recovery tests were performed. Three samples (twelve aliquots from each) that capture the age spread of the profile were selected. As in the case of the preheat plateau, aliquots were bleached twice and dosed with levels approximating those naturally occurring; ~65 Gy (SER16/2/1), ~69 Gy (SER16/2/3), and ~92 Gy (SER16/2/9). Almost all disks recovered the administered dose within uncertainty (Figure 6.4), with an average measured to given dose ratio of 0.94 ± 0.06 ($n = 36$, Table 6.1), demonstrating the suitability of the quartz SAR protocol to recover a laboratory administered dose.

Table 6.1. Residual, dose recovery and fading results for selected samples. Fading values and errors reported as a mean calculated based on three aliquots. * = residual subtracted dose recovery ratio.

Sample	Quartz	Polymineral			
	Dose recovery*	Residual dose (Gy)	Dose recovery*	IR ₅₀ g-value (%)	pIRIR ₂₂₅ g-value (%)
SER16/2/1	0.96 ± 0.06	-	-	-	-
SER16/2/3	0.91 ± 0.06	-	-	-	-
SER16/2/7	-	-	-	13.0 ± 0.9	2.1 ± 1.1
SER16/2/9	0.94 ± 0.06	1.10 ± 0.16	1.08 ± 0.04	-	-
SER16/2/10	-	1.25 ± 0.31	0.87 ± 0.05	16.3 ± 0.9	0.9 ± 1.1
SER16/2/12	-	-	-	11.9 ± 1.0	2.1 ± 1.2
SER16/2/17	-	2.07 ± 0.17	0.87 ± 0.04	10.2 ± 0.9	2.5 ± 1.1
SER16/2/23	-	1.23 ± 0.16	-	5.4 ± 1.2	1.8 ± 1.0
Average	0.94 ± 0.06	1.41 ± 0.20	0.92 ± 0.04	11.37 ± 0.99	1.87 ± 1.11

6.2.3.3. Quartz signal assessment and provenance

The quartz OSL signal comprises a number of discrete components, fast, medium and slow (e.g. Smith & Rhodes 1994; Bailey *et al.* 1997). Signal from the fast component is preferred for dating because it bleaches rapidly in nature and is thermally stable (Wintle and Murray, 2006). To quantitatively test for the dominance of the fast component in the initial part of the OSL signals, the fast ratio (Durcan and Duller, 2011) was calculated with the R `calc_FastRatio` script (King *et al.*, 2019). In addition, continuous-wave OSL signals were fitted with the sum of exponentials using the `fit_CWCurve` script (Kreutzer, 2019b) to assess any variability in the number of components identified, and the relative contribution of signal from the various components to the total OSL signal.

The majority of measured quartz signals decayed rapidly to background levels within a few seconds (Figure 6.5A), and qualitatively, this suggests dominance of the fast component. This qualitative assessment is confirmed by the fast ratio, calculated for both natural and regenerated signals, selected representative samples from Surduk 2A and Surduk 2B (SER16/2/1, SER16/2/3, SER16/2/4, SER16/2/7, SER16/2/8, SER16/2/9, SER16/2/23, and SER16/2/20). Averages above 20 were calculated for all samples, except for the sample SER16/2/8. However, there was a lot of variability between individual disks especially in the samples from Surduk 2B, e.g. for SER16/2/23 fast values range between 8.3 ± 2.9 and 357.9 ± 530.5 .

Sample SER 16/2/8, had a notably less bright OSL signals and decayed more slowly than other samples (Figure 6.5D), with 13 out of 15 signals displaying fast ratio below 20 (FR average = 13.1 ± 2.3). This suggests that signal from the fast component does not dominate the initial part of the OSL signal, which may result in erroneous D_e determination (Durcan and Duller, 2011). On this basis, quartz D_e s for this sample are considered unreliable.

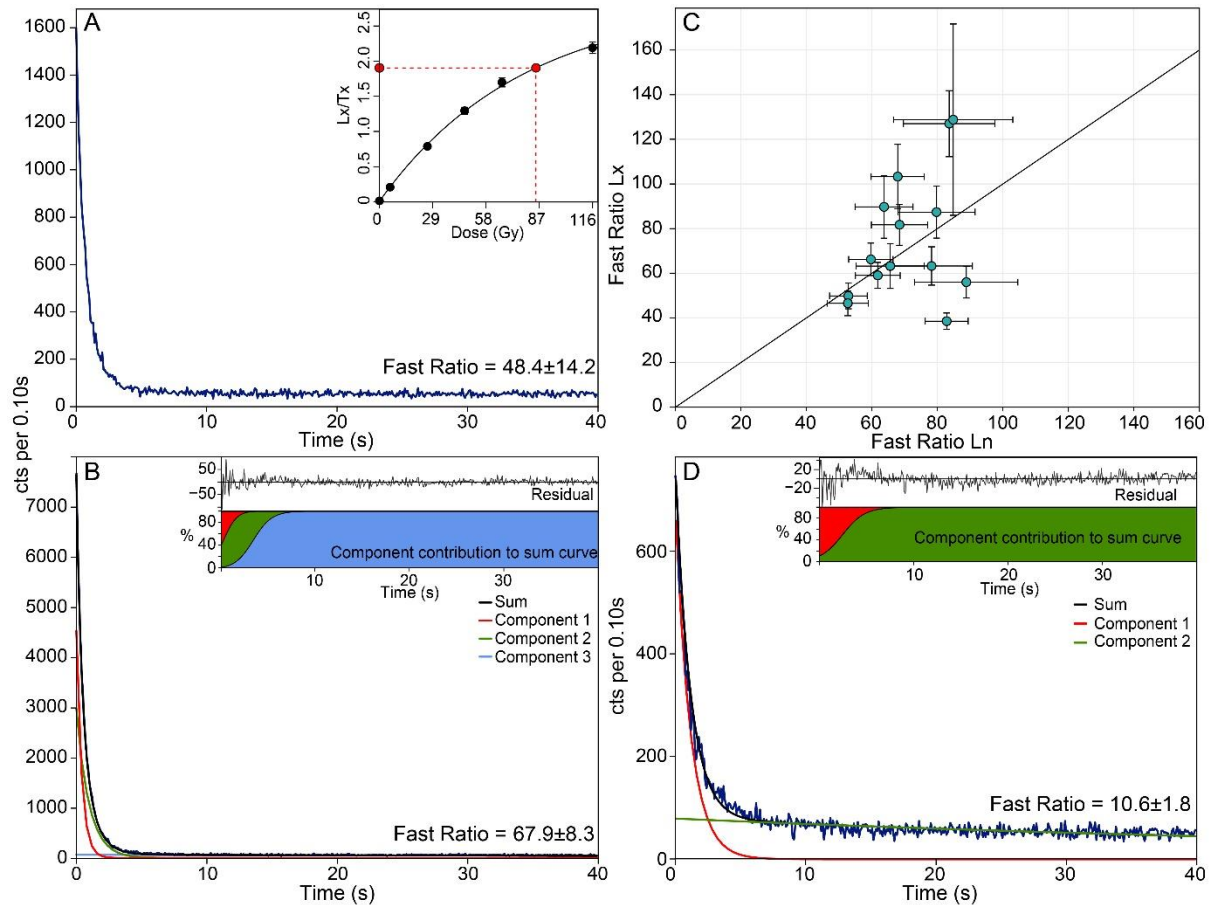


Figure 6.5. A. Decay and dose response curves for quartz (SER16/2/4). B. Decay curve for a typical quartz disk from sample SER16/2/7 with fitted components; insert shows component contributions to the total curve and residuals from the component fitting. C. Fast ratio from the natural signal measurement as a function of fast ratio from the nearest regeneration point for sample SER16/2/7. D. Decay curve for typical quartz disk from sample SER16/2/8 with fitted components; insert shows component contributions to the total curve and residuals from the component fitting. All fast ratios are presented with absolute error values.

The application of routinely applied tests such as preheat plateau, dose recovery, and the fast ratio provides grounds for signal and rejection, but does not provide insights into the cause of the signal problems. One avenue to explore is sediment geochemical composition to investigate any potential causes of this abrupt shift in quartz behaviour. While much work has been undertaken to establish links between provenance and luminescence dating (cf. Gray *et al.*

2019), only a few studies have looked at geochemical properties for comparison (Götte and Ramseyer, 2012; Rodrigues *et al.*, 2019; Stevens *et al.*, 2013a).

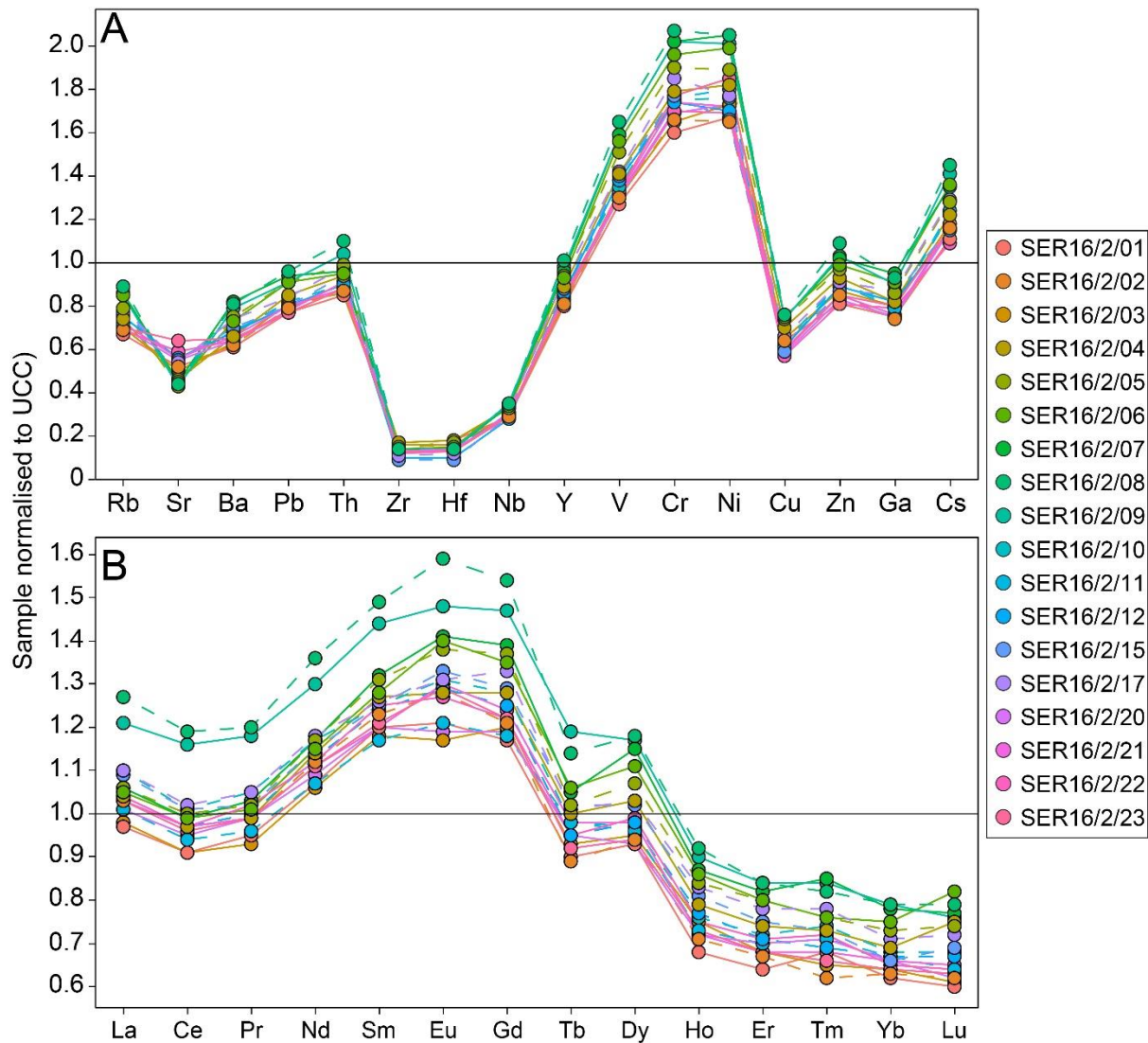


Figure 6.6. Bulk sample trace elements UCC-normalised spider diagrams for Surduk 2.

A) large-ion lithophile elements (LILE) and high-field-strength elements (HFSE) elements B) Light Earth Elements (LREE) and Heavy Earth Elements (HREE).

Bulk sample geochemical data from ICP analyses were examined in more detail. Trace elements, normalised relative to the Upper Continental Crust (UCC), are shown in Figure 6.6A negative anomaly relative to UCC can be seen for Rb, Ba, and Sr for all the Surduk 2 samples, which is likely related to the removal of these elements as a part of the weathering process and/or low

concentrations of feldspars in the samples. The relatively high enrichment of transitional elements (V, Cr, and Ni; Figure 6.6A) suggest a mafic character of the source rocks (Bracciali *et al.*, 2007; Gasparon *et al.*, 1993), especially in samples SER16/2/7, SER16/2/8 and SER16/2/9. Further, sample SER16/2/8 is also strongly enriched in all Light Rare Earth Elements (LREE) especially Eu, and has one the higher Eu anomaly (0.77, Appendix G). The Eu anomaly, calculated by Eu/Eu^* (where Eu^* is $(\text{Sm}_N \cdot \text{Gd}_N)^{0.5}$), provides a measure of Eu^{2+} fractionation from Eu^{3+} relative to the neighbouring elements in chondrite normalised Rare Earth Elements (REE). In a sedimentary setting the calculated values are indicative of source rock types (Kasanzu *et al.*, 2008), with negative anomaly associated with felsic rocks (feldspar bearing rocks), and no anomaly with mafic inputs (Cullers, 1994; Gallet *et al.*, 1998; Gao and Wedepohl, 1995). The negative Eu/Eu^* values suggest felsic inputs in all samples, though samples with the highest values (e.g. SER16/2/8) indicate incorporation of more mafic material. Thus, these samples might have slightly different source rocks, or additions from another source that is affecting the bulk sample geochemical signals. While links between provenance change and quartz signal characteristics are not clear yet, one mechanism could be envisaged through short travel distance of the small additional source inputs that would preclude quartz sensitisation (Fitzsimmons, 2011; Pietsch *et al.*, 2008). It is beyond the scope of this paper to explore the properties (e.g. components, sensitivity) of the luminescence signal in quartz, and how these are influenced by changes in geochemistry of the sediment or the provenance. However, this section shows the potential for linking geochemical properties with luminescence properties and highlights the need for further investigation.

On the basis of preheat plateau tests, dose recovery tests, the fast ratio, and bulk sample geochemistry, quartz OSL signals are considered suitable for dating for most of the samples in Surduk 2A, where calculated D_e s are less than 100 Gy, and are not in saturation. Therefore, ages from Surduk 2A are based on quartz signals, apart from samples SER16/2/7 and SER16/2/8, which are excluded from further analyses due to the poor preheat test and recycling ratio

performances (SER16/2/7), and non-dominance of the fast component (SER16/2/8). In section Surduk 2B, quartz D_e values exceed 175 Gy for all samples (Table 6.2). Multiple studies have suggested that quartz OSL ages become less reliable when the D_e is found in the 100–200 Gy bracket (e.g. Buylaert *et al.* 2012) due to signal saturation, and the large asymmetric uncertainties that result from interpolating onto the asymptote of the dose response curve (e.g. Figure 6.5A). Therefore, for samples with D_e s above 100 Gy and SER16/2/7, the D_e was determined using 4–11 μm polymineral fraction and the pIRIR signal.

Table 6.2. Samples, depths, radionuclide concentrations, dose rates, D_e values and the final luminescence ages obtained from the 4-II μm quartz (OSL protocol) and polymineral fractions (pIRIR₂₂₀ protocol). Values are presented to 2 decimal places, and all calculations were made prior to rounding. Based on the results of the fading correction no fading corrections have been made and therefore the pIRIR₂₀₀ age reflects uncorrected age. * = overdispersion.

Sample	Depth (m)	Unit	U (ppm $\pm$ 1 σ)	Th (ppm $\pm$ 1 σ)	Rb (ppm $\pm$ 1 σ)	K (% $\pm$ 1 σ)	QUARTZ					POLYMINERAL			
							Cosmic dose rate (Gy/ka)	Total dose rate (Gy/ka)	OD %*	D_e (Gy)	OSL age (ka)	Total dose rate (Gy/ka)	OD %*	D_e (Gy)	pIRIR ₂₂₀ age (ka)
SER16/2/1	1.5	II	1.2 $\pm$ 0.2	9.7 $\pm$ 0.9	74.6 $\pm$ 7.5	1.9 $\pm$ 0.2	0.18 $\pm$ 0.02	3.2 $\pm$ 0.2	9	64.5 $\pm$ 1.9	20.2 $\pm$ 1.5	-	-	-	-
SER16/2/2	1.8	II	1.2 $\pm$ 0.2	9.3 $\pm$ 0.9	76.7 $\pm$ 7.7	2.1 $\pm$ 0.2	0.17 $\pm$ 0.02	3.4 $\pm$ 0.2	1.5	67.7 $\pm$ 0.9	20.1 $\pm$ 1.4	-	-	-	-
SER16/2/3	2.1	II	2.5 $\pm$ 0.2	9.2 $\pm$ 0.9	78.6 $\pm$ 7.9	2.3 $\pm$ 0.2	0.16 $\pm$ 0.02	3.7 $\pm$ 0.3	3.3	70.1 $\pm$ 1.2	18.8 $\pm$ 1.3	-	-	-	-
SER16/2/4	2.4	II	2.2 $\pm$ 0.2	10.0 $\pm$ 1.0	83.4 $\pm$ 8.3	2.5 $\pm$ 0.2	0.16 $\pm$ 0.02	3.9 $\pm$ 0.3	5.6	86.4 $\pm$ 1.9	22.3 $\pm$ 1.6	-	-	-	-
SER16/2/5	2.7	II	2.1 $\pm$ 0.2	10.0 $\pm$ 1.0	87.8 $\pm$ 8.8	2.3 $\pm$ 0.2	0.15 $\pm$ 0.02	3.6 $\pm$ 0.3	4.4	82.0 $\pm$ 2.2	22.5 $\pm$ 1.7	-	-	-	-
SER16/2/6	3.0	II	2.1 $\pm$ 0.2	10.2 $\pm$ 1.0	94.9 $\pm$ 9.5	2.3 $\pm$ 0.2	0.15 $\pm$ 0.02	3.6 $\pm$ 0.3	7.5	85.3 $\pm$ 2.1	23.4 $\pm$ 1.7	-	-	-	-
SER16/2/7	3.3	II	2.0 $\pm$ 0.2	10.3 $\pm$ 1.0	95.8 $\pm$ 9.6	2.4 $\pm$ 0.2	0.14 $\pm$ 0.01	-	-	-	-	4.4 $\pm$ 0.3	2.6	99.2 $\pm$ 1.4	22.6 $\pm$ 1.5
SER16/2/8	3.6	II	2.1 $\pm$ 0.2	11.8 $\pm$ 1.2	100.0 $\pm$ 10.0	2.4 $\pm$ 0.2	0.14 $\pm$ 0.01	4.0 $\pm$ 0.3	5.4	84.6 $\pm$ 2.0	21.4 $\pm$ 1.6	-	-	-	-
SER16/2/9	3.9	II	2.1 $\pm$ 0.2	11.1 $\pm$ 1.1	95.5 $\pm$ 9.5	2.4 $\pm$ 0.2	0.13 $\pm$ 0.01	3.8 $\pm$ 0.3	7.4	92.7 $\pm$ 2.4	24.3 $\pm$ 1.8	-	-	-	-
SER16/2/10	4.4	IV	1.9 $\pm$ 0.2	9.8 $\pm$ 1.0	81.1 $\pm$ 8.1	1.9 $\pm$ 0.2	0.14 $\pm$ 0.01	3.2 $\pm$ 0.2	0	175.7 $\pm$ 3.6	54.4 $\pm$ 3.9	3.8 $\pm$ 0.2	9	174.3 $\pm$ 5.9	45.5 $\pm$ 3.3
SER16/2/23	4.8	IV	1.9 $\pm$ 0.2	9.5 $\pm$ 0.9	78.5 $\pm$ 7.8	1.8 $\pm$ 0.2	0.13 $\pm$ 0.01	3.1 $\pm$ 0.2	17	120.6 $\pm$ 7.5	38.6 $\pm$ 3.6	3.7 $\pm$ 0.2	3.6	176.2 $\pm$ 2.8	47.3 $\pm$ 3.1
SER16/2/12	5.2	IV	1.8 $\pm$ 0.2	9.7 $\pm$ 1.0	83.8 $\pm$ 8.4	1.9 $\pm$ 0.2	0.13 $\pm$ 0.01	3.2 $\pm$ 0.2	4.6	169.9 $\pm$ 3.9	53.1 $\pm$ 3.9	3.8 $\pm$ 0.2	4	179.8 $\pm$ 3.3	47.3 $\pm$ 3.1
SER16/2/22	5.5	IV	2.0 $\pm$ 0.2	9.7 $\pm$ 1.0	76.7 $\pm$ 7.7	1.8 $\pm$ 0.2	0.12 $\pm$ 0.01	-	-	-	-	3.8 $\pm$ 0.2	0	187.6 $\pm$ 2.5	49.5 $\pm$ 3.2
SER16/2/21	5.8	IV	2.0 $\pm$ 0.2	9.4 $\pm$ 0.9	80.9 $\pm$ 1.0	1.8 $\pm$ 0.2	0.12 $\pm$ 0.01	-	-	-	-	3.5 $\pm$ 0.2	1.3	186.2 $\pm$ 2.4	49.8 $\pm$ 3.2

SER16/2/20	6.1	IV	1.9±0.2	9.4±0.9	78.4±7.8	1.8±0.2	0.12±0.01	3.1±0.2	0	200.1±3.9	64.8±4.7	3.7±0.2	0	191.8±2.6	52.0±3.4
SER16/2/15	6.4	IV	1.9±0.2	10.1±1.0	85.8±8.6	1.9±0.2	0.11±0.01	-	-	-	-	3.8±0.2	2	196.2±2.6	50.9±3.3
SER16/2/17	7.2	V	2.0±0.2	10.5±1.0	88.8±8.9	1.8±0.2	0.11±0.01	3.2±0.2	4	193.3±5.0	59.78±4.5	3.9±0.2	0	199.3±2.7	51.3±3.4

6.2.4. pIR-IRSL measurements

D_e s from polymineral aliquots were calculated using a modified pIRIR SAR protocol (after Thomsen *et al.* 2008; Buylaert *et al.* 2012). In all cases, after a preheat, IR₅₀ and pIRIR_{elev} signals were measured for 200 seconds. The same sequence was followed for the test dose measurement with the addition of a 290 °C ‘hot-bleach’ (for 200 seconds) at the end of each cycle. Signal from the first 2 seconds of stimulation were integrated, with the background taken from the final 100 seconds of measurements were subtracted. An exponential function was used to fit dose response curves.

6.2.4.1. Preheat temperature selection

A number of loess luminescence studies from the Carpathian Basin have reported problems with dose recovery when using an elevated temperature pIRIR protocol (Murray *et al.*, 2014; Schatz *et al.*, 2012; Stevens *et al.*, 2011; Újvári *et al.*, 2014a), especially the 320 °C preheat – 290 °C stimulation temperature combination. Further, research by Roberts (2012) demonstrated the influence of preheat temperature in the pIRIR protocol on the final D_e value, and therefore the importance of a preheat plateau test for feldspar and polymineral samples. The impact of temperature on D_e s was tested through preheat plateau (Figure 6.7). Six preheat and elevated pIRIR temperature combinations (three aliquots per each) were analysed, with the pIRIR measurement temperature ~25-30 °C lower than the preheat temperature. For preheats above 280 °C, higher D_e s are measured with the pIRIR₂₉₀ protocol (preheat of 320 °C) producing D_e s almost twice as large (274 ± 76 Gy) as those in the 225-280 °C temperature range (average 153 ± 5 Gy). These results support observations of Murray *et al.* (2009) and Roberts (2012) who also noted changes in D_e s with an increased preheat temperature, which is most likely resulting from sensitivity change occurring between Ln and Tn cycles, which cannot be measured and therefore accounted for (Roberts, 2012). The overlapping D_e values for 225-280 °C

preheats suggests the preheat plateau is achieved for these temperatures. Therefore, two of the lower temperatures, 220 and 250 °C, were selected for further dose recovery testing.

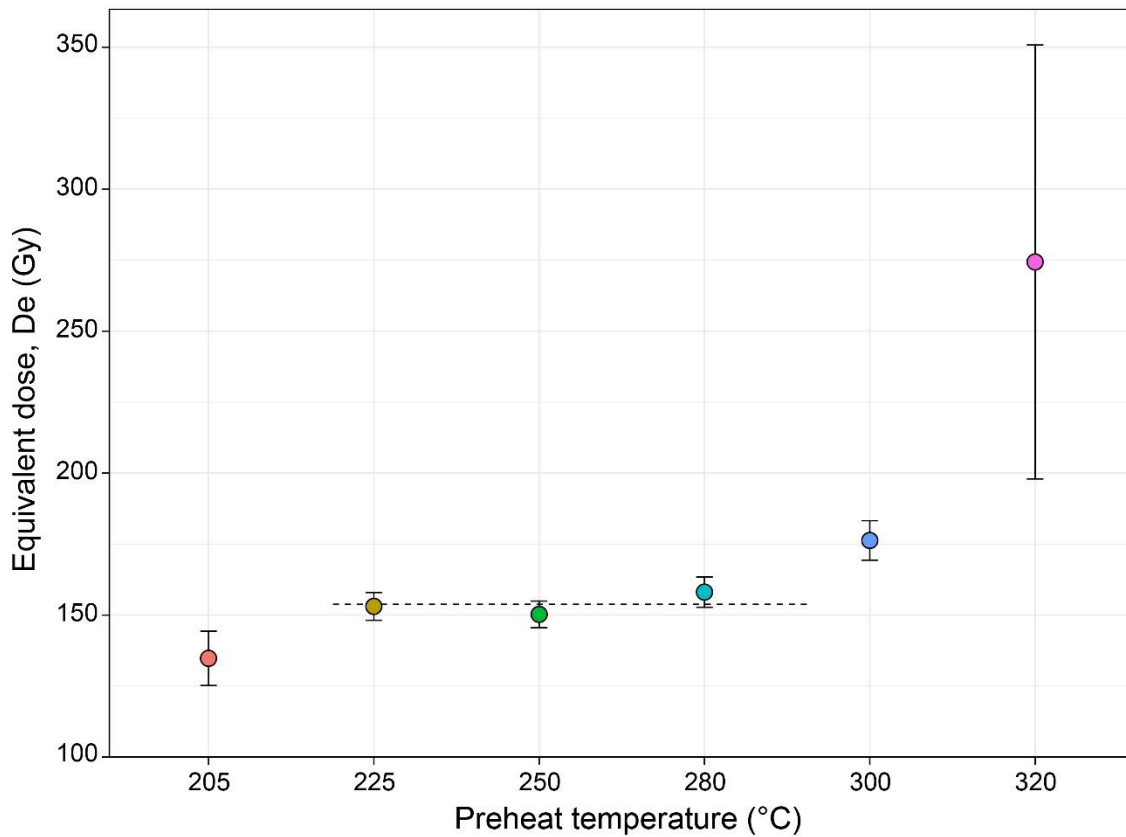


Figure 6.7. D_e dependency on preheat temperature for sample SER16/2/9. The average D_e and standard deviation of three aliquots at each temperature are shown. Note the preheat plateau (dashed line) marked for the temperature range 225-280 °C.

6.2.4.2. Residuals

Buylaert *et al.* (2011) and Sohbati *et al.* (2012) indicated that parts of the feldspar signal may be unbleachable, which may affect the ability to recover given doses. Further, if these ‘residual’ components are large enough they could have an effect on D_e calculation, and therefore age. While many regional loess studies have reported minimal unbleachable components (Murray *et al.*, 2014; Schatz *et al.*, 2012; Újvári *et al.*, 2014a), some have shown quite large residual signals e.g. 15-20 Gy (Austria; Thiel *et al.* 2011) and up to 40 Gy (in

some Serbian samples; Stevens *et al.* 2011) demonstrating the importance of testing for this component.

To test the size of the residual component in the Surduk 2 samples, 6 aliquots from four samples, SER16/2/9, SER16/2/10, SER16/2/17, SER16/2/23, were bleached in daylight for 7 days (during May in the UK), and measured using the pIRIR₂₂₀ protocol. Of the 24 aliquots measured, 18 passed the recycling ratio, but none passed a 5% recuperation ratio. As the initial assessment of the signal suggested small natural signals, all recuperation values were converted into absolute values (in Gy) to test for absolute size.

The average residual component measured is 1.41 ± 0.20 Gy ($1.10 \pm 0.16 - 2.07 \pm 0.17$ Gy range; Table 6.1), equivalent to ~ 0.4 ka (when calculated using the average polymineral dose rate). These results show that the unbleachable component has a negligible impact on the final ages. It is not possible to compare these values with the previous Surduk 1 study as the residual test was not performed (Fuchs *et al.*, 2008). Previously reported Serbian values range between 1 and 40 Gy (Bösken *et al.*, 2017; Murray *et al.*, 2014; Stevens *et al.*, 2011), and along with our results, demonstrate that residual components are sample and site specific, and should be routinely assessed.

6.2.4.3. Dose recovery

As with quartz, the suitability of the pIRIR protocol was tested using a dose recovery test. First two pIRIR protocols, pIRIR₂₀₀ (225 °C preheat) and pIRIR₂₂₅ (250 °C), were tested using sample SER16/2/9. Six aliquots were bleached in daylight for 7 days (during May in the UK), irradiated with a laboratory beta-dose approximating their natural one, and measured using the two protocols. Figure 6.8 shows that the pIRIR₂₂₅ protocol struggled to recover the given dose with an average given to measured ratio of 1.38 ± 0.06 . Aliquots measured using the pIRIR₂₀₀ protocol recovered the laboratory dose, giving an average ratio of 1.08 ± 0.04 . Subtracting the average residual value from the measured equivalent

dose prior to the calculation of the dose recovery, takes the ratios down to 1.36 ± 0.06 for pIRIR_{225} , while the pIRIR_{200} remains unchanged due to the very small size of residual dose. These results show that the lower preheat temperature better recovers a known dose for this suite of 2 samples.

Following selection of the pIRIR_{200} protocol an additional twelve aliquots from samples SER16/2/10 and SER16/2/17, were analysed following the same preparation and measurement protocol. The average measured to given dose ratio for these samples was 0.92 ± 0.04 ($n = 18$) suggesting a satisfactory pIRIR protocol for D_e measurement.

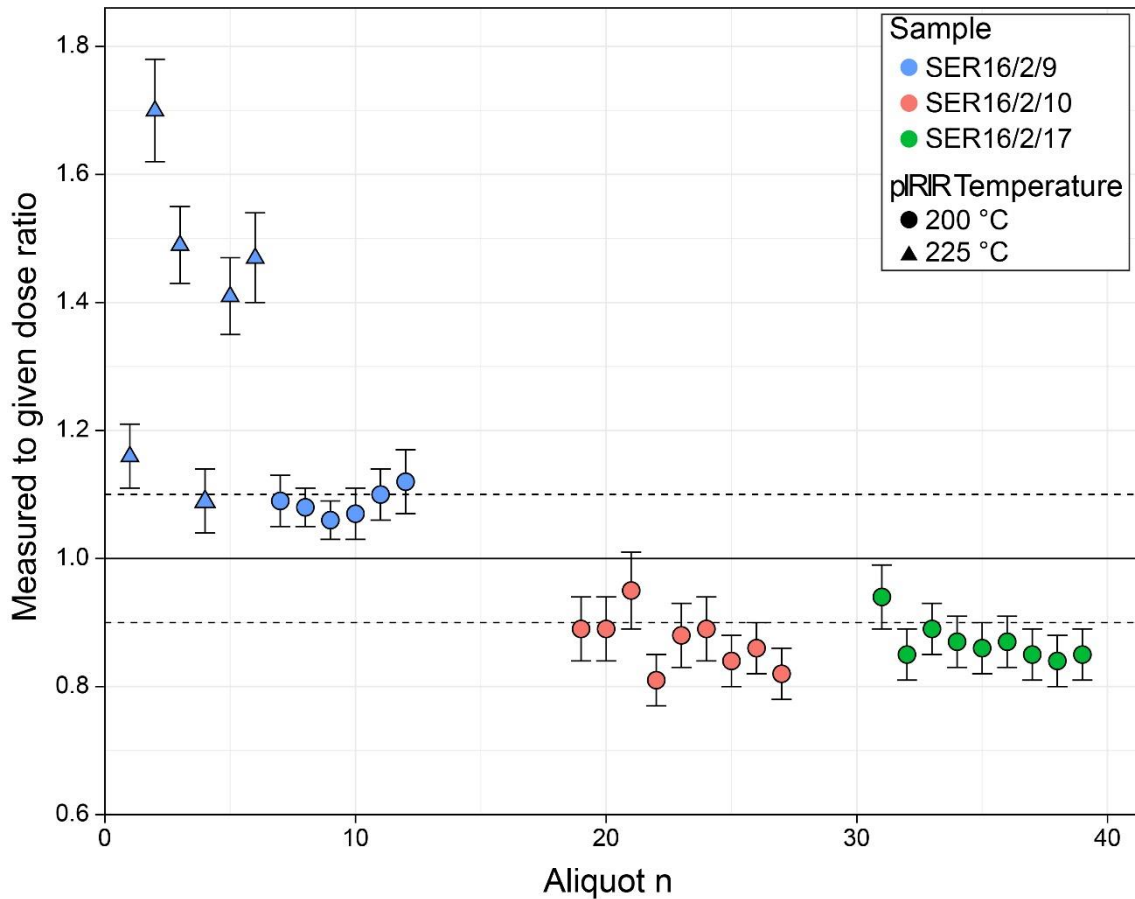


Figure 6.8. Polymineral dose recovery for samples SER16/2/9, SER16/2/10, and SER16/2/17. Note dose recovery tests for the pIRIR_{220} and pIRIR_{225} protocols were carried out using sample SER16/2/9. Dotted lines mark $\pm 10\%$ from unity. All samples had a residual dose subtracted prior to the calculation.

6.2.4.4. Laboratory fading

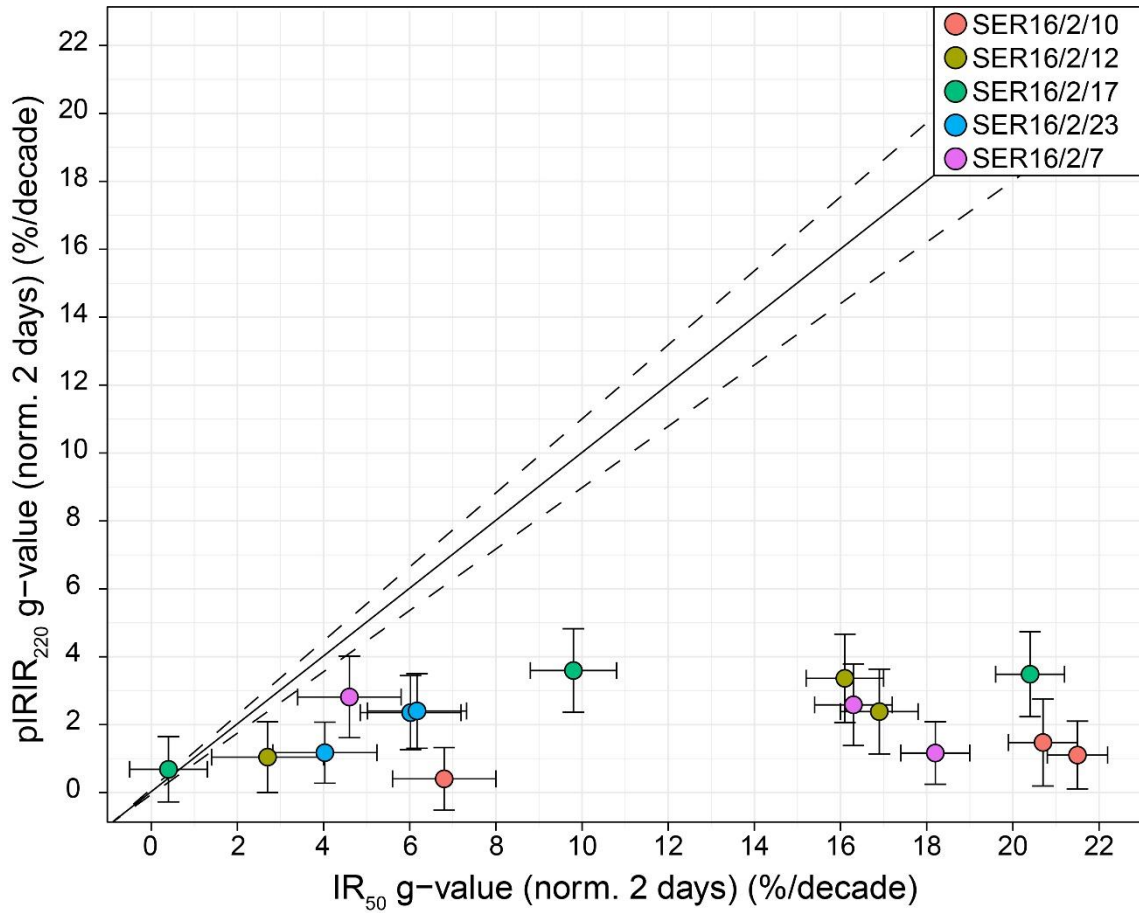


Figure 6.9 Calculated fading rates for the IR₅₀ and pIRIR₂₀₀ luminescence signals for all aliquots.

Laboratory fading rates ($g_{2\text{days}}$) were tested for the pIRIR₂₀₀ signal, using the same protocol used for D_e measurements. Following Auclair *et al.* (2003) three aliquots per sample were irradiated with a fixed dose (~90 Gy), a test dose (~40 Gy) and measured following a series of pauses (0, 1, 10, 100 and 1000 hours). The mean fading rates for the IR₅₀ and pIRIR₂₀₀ signals are $11.37 \pm 0.99\%$ /decade and $1.87 \pm 1.11\%$ /decade ($n = 15$, 5 samples) respectively. The range of the fading rates for the IR₅₀ signal varies between $0.43 \pm 0.94\%$ /decade and $21.53 \pm 0.74\%$ /decade, whereas the pIRIR₂₀₀ results range from $0.27 \pm 0.92\%$ /decade and $3.46 \pm 1.23\%$ /decade (Figure 6.9, Table 6.1). These results demonstrate that IR₅₀ signals undergo high rates of fading at Surduk 2. In contrast, fading rates for the pIRIR₂₀₀ are

sufficiently low that they do not require a fading correction, following the arguments of Buylaert *et al.* (2012) and Thiel *et al.* (2011).

6.2.5. D_e and age calculation

All measured aliquots ($n = 345$) were screened using signal recuperation ($<5\%$), a recycling ratio (Murray and Wintle, 2000), and additionally for quartz, an OSL IR depletion ratio (Duller, 2003). In total 24 signals were rejected due to a failed recycling ratio, and 6 signals failed recuperation. All but 5 quartz signals passed the IR depletion ratio. Overdispersion (Table 6.2) was found to be below 10% (except for the quartz sample SER16/2/23) and therefore all equivalent doses were calculated using the Central Age Model (Galbraith *et al.* 1999; CAM). CAM D_e s were divided by the environmental dose rate to derive the age. As discussed, D_e s were calculated from quartz for Surduk 2A samples, with the exception of SER16/2/7 and SER16/2/8. For all other samples, polymineral pIRIR signals were used.

6.2.6. Age depth-model and MARs

All final luminescence ages were re-calculated using Bayesian and inverse modelling (Zeeden *et al.*, 2018a), which separates systematic and random errors of luminescence ages. This model creates probability density functions for both types of error but models only the random component of the uncertainty, making this approach better suited for the analysis of luminescence ages than other Bayesian models such as OxCal (Bronk Ramsey, 1995). Due to the lack of the overlap and to uncertainty regarding the sediment thickness, two separate models were created: one for the Surduk 2A and the second for the Surduk 2B. These age-depth models provide a basis for calculating sediment accumulation rates, as well as a better visual representation of the age distribution throughout the profile.

Loess-palaeosol sequences can preserve information about dust fluxes, yet to date no sites from Europe have been included in the global palaeodust cycle modelling efforts (Albani *et al.*, 2015), mostly resulting from the lack of high resolution chronologies. To aid those efforts a number of loess studies (Perić *et al.*, 2019; Stevens *et al.*, 2016; Újvári *et al.*, 2015) are converting age-depth models into MARs. Here, modelled luminescence ages were used to calculate MARs (Kohfeld and Harrison, 2003) using the following equation

Equation 6.1 Mass accumulation rate equation.

$$\text{MAR (g m}^{-2} \text{ a}^{-1}) = \text{SR} \times f_{\text{eol}} \times \rho_{\text{dry}} \quad (1)$$

where SR is the sedimentation rate (m a^{-1}), f_{eol} is the fraction of the sediment that is aeolian in origin, and ρ_{dry} is the bulk density of dry sediment (g m^{-3}). As the sediment is interpreted as loess and therefore aeolian in origin, $f_{\text{eol}} = 1$. A bulk density value of 1.5 g cm^{-3} was used in all calculations based on the reported estimates of loess bulk density in Hungary and Serbia (Perić *et al.*, 2019; Újvári *et al.*, 2010a). Finally, in desert research it has been shown that using only mean ages to construct sedimentation rates for sand dune accumulation may provide an inaccurate picture of aeolian and climatic history (Leighton *et al.*, 2014), therefore for the first time in loess research two MARs are calculated based on mean and minimal sedimentation rates. Mean sedimentation rates are calculated as $\text{SR}_{\text{mean}} = (x_1 - x_2) / (y_1 - y_2)$, where x_{1-2} are two depths and y_{1-2} corresponding ages in the profile. The $\text{SR}_{\text{min}} = (x_1 - x_2) / ((y_1 + \sigma_1) - (y_2 + \sigma_2))$ also includes age errors for each relative age.

To ensure a meaningful and fair comparison of MARs between loess studies, only sites with a high-resolution, absolute chronology were selected. Further, sites where the luminescence chronology used an IR_{50} signal which had not been tested for fading were also excluded. Therefore three sites Crvenka (Stevens *et al.*, 2011), Dunaszekcső (Újvári *et al.*, 2017), and Titel (Perić *et al.*, 2019) were selected for MAR assessment.

6.3. Palaeoenvironmental results and discussion

6.3.1. A new chronology and sedimentation rates for the Surduk 2 loess-palaeosol sequence

Unmodelled quartz and polymineral pIRIR₂₀₀ luminescence ages for Surduk 2 are presented in Table 6.2. The preferred (Quartz signal assessment and provenance discussion) unmodelled and modelled ages are presented in Figure 6.10 and Appendix M Table S2. Sixteen ages span from the top of the transitional palaeosol Unit (III) to 1.5 m below the modern day surface. All but one age come from loess Unit II, with the youngest age 19.03 ± 1.03 ka. The bottom age, for the transitional zone between palaeosol and loess, places its burial at 52.55 ± 2.71 ka.

The ages for both parts of the profile form two stratigraphically-consistent depositional groups. The first (Surduk 2A) covers 1.5 m within the top ~4 m and represents the period between 19.03 ± 1.03 and 24.62 ± 1.31 ka. The second group (Surduk 2B) consists of eight samples, spread over 2.8 m, with ages between 44.99 ± 2.20 and 52.55 ± 2.71 ka. These two groups are separated by a sampling gap that is estimated to be between 1 and 1.5 m. The comparison of ages above and below shows relatively rapid accumulation rates and suggests that within that packet of sediment a change occurred. Without further high resolution chronological investigation at this stage it is not possible to definitively determine whether this gap represents a period of sediment accumulation lows, driven by environmental or climatic factors, or if this is an erosion boundary between different periods of dust accumulation. However, it is most likely that an erosional boundary is present above LILL2, supporting a previously argued notion that loess sequences are neither continuous nor homogenous, and are likely to preserve disturbances in deposition (Stevens *et al.*, 2008, 2018).

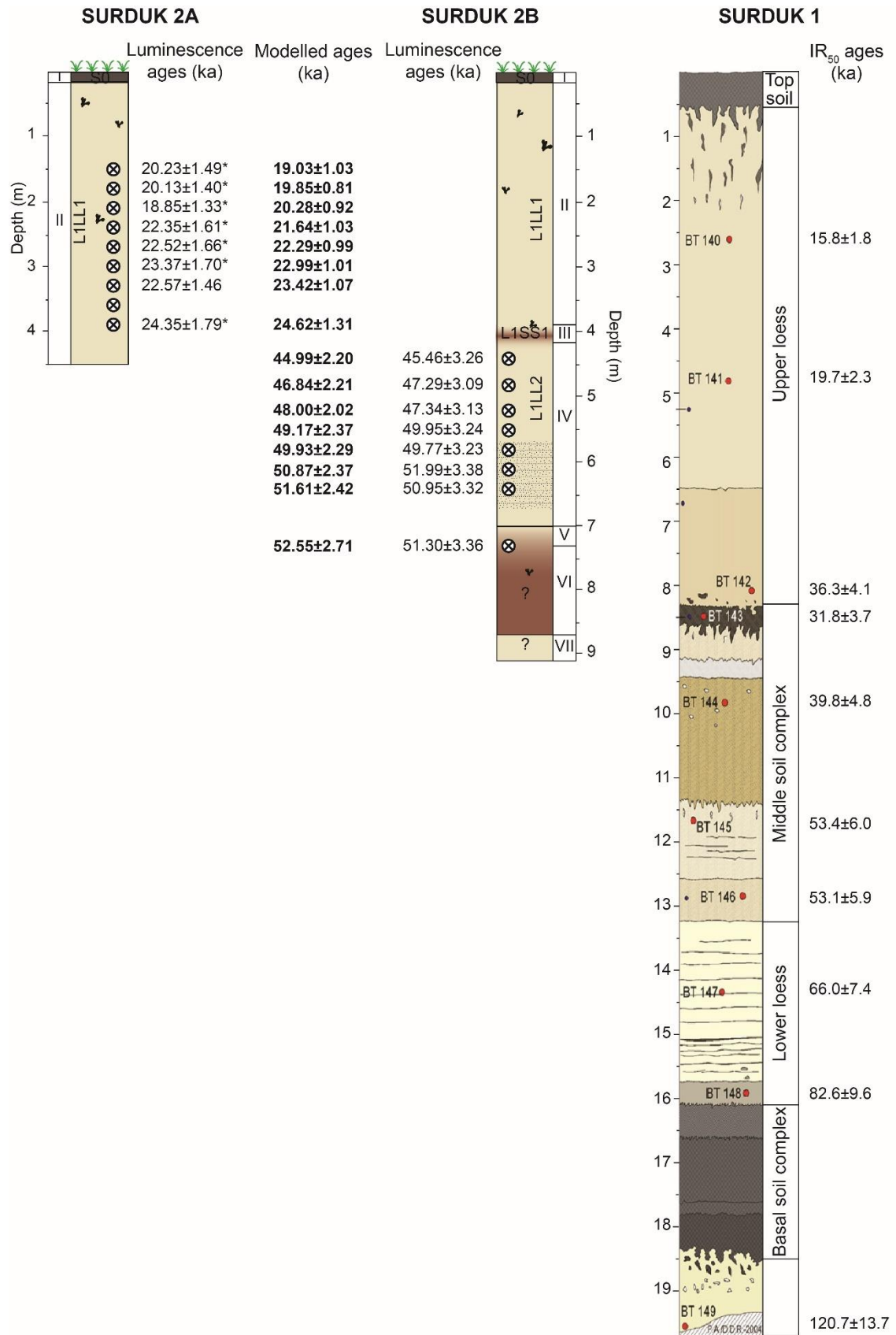


Figure 6.10. Schematic stratigraphic diagram for Surduk 1 (Antoine *et al.*, 2009a; Fuchs *et al.*, 2008) **and Surduk 2**. For the Surduk 2 quartz OSL (marked by *), polymineral pIRIR₂₂₀, and Bayesian modelled ages (bold) are presented.

6.3.2. Comparison with other sites and implications

The oldest age obtained from Surduk 2B comes from the transitional palaeosol-loess zone near the bottom of the profile and dates sediment burial to 52.55 ± 2.71 ka. The calcification and compaction of the palaeosol below precluded collection of samples and determination of the beginning of deposition for this part of the profile/sequence. The comparison of the basal parts between Surduk 1 and 2, shows a large age discrepancy (Figure 6.10). Based on stratigraphical position bottom palaeosol at Surduk 2B can correspond either with the “Basal soil complex” or the “Middle soil complex” at Surduk 1, and therefore be interpreted as either S1 or LISS2 palaeosol.

The loess deposition on top of the “Basal soil complex” at Surduk 1 was dated to 82.6 ± 9.0 ka (Figure 6.10). Due to the blanket nature of loess deposition it is highly unlikely that there is a ‘real’ ~30 ka discrepancy between Surduk 2 and Surduk 1 deposits, especially that they are located so closely together. The luminescence investigation at Surduk 1 did not test the IR₅₀ signal for fading and ages were not corrected (Fuchs *et al.*, 2008). Fading tests at Surduk 2 show that the polymineral IR₅₀ signal is athermally unstable (Figure 6.9). Similar fading behaviour can be expected from Surduk 1, and it is likely that Surduk 1’s chronology underestimates the true ages. Therefore the age of 82.6 ± 9.0 ka for the “Basal soil complex” at Surduk 1 is likely to be too young. However, without fading rate data for those samples, combined with the old age of the samples (and therefore the difficulties correcting the non-linear part of the dose response curve) it is not reasonable to speculate the degree of under-estimation of each age at Surduk 1 in Fuchs *et al.* (2008). Nonetheless taking the fading rates broadly into consideration and the depths of the units at both

profiles, it is likely that the Unit VI palaeosol at Surduk 2B corresponds with the “Middle soil complex” at Surduk 1, dated to 36.3 ± 4.1 ka (Fuchs *et al.*, 2008).

Nevertheless if the correlation based on stratigraphy was correct it would suggest favourable pedogenic conditions at Surduk 2B persisting until 52.55 ± 2.71 ka, and no loess deposits corresponding to an initial climate deterioration seen across the region and associated with MIS 3 (Bokhorst *et al.*, 2011; Panagiotopoulos *et al.*, 2014; Wegwerth *et al.*, 2016). This could be a result of repeated erosional events at Surduk 2, possible due to the geomorphic position of the site. Alternatively a number of loess profiles in central Europe e.g. Stalać (Bösken *et al.*, 2017), Süttő (Novothy *et al.*, 2009), and Stari Slankamen (Schmidt *et al.*, 2010), indicate persistent pedogenesis until the MIS 3 stage, which may have also occurred at Surduk. However without further geochronological investigation at Surduk 1 it is not possible to determine if stratigraphic the discrepancy between Surduk 1 and 2 palaeosols represents multiple erosional event at Surduk 2, pedogenic conditions differences or the chronological discrepancy.

Following the transitional unit, primary loess deposition begun at Surduk 2B after 52.55 ± 2.71 ka and lasted at least until 44.99 ± 2.20 ka (Figure 6.10). At the beginning of this period the mass accumulation rates were the highest in the profile $1288 \text{ g m}^{-2} \text{ a}^{-1}$ (mean; minimum = $163 \text{ g m}^{-2} \text{ a}^{-1}$), after which they decreased in a step like manner all the way up the Unit IV (Figure 6.11). However, there are two brief periods of increased accumulation between 49.93 ± 2.29 and 49.17 ± 2.37 ka (mean $591 \text{ g m}^{-2} \text{ a}^{-1}$ and min. $174 \text{ g m}^{-2} \text{ a}^{-1}$) and 48.00 ± 2.02 and 46.84 ± 2.21 ka (mean $514 \text{ g m}^{-2} \text{ a}^{-1}$ and min. $173 \text{ g m}^{-2} \text{ a}^{-1}$). This indicates temporary environmental deterioration or increased supply of material during the early MIS 3. While a decrease in MAR values is also seen in Crvenka over this period (Stevens *et al.*, 2011), the lack of a temporary increase could be attributed to the lower chronological resolution of the study or the site's position. We propose that the increase in accumulation

was locally driven and probably related to the site's proximity to the Danube and sediment source. Further, it is important to note that while mean rates show a relatively large change in the MAR values, e.g. from 607 to 479 $\text{g m}^{-2} \text{a}^{-1}$, the difference in minimum rates is very small (176 and 171 $\text{g m}^{-2} \text{a}^{-1}$). Seeing that these rates are almost three times lower and do not really show corresponding trends, this highlights that care must be taken when interpreting MARs, especially when only mean rates are presented.

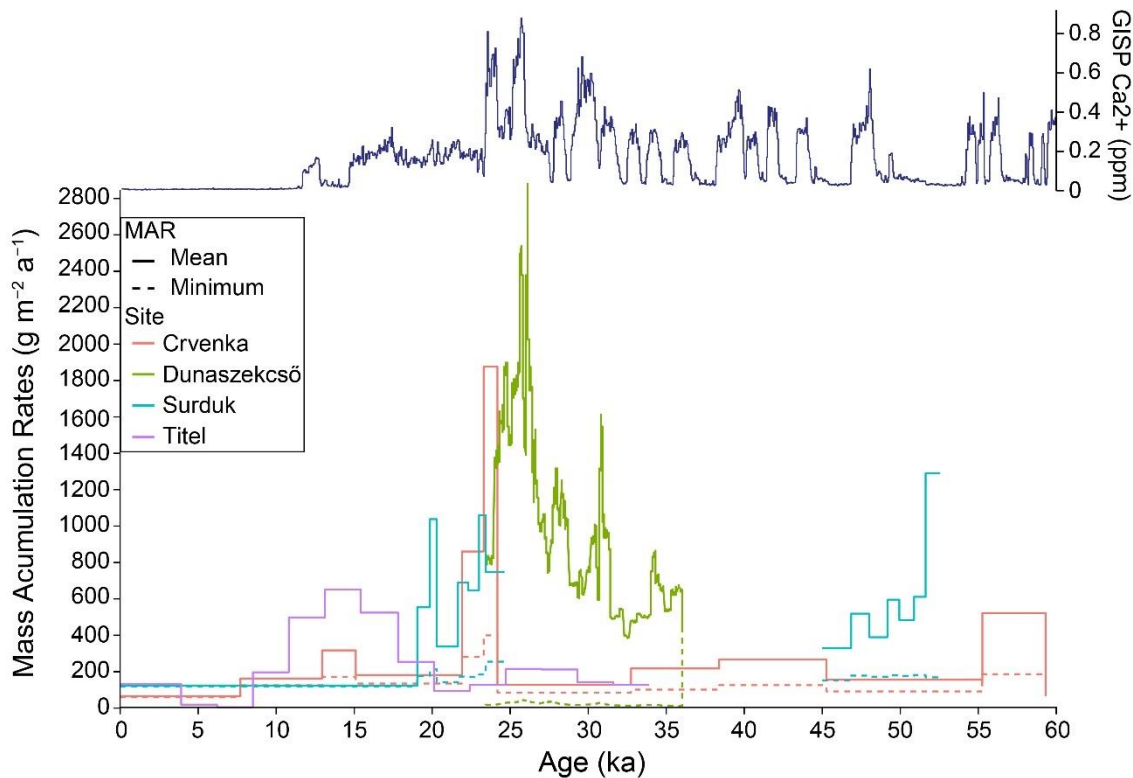


Figure 6.11. Mass Accumulation Rates (MAR) as a function of age for the loess-palaeosol profile at Surduk 2, plotted against results from Titel (Perić *et al.*, 2019), Dunaszekcső (Újvári *et al.*, 2017), Crvenka (Stevens *et al.*, 2011), and GISP Ca^{2+} record (Rasmussen *et al.*, 2014). The geographic location of these sites in relation to Surduk 2 is shown in Figure 6.1.

A hiatus in luminescence ages is observed between 44.99 ± 2.20 and 24.62 ± 1.31 ka. At present it is not possible to determine the source of this discrepancy (sedimentary hiatus or sedimentation slowdown) nor the exact position of the gap. Consequently, the record

of the early MIS 3 sedimentation is missing from Surduk 2. The MIS 3 period was considered a climatically milder and more stable component of the previous interglacial (Wegwerth *et al.*, 2015), but containing pronounced oscillations (Fischer *et al.*, 2019; Hoffecker, 2009). At other loess profiles, e.g. Belotinac (Obreht *et al.*, 2014), Crvenka (Stevens *et al.*, 2011; Zech *et al.*, 2013), Dunaszekcső (Újvári *et al.*, 2014a), Stari Slankamen (Schmidt *et al.*, 2010), Stalać (Bösken *et al.*, 2017), or Tokaj (Schatz *et al.*, 2012), it is associated with palaeosol development. A hint of a weak pedogenic horizon was observed in the field above the sample SER16/2/10 but this part of the section was not accessible at the time.

In the later parts of MIS 3, the climate in the region is suggested to have been progressively deteriorating, with colder temperatures, increased precipitation, and changes in vegetation cover (Kageyama *et al.*, 2006; Sümegi *et al.*, 2013, 2019; Zech *et al.*, 2013). This can be seen represented at other sites such as Dunaszekcső (Újvári *et al.*, 2017) or Titel (Perić *et al.*, 2019) by an increase in MAR values, which is expected as the ice-sheets grow to their maximum extent. Taking this regional picture into consideration, we suggest that Surduk 2 contains a sedimentological hiatus, and if a palaeosol was present, it has likely been eroded. It is not possible to determine how much sediment has been removed as only the remaining features are datable. However, a further higher resolution chronological investigation should be able to identify when exactly the gap occurs.

The top part of Unit II preserves ~5.5 ka of dust accumulation and represents the prelude to, and the main part of the Last Glacial Maximum (LGM). While not particularly thick in comparison to other loess sections recording this period of accumulation, it still indicates progressive and relatively rapid sediment accumulation from 24.62 ± 1.31 ka (mean $744 \text{ g m}^{-2} \text{ a}^{-1}$; Figure 6.11). This period of deposition also corresponds to a potential shift in provenance. Bulk sample geochemical analyses (Figure 6.6) suggest sediment at that time

had slightly more mafic and/or less felsic source rock inputs. The analysis did not imply complete change in provenance but rather small contributions from other source. This temporary shift combined with a short-distance transport could indicate sediment delivered to the site from relatively proximal rocks, likely linked to landscape instability during the build up to the LGM.

Following this period at 23.42 ± 1.07 ka (Figure 6.11) MARs raised to the second highest values for Surduk 2 (mean $1058 \text{ g m}^{-2} \text{ a}^{-1}$), indicating increased environmental instability. High MARs did not persist for long and begun to drop after 22.99 ± 1.01 ka and continued to fall until 20.28 ± 0.92 ka (mean $333 \text{ g m}^{-2} \text{ a}^{-1}$). This was followed by a temporary rise to the second highest rate at Surduk 2A (mean $1036 \text{ g m}^{-2} \text{ a}^{-1}$ and min. $207 \text{ g m}^{-2} \text{ a}^{-1}$) that lasted until 19.85 ± 0.81 ka. These results indicated that even during the LGM, which is thought to be the period of highest sediment accumulation, the deposition was not constant.

The values at Surduk 2 are as much as five times greater than those shown for this period at the nearby Titel Plateau (Perić *et al.*, 2019), exceeded even by the conservative minimum values of $207 \text{ g m}^{-2} \text{ a}^{-1}$. While the Surduk 1 profile does not fully capture a chronology for this period, it still suggests increased wind speeds or delivery of coarser material to the system as a higher proportion of sands and reduction of clay is noted (Antoine *et al.*, 2009a), further supporting a lack of vegetation and cold/windy conditions.

The uppermost sample at Surduk 2, located 1.5 m below the modern land surface, indicates loess deposition at 19.03 ± 1.03 ka (Figure 6.10). It is expected that during deglaciation and a transition to the Holocene, sediment availability declined and depositional rates decreased as vegetation became more established. The transition to the Holocene palaeosol is not strongly marked or visible. A lack of thick well developed Holocene soil, as well as a thicker deglaciation loess unit, is also seen at Surduk 1. Moreover, considering

human activities on the modern land surface at both localities, it is likely that Holocene soil (S0) has been removed as part of agricultural processes.

6.3.3. Comparison with Greenland and implications for MARs interpretations

A number of studies have attempted to link central European loess deposits with Greenland dust records based on geochemistry (Újvári *et al.*, 2015), MARs (Újvári *et al.*, 2017), particle size (e.g. Rousseau *et al.* 2002; Antoine *et al.* 2009), and models (e.g. Sima *et al.* 2009) to show its contributions into the global dust record. Figure 6.11 shows MARs from four sites around the Southern part of the Carpathian Basin plotted against dust records from Greenland (Rasmussen *et al.*, 2014). Firstly, and most notably, it can be observed that peaks and troughs in accumulation do not always overlap. While some broad similarities are seen, records often conflict each other, e.g. Surduk 2 MARs show increased accumulation followed by a decrease at around 23 ka, however at the same time at Crvenka rates fall dramatically and stabilise for several thousands of years. It must be pointed out that with higher dating resolution less of the sedimentary sequence is averaged, hence records from sites such as Dunaszekcső show much more detail and variability by comparison. Even if broad trends can be seen there appears to be Carpathian Basin wide heterogeneity, with no obvious trends in accumulation seen over relatively short distances. This suggests that loess does not develop as a blanket feature at the same time across the landscape, as sediment is not transported to the sites uniformly. The comparison between sites in the Carpathian Basin, thus suggests that accumulation at each site is likely driven by short-distance transport and local factors, such as sediment availability on floodplains.

When further compared with the dust record from Greenland (Figure 6.11) the picture is quite complex. The MARs patterns seen in the Carpathian Basin do not always mirror trends in Greenland. For example, during the drop in accumulation between 51.61 ± 2.42

and 50.87 ± 2.37 ka at Surduk 2 (shift from 1288 to $607 \text{ g m}^{-2} \text{ a}^{-1}$) values in Greenland remained relatively constant. At the same time while Surduk 2 notes high rates of accumulation the dust flux in Greenland is low. However, the drop-rise pattern between 50-47 ka at Surduk 2 approximates pattern seen in Greenland. In both cases increases in MARs at Surduk 2 proceed changes in Greenland, though dust flux ceased at the same time. The same pattern is also observed for peaks at 20.28 ± 0.92 ka at Surduk 2A and smaller peak at ~ 28 ka at Dunaszekcső (Újvári *et al.*, 2017). It could be therefore argued that for some instances the record from Carpathian Basin is proceeding the changes that are eventually picked up in Greenland.

Lastly, it is important to note how much variability is seen between the mean and minimum MAR rates. Calculating minimum MAR values takes into account the uncertainty of ages and enables a fuller exploration of the geomorphologic signal. For the most part, the same trends are still seen between minimum and mean values but the discrepancy between the two values can reach almost two orders of magnitude (e.g. Dunaszekcső). This approach is not taken to discredit the mean values, but to highlight that the true MAR values are somewhere in-between the minimum and maximum (which is often impossible to calculate). Therefore, while the trends can be explored when using mean values alone, interpretation of values where only mean values are presented should be taken with caution, especially when comparing with other dust records, such as Greenland. Finally, this point is particularly pertinent to the debate surrounding the contributions of European loess deposits to the dust recorded in Greenland (Albani *et al.*, 2015; Sima *et al.*, 2009; Újvári *et al.*, 2015, 2017). It is unlikely that a sole site was contributing greatly, but the lack of overlapping trends between sites and the discrepancy between minimum and mean rates suggest that European loess contributions are periodic, and secondary. However, more sites with higher resolution chronologies are needed to unpack this complex dust record, and its contribution to global dust archives

6.4. Conclusions

This study presents a new high-resolution chronology for the loess-palaeosol sequence at Surduk 2, based on 13 quartz OSL and 10 polymineral pIRIR₂₂₀ ages, that provides a basis for a broad review of the palaeoenvironmental record preserved at this site. The modelled luminescence ages based on both protocols bracket the primary loess deposition between 52.55 ± 2.71 and 19.03 ± 1.03 ka. The results, however, suggest that this record is not continuous and contains a hiatus that occurred after 44.99 ± 2.20 ka and prior to 24.62 ± 1.31 ka. The bulk sample elemental analysis identified a potential abrupt but small provenance shift that occurred between 24.62 ± 1.31 and 23.42 ± 1.07 ka. Further, the high-resolution chronology provides a basis for MARs calculation for Surduk 2 and comparison with other sites from the Carpathian Basin, Crvenka (Stevens *et al.*, 2011), Dunaszekcső (Újvári *et al.*, 2017), Titel (Perić *et al.*, 2019), and Greenland (Rasmussen *et al.*, 2014). The analysis demonstrates that sites experienced increased periods of accumulation at different times, showing that sites' depositional histories are not uniform, despite their relatively close locations. Therefore preserved loess sequences likely depend on the site's geomorphological position and palaeotopography, which control appearance and intensity of erosional and pedogenic process (Marković *et al.*, 2018a; Vandenberghe *et al.*, 2014). While European loess contributions to Greenland are still debated, these results suggest that they do not play a major role. Finally, we suggest that additional chronological analysis is needed to identify the exact position of the hiatus and to determine how long was this site stabilised for prior to 53 ka and whether it experienced pedogenically favourable conditions continuously since the last interglacial.

SUMMARY: Paper 3

Chapter 6 addresses Research Question 1 by producing a high-resolution chronology for Surduk 2, and therefore providing a basis for investigating the timing of loess deposition during the late Quaternary in Serbia (**Objective 1**). By combining chronological results with MARs, this paper compares the periods of activation and sediment deposition across the Carpathian Basin.

The results of this paper demonstrate that Surduk 2 does not preserve a continuous record of loess deposition. Instead it shows that Surduk 2 preserves a sedimentary hiatus that occurred after 48 ± 2 ka. The primary loess deposition establishes shortly before 24.78 ± 1.41 ka and continues until at least the late LGM. The constructed chronology provides a basis for a MAR calculation which also shows that the deposition was highly variable throughout the late Quaternary. This confirms previous suggestions that loess profiles, as any other sedimentary archive, are not continuous, and treating them as such only leads to a misinterpretation of proxy signals and distortion of the palaeopicture. Moreover, this highlights the need for high resolution chronological approaches in loess studies.

The analysis of the MARs at Surduk 2, and comparison with other sites from the Carpathian Basin, reveals that accumulation periods are not consistent in timing or rates across the region. The periods of accumulation increase, and low stands are also not in correlation with Greenland dust records, showing that loess deposition is likely driven by local drivers, such as local winds, sediment supply, or topography.

Chapter 7: Geochemistry results

7.1. Introduction

The methodology described in Chapter 3 produced a variety of datasets, which are predominantly discussed in Chapter 7. This chapter presents results of the geochemical analyses, focusing primarily on the interpretation of the U-Pb and Hf zircon data. The results presented here will be discussed in Chapter 8.

7.2. Results

7.2.1. Grain numbers

In the analysis of zircons for determination of their age of formation, there is still a lack of consensus regarding what constitutes a minimum number of grains required for analysis and comparison in a single grain study. A number of studies have been published arguing for various minimum number of zircons per sample, from 35 (Andersen, 2005) to 800 (Licht *et al.*, 2016) and anything in between.

Based on probability equations Vermeesch (2004) recommended that c. 117 grains should be analysed in order to have a 95% chance of detecting all populations in a sample comprising 20 populations each making up 5% of the total. However, he suggested that this may vary depending on the investigated material and the distribution of each population. As at present it is not known how many age populations are contributing to the Danubian loess, the Vermeesch (2004) recommendation was followed in this research. In practice, more grains were analysed in most samples, but many grains showed significant discordance and/or common Pb content, in part due to the small size of the zircon. For this reason, some samples have fewer analyses than desired. However, in all cases they exceed the recommended 70 grains of Andersen (2005), which based on the

statistical analysis and numerical simulations suggests that this would achieve a 95% chance of sampling all populations > 1-2 % of the total.

Additionally, only some studies have used other provenance methods, e.g. heavy mineral assemblages (Bird *et al.*, 2015; Stevens *et al.*, 2013b), garnets (Fenn *et al.*, 2018), and rutile (Újvári *et al.*, 2013) in conjunction with zircon U-Pb ages analysis. In this study all U-Pb zircon samples are also analysed for Hf isotope composition. These results are also supported by bulk sample geochemical analysis and luminescence data, therefore potentially overcoming the need for large (>200) U-Pb datasets.

7.2.2. Modern Rivers

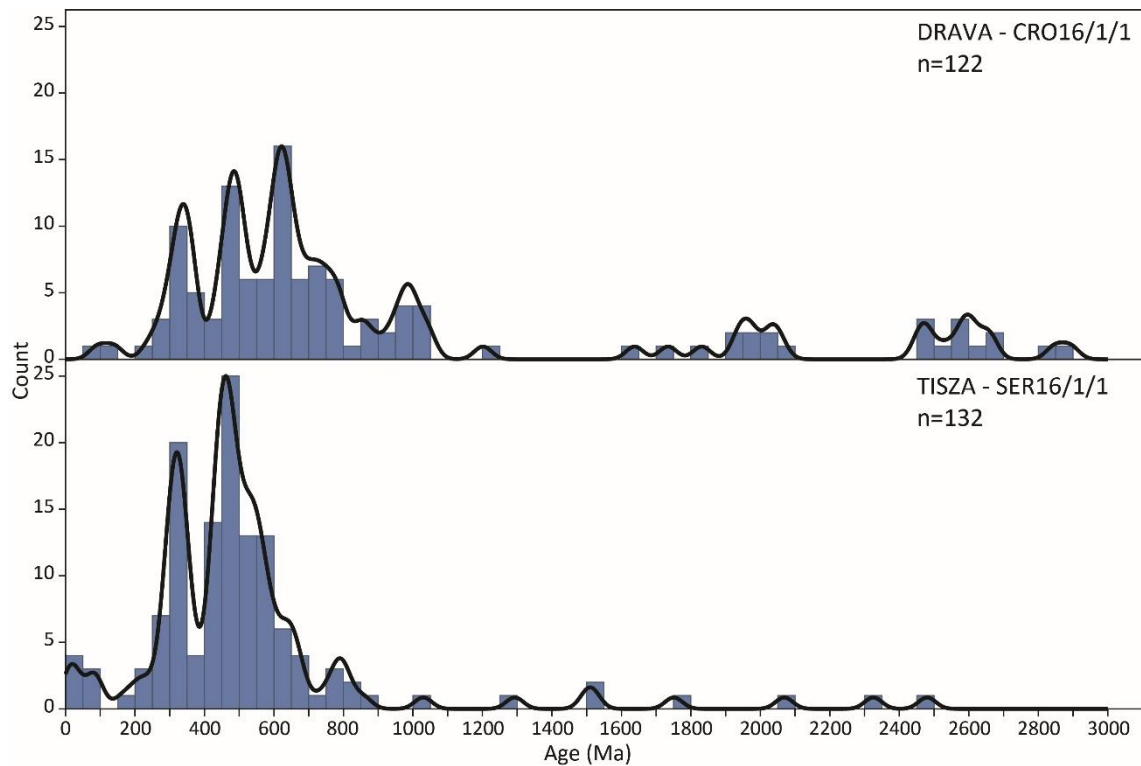


Figure 7.1 Zircon U-Pb Kernel Density Estimator (KDE) diagram for modern Tisza and Drava Rivers. Kernel bandwidth 30, histogram binwidth 50.

The results of the U-Pb dating of detrital zircons from modern sandy-silty alluvium of the Danube's tributaries are shown in Figure 7.1. The majority of the grains contributing to

Drava's zircon age distribution fall in the 200-1100 Ma bracket. Three well-defined age populations at c. 340 Ma, c. 490 Ma, and c. 620 Ma can be observed. Interestingly, there are several distinct, smaller groupings of Tonian, Palaeoproterozoic and Archaean age (c. 990 Ma, c. 2040 Ma, c. 2600 Ma and c. 2900 Ma), and a small Cretaceous population.

Tisza's zircon ages are dominated by grains younger than 800 Ma (Figure 7.1). These have two major age populations at c. 330 Ma and c. 460 Ma. There is also a large contribution of grains of ~550 Ma, 650 Ma and 800 Ma ages, however apart from the last of these, they do not form strong distinct peaks. Lastly, the Tisza sample contains zircons with young ages, in the Miocene (~16 Ma) and Upper Cretaceous (80 Ma).

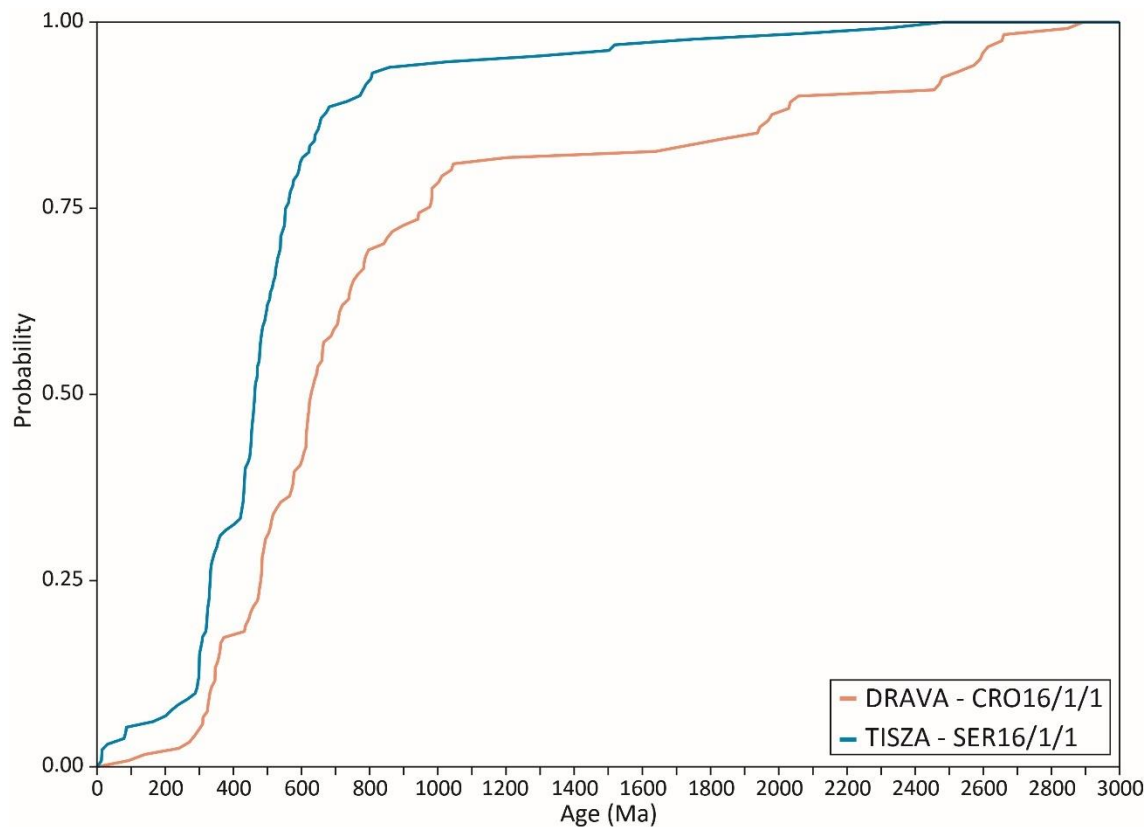


Figure 7.2 Age distributions for detrital zircons in the modern Tisza and Drava Rivers presented as a cumulative percentage.

The KDE diagrams (Figure 7.1) indicate that the sediments from two rivers have quite different zircon age distributions. Plotting ages as cumulative distributions (Figure 7.2),

shows that the distributions have only some similarities. Approximately 80% of the Tisza's age distribution is composed of grains dated to 300-700 Ma. In comparison, the results from the Drava show ~60% of grains in the 450-1050 Ma bracket. Additionally, the Drava receives almost 20% of its zircon age distribution from Mesoproterozoic or older grains, whereas the Tisza contains more Mesozoic and younger grains.

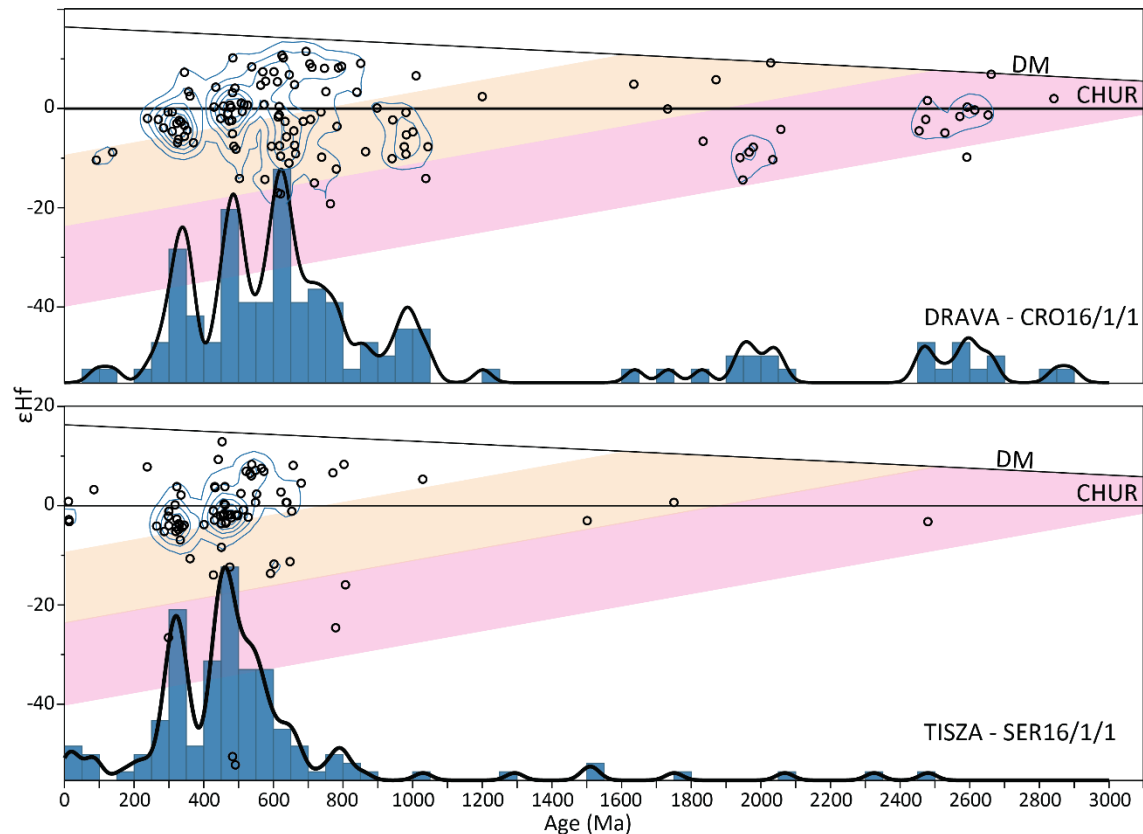


Figure 7.3 ϵ_{Hf} plotted against U-Pb age for detrital zircons in the modern Tisza and Drava rivers. Shaded areas represent the evolution of ϵ_{Hf} through time with the Vervoort *et al.* (1999) depleted mantle model; 2500-3300 Ma Archaean crust (pink) and 1600-2500 Ma Palaeoproterozoic crust (orange).

The results of the *in situ* zircon Hf analyses for both rivers are presented in Figure 7.3, with the marked Chondritic Uniform Reservoir (CHUR) and the depleted mantle (DM) evolution lines. Zircons typically contain several weight % Hf, but only a few parts per million Lu, resulting in very low $^{176}\text{Lu}/^{177}\text{Hf}$ ratios, and slow ingrowth of radiogenic ^{176}Hf .

Depleted mantle model ages can be derived by back-calculating the $^{176}\text{Hf}/^{177}\text{Hf}$ composition of the zircon to the time of its growth using the measured $^{176}\text{Lu}/^{177}\text{Hf}$, then projecting back in time using a model $^{176}\text{Lu}/^{177}\text{Hf}$ ratio representing an average crustal value. The point at which the projected line intersects the depleted mantle growth line represents a model crustal residence age for the hafnium which ultimately entered the zircon lattice. Here, the average passive margin mud $^{176}\text{Lu}/^{177}\text{Hf}$ value of 0.012 (Vervoort *et al.*, 1999) is used as an estimate of average crustal $^{176}\text{Lu}/^{177}\text{Hf}$. The shaded areas on the ϵHf -age diagrams mark the theoretical evolution paths for reworking of pre-existing crust, separated from a depleted mantle during the Archaean and Palaeoproterozoic, derived assuming an average $^{176}\text{Lu}/^{177}\text{Hf}$ value of 0.012. A strong deviation from the CHUR, and a dip into Palaeoproterozoic/Archaean fields (strongly negative ϵHf values), indicates involvement, or at least partial contributions, of the older crustal material (Chauvel *et al.*, 2014). Importantly zircons can grow in a variety of magmatic settings, therefore some ϵHf values representing “pure” juvenile magmas or crustal-reworking, while in some cases mixing of both signals through intrusion of melts is represented.

For Drava sediments the age populations recognised in the KDE plots appear as discrete populations in ϵHf -age space. The c. 340 Ma population plots just below CHUR line, with ϵHf as low as -7, while the c. 490 Ma populations lies close to the CHUR line indicating that Palaeoproterozoic and older crust was not involved in their formation to any significant extent.

The c. 620 Ma age population includes a cluster of grains with negative ϵHf , as low as -17, while a population at c. 1000 Ma also has negative ϵHf , as low as -13. These populations are consistent with zircon growth from melts which include a component of Palaeoproterozoic or older crust. A poorly-defined grouping of grains from c. 850 to 500 Ma has positive ϵHf , from +5 to +15. These are likely to represent Neoproterozoic oceanic

arc terranes, likely recycled through one or more previous sedimentary cycles, though with small possibility of basement rocks eroded by the rivers.

Finally, two populations at c. 2500 and 2000 Ma are seen. The c. 2000 Ma population is scattered, but a cluster of data plots below the CHUR line, within the field of Archaean crust, suggesting that these zircons formed during melting of older crust, rather than in a new cycle of crustal growth.

In the case of the modern Tisza sediments, the discrete populations in ϵHf -age space also replicate the populations seen on the KDE plots. The majority of the c. 330 Ma population plots just below the CHUR line ($\epsilon\text{Hf} = -3$), with only a couple of strongly negative grains ($\epsilon\text{Hf} < -10$). The 460 Ma populations plot much closer to the CHUR line ($\epsilon\text{Hf} = -1.5$), however there are a few grains with both grains with strongly negative ϵHf as well as grains with positive ϵHf . The c. 330 Ma and c. 460 Ma populations plot on the upper boundary of the field for Palaeoproterozoic crust, indicating that Palaeoproterozoic and older crust was involved in their formation to any significant extent.

As noted from the KDE diagrams there are no significant Neoproterozoic or Archaean age populations in the modern Tisza sample (Figure 7.1). A small cluster of grains can be observed at around c. 500-650 Ma, most of which have positive ϵHf typical of oceanic arcs (c. +5), however a few grains with negative ϵHf , from -11 to -13, can be seen.

7.2.3. Croatia

7.2.3.1. Zircon U-Pb ages and Hf isotopes

All samples from Erdut are dominated by a zircon population in the 300-700 Ma range, with additional tails in the 800-1100 Ma range (Figure 7.4). Minor contributions from grains of Mesoproterozoic, Palaeoproterozoic and Archaean ages are also seen. Samples CRO16/2/15, CRO16/2/21 and CRO16/2/9 contain very young, Eocene grains. In most

samples the zircons of ~340 Ma age are the most abundant, but two additional dominant populations are observed at ~450 Ma, and ~620 Ma. The proportion of each population varies between samples. For example, in samples CRO16/2/21, CRO16/2/11 and CRO16/2/9 the Ordovician population is less prominent. In samples CRO16/2/12 and CRO16/2/9 a population of Triassic and Jurassic grains is noted, which is absent from all other samples.

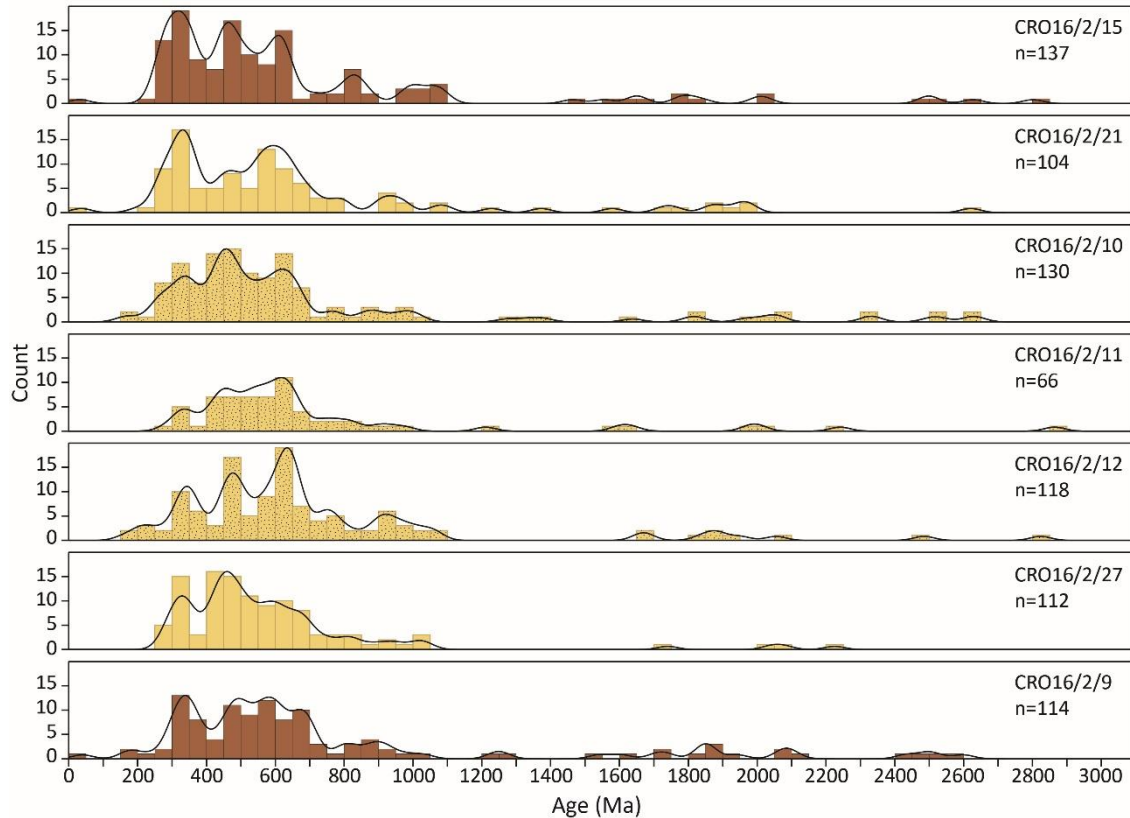


Figure 7.4 Zircon U-Pb Kernel Density Estimator (KDE) diagram for Croatia loess-palaeosol profile. Samples are presented in stratigraphic order and colours denote loess (yellow), palaeosol (brown), and fluvial unit (dotted) samples. Kernel bandwidth 30, histogram binwidth 50.

There is noticeable variability between samples. For example, a Permian (~280 Ma) age population appears in samples CRO16/2/15 and CRO16/2/21. This is additionally seen in the cumulative percentages (Figure 7.5), where grains <400 Ma contribute to almost 30% of the age distributions of these samples. CRO16/2/9 and CRO16/2/10 plot close together

in the 900-2100 Ma part of the cumulative curve (Figure 7.5). Additionally, in the bottom two samples (CRO16/2/27 and CRO16/2/9) all three dominant populations become uniform, with a fairly even distribution of grains in all histogram bins. In fluvial samples CRO16/2/11 and CRO16/2/12 the contributions of the Carboniferous population (~340 Ma) are reduced.

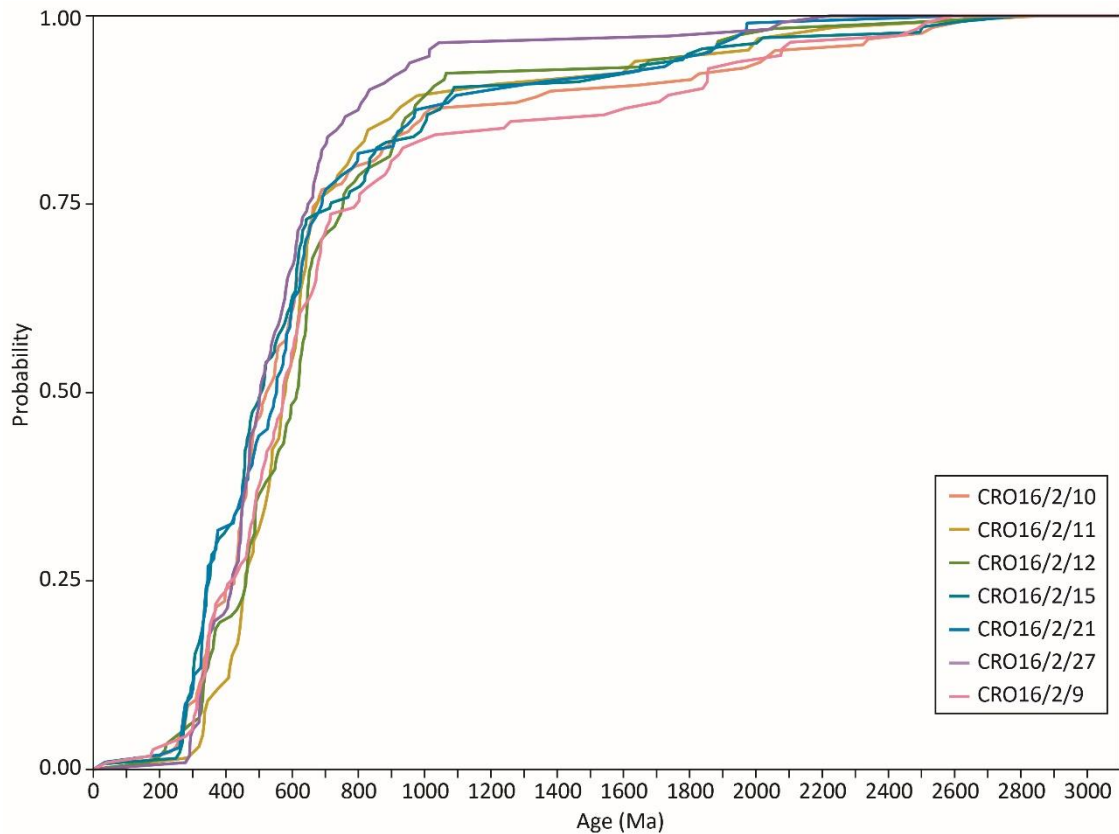


Figure 7.5 Age distributions for individual Croatian samples presented as a cumulative percentage.

Figure 7.5 also shows that there are some differences in the shapes of the cumulative age distributions. Sample CRO16/2/27 has limited contributions from older grains, with ~85% of the distribution driven by grains <700 Ma. On the other hand, grains >700 Ma contribute ~25-30% to the age distribution in sample CRO16/2/9.

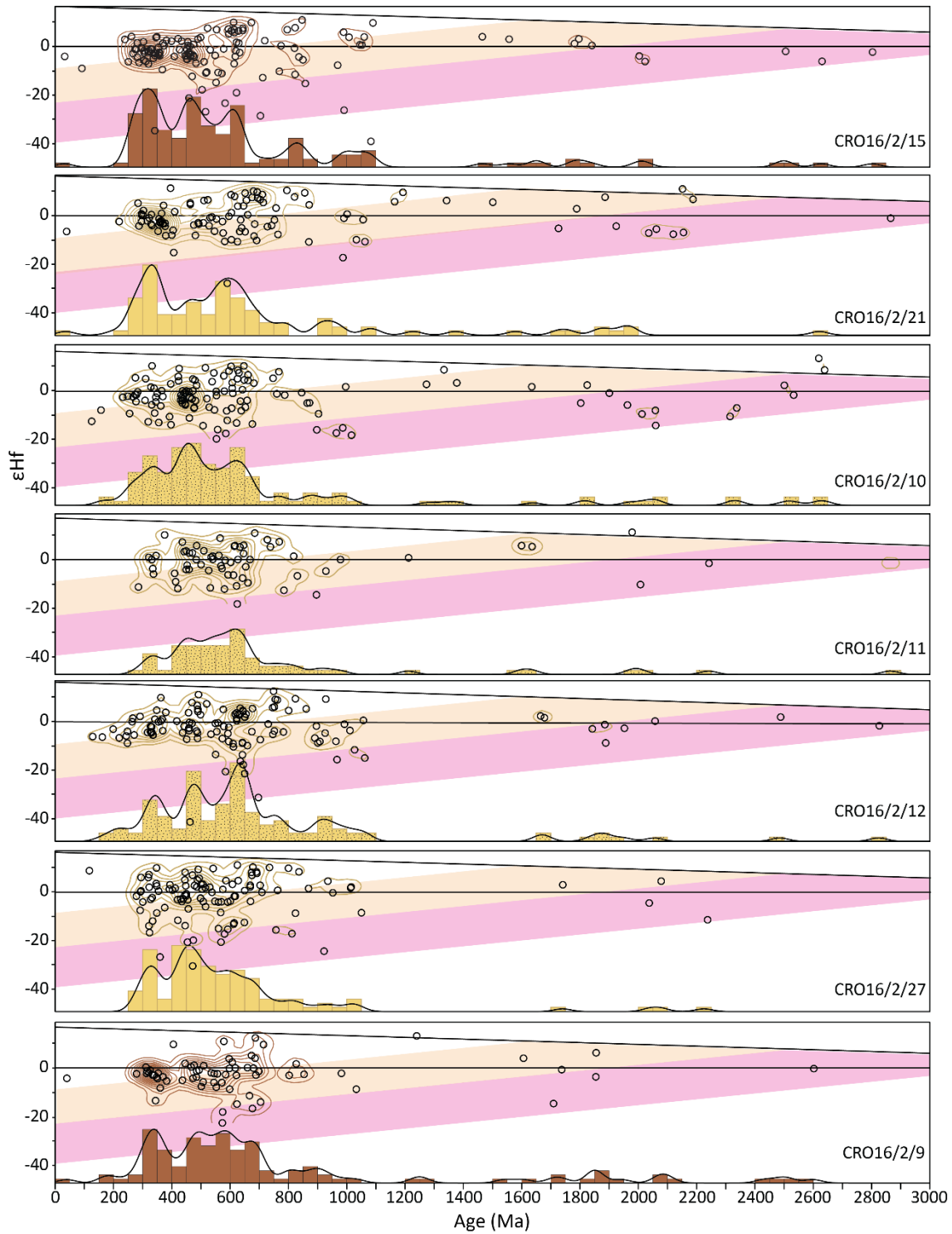


Figure 7.6 Detrital zircon U-Pb age plotted with ϵ_{Hf} vs U-Pb age loess and palaeosol for samples at Erdut. Areas represents the evolution of Hf in crust through time for 2500 - 3330 Ma Archean crust (pink), and 1600 - 2500 Ma Palaeoproterozoic crust (orange).

Hf analysis of zircon grains from Erdut (Figure 7.6) shows the variability in Hf-isotope composition of grains contributing to the individual age populations. Of particular interest are the variations between three age populations seen on the KDE plots, at c. 340 Ma, 450 Ma and 600 Ma. The differences can be seen mostly from the proportion of juvenile crust and mature crust grains for the same age population, which are outlined below.

The ϵHf -age distributions for all samples show a number of similarities. For the most part, c. 340 and 450 Ma populations plot just below the CHUR line, showing mildly negative to slightly positive ϵHf , while the third population (c. 620 Ma) is in general showing two trends; a cluster with slightly positive ϵHf values, and a scatter to more negative values. Both 340 and 450 Ma populations may reflect zircon growth in magmas derived by melting of Neoproterozoic mafic crust.

In sample CRO16/2/15 both 340 and 450 Ma age populations have mildly negative ϵHf values, as low as -10, although the c. 450 Ma population has a few grains scattering towards more negative, crust-dominated values. In the third population (c. 620 Ma), while there are some grains with values as low as -23, around 70% is contributed by grains with arc-like signatures ($\epsilon\text{Hf} > 4$). The positive and mildly negative ϵHf data can be explained by new crustal growth, or melting of Neoproterozoic or Mesoproterozoic crust, however, some involvement of melts derived from Palaeoproterozoic or older crust is required to explain the more negative values shown by some data points, especially at c. 620 Ma.

In all fluvial samples (CRO16/2/10, CRO16/2/11 and CRO16/2/12) juvenile grains contribute 40-50% to the distribution of zircons in the c. 610 Ma population, with values as high as $\epsilon\text{Hf} = 16$ in CRO16/2/12, indicating mantle derived source rocks. However, there are contributions of grains with $\epsilon\text{Hf} = -19$, $\epsilon\text{Hf} = -18$, and $\epsilon\text{Hf} = -21$, in CRO16/2/10, CRO16/2/11

and CRO16/2/12 respectively. Moreover, in CRO16/2/12 there is a distinct gap between the juvenile and mature populations in the c. 610 Ma population.

The c. 340 Ma peak in sample CRO16/2/27 is predominantly composed (56%) of grains with ϵHf scattering around 0; however the values range from -3 to -16. A poorly-defined grouping of grains from c. 400 to 500 Ma has have an almost continuous spread of values ϵHf , from 10 to -30. The c. 610 Ma population is relatively muted in CRO16/2/27, and grains contributing to this age range have almost exclusively negative ϵHf (>70%) with values reaching $\epsilon\text{Hf} = -20$ requiring a contribution from melts of Palaeoproterozoic or older crustal material.

7.2.3.2. Bulk sample geochemistry

Selected REE and trace elements in samples from Erdut are plotted normalised to the Upper Continental Crust values (Figure 7.7) (Taylor *et al.*, 1983). Figure 7.7A shows the large-ion lithophile elements (LILE) such as Rb, Ba, Sr, and high-field-strength elements (HFSE) for example Zr, Hf, Nb, Th, Y.

For all elements apart from Th, Zr, Hf, Nb and Y (Figure 7.7A), there is significant inter-sample variability in the distribution. The same patterns for Zr and Hf in Erdut indicate that their concentration is likely driven by zircon minerals. The HFSE elements are, broadly speaking, depleted in all samples, apart from CRO16/2/9, potentially suggesting mafic source rocks, but also some changes in provenance. The transition elements V, Cr, and Ni show a strong positive anomaly, while Cu and Zn a negative one.

All samples are slightly depleted in Rb, and Ba and strongly depleted in Sr, especially sample CRO16/2/9, relative to UCC. This could be explained by Sr solubility and removal as a part of the weathering process, but this could also indicate a low concentration of

feldspar in the samples. Interestingly, samples CRO16/2/21, CRO16/2/17 and CRO16/2/20 are less depleted than others.

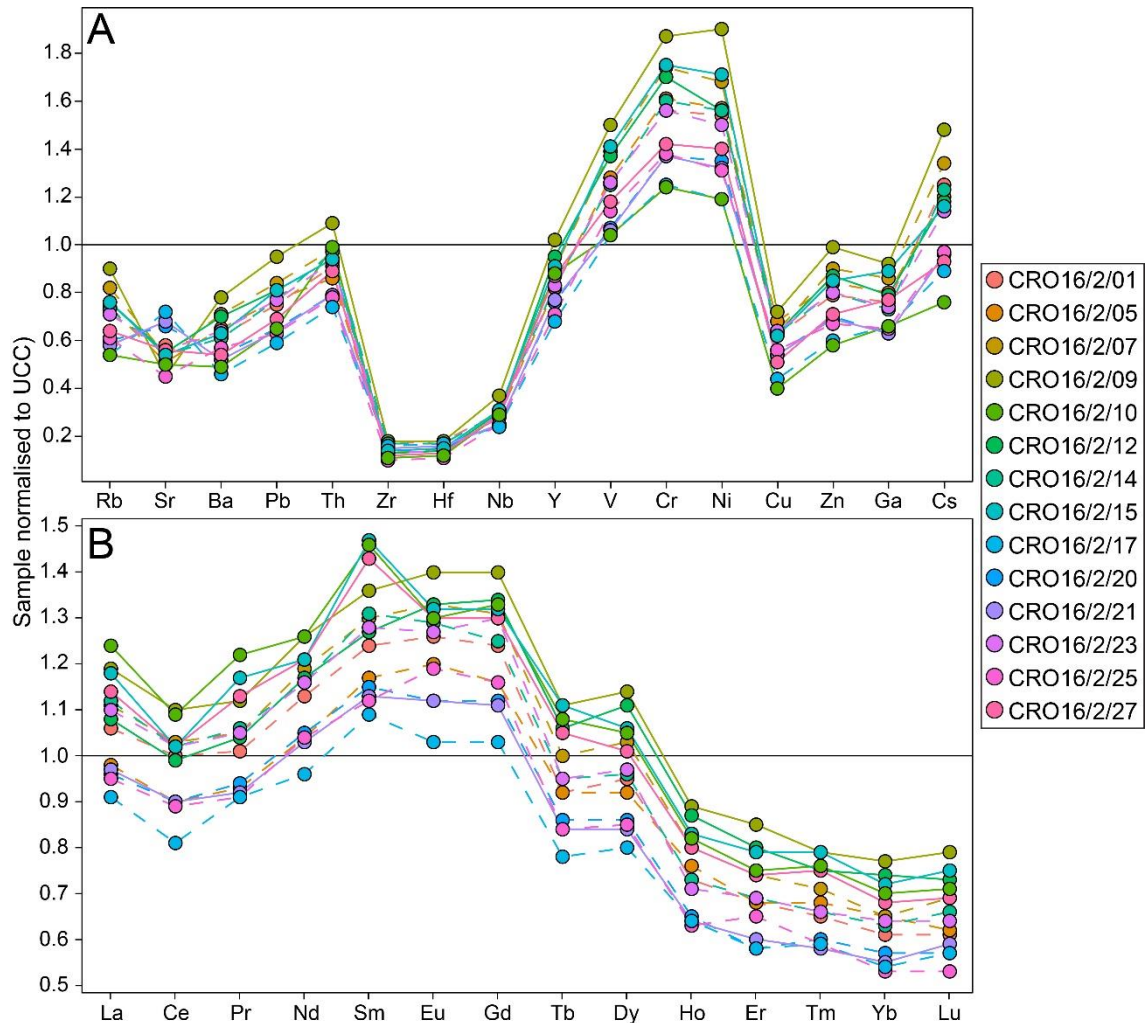


Figure 7.7 UCC-normalised bulk sample trace elements diagram for Erdut. A) LILE and HFSE elements B) REE. Samples corresponding zircon U-Pb ages and Hf data are marked as solid lines.

There is significant inter-sample variability in relation to the UCC (Figure 7.7B). In general, Light Rare Earth Elements (LREE) are slightly enriched in samples from Erdut compared to the UCC, however samples CRO16/2/17, CRO16/2/25, CRO16/2/5, CRO16/2/17, CRO16/2/20, and CRO16/2/21 are slightly depleted in La, Ce, and Pr. On the other hand, Heavy Rare Earth Elements (HREE) show as slightly depleted, but a somewhat flat profile

in all samples. The exceptions are Tb and Dy where half of the samples are enriched and half are depleted.

Sample CRO16/2/9 from the top of the penultimate palaeosol shows a completely different pattern of trace element distribution compared with the remaining samples.

7.2.4. Serbia

7.2.4.1. Zircon U-Pb ages and Hf isotopes

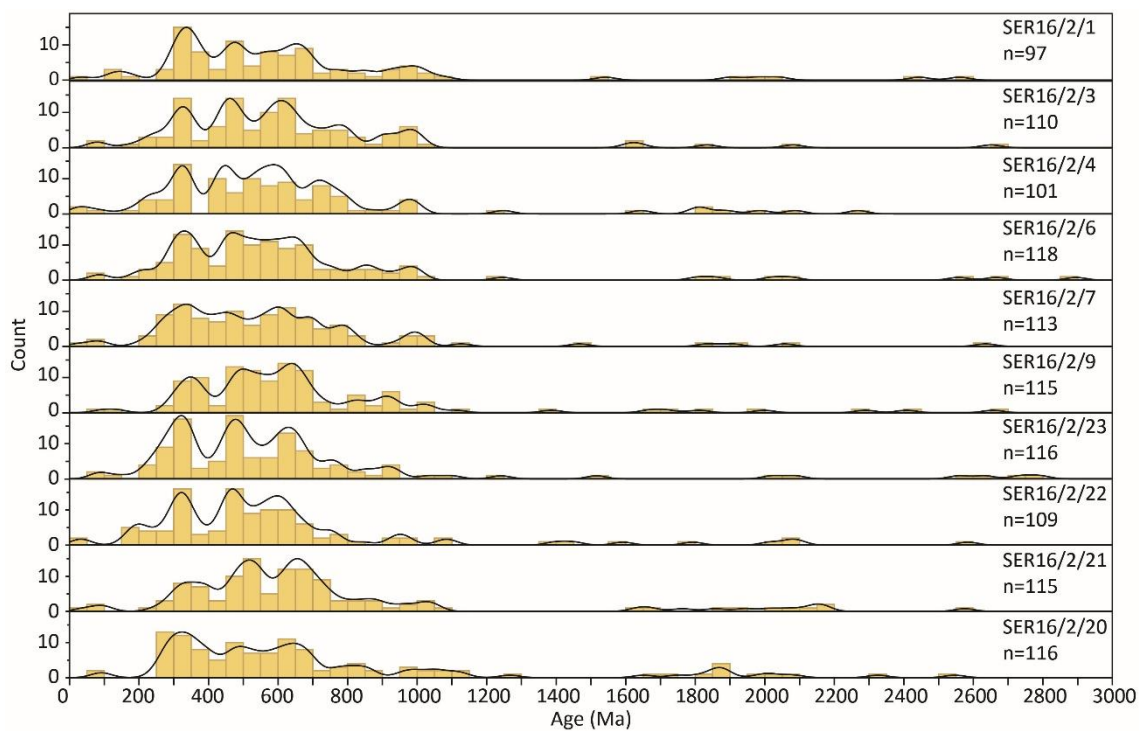


Figure 7.8 Zircon U-Pb Kernel Density Estimator (KDE) diagram for Surduk 2 loess-palaeosol profile. Samples are presented in stratigraphic order. Kernel bandwidth 30, histogram binwidth 50.

The KDE diagram (Figure 7.8) shows that the Surduk 2 loess samples share many similarities in their zircon age distributions. Broadly three populations at c. 330 Ma, c. 470 Ma and c. 630 Ma can be observed, however they are not equally prominent in all samples. The c. 330 Ma population is the most abundant in all samples apart from SER16/2/9 and SER16/2/21. The third peak is Neoproterozoic in age, between c. 590 and 670 Ma in all

samples. All samples appear to have relatively large tails in the distribution, with a significant proportion of grains in the 700-1150 Ma range (Figure 7.8). Additionally, samples SER16/2/23, SER16/2/21, and SER16/2/20 include older Palaeoproterozoic grains (1600-2200 Ma).

A population at ~990 Ma is present in all samples, but is particularly prominent in samples SER16/2/1, SER16/2/3, SER16/2/4, and SER16/2/7. Finally, all Surduk 2 samples contain Mesozoic and younger zircon grains, e.g. Oligocene (~30Ma; SER16/2/1, SER16/2/4, SER16/2/22), Upper Cretaceous (~85Ma; SER16/2/3, SER16/2/6, SER16/2/7, SER16/2/23, SER16/2/21, SER16/2/20) and Lower Cretaceous (SER16/2/1 and SER16/2/9).

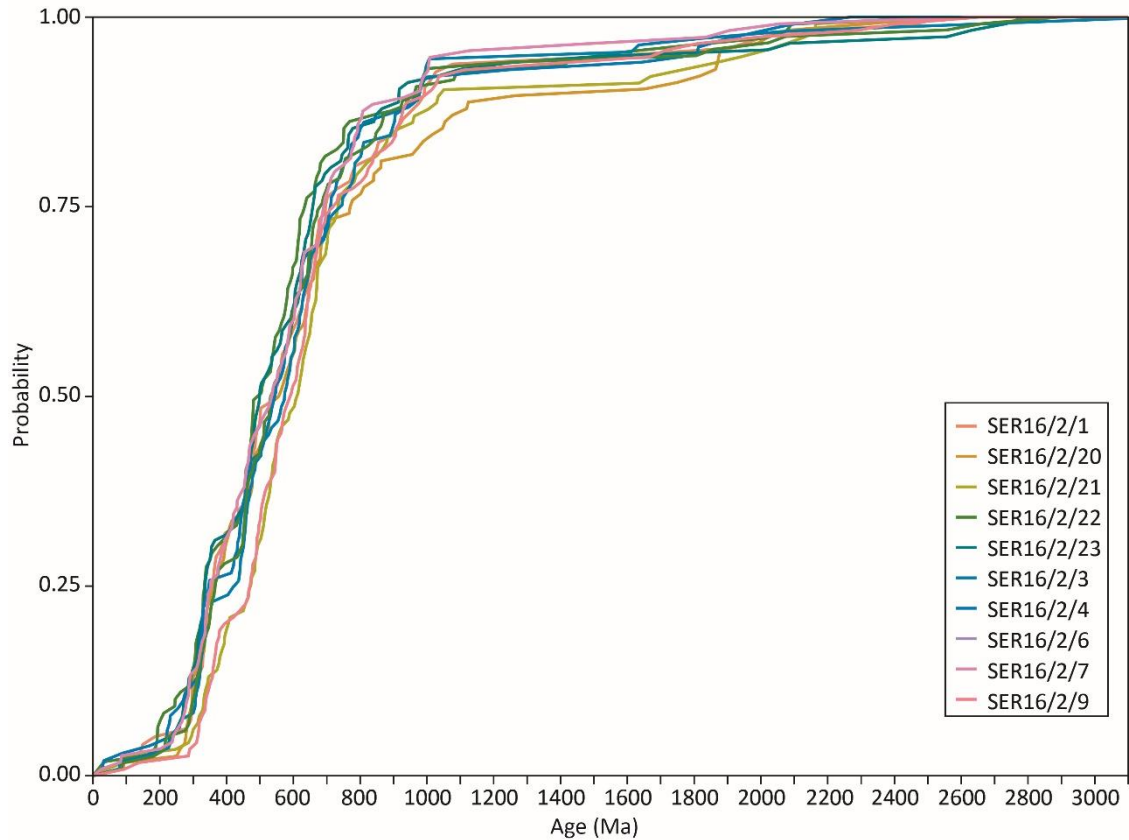


Figure 7.9 Age distributions for individual Serbian samples presented as a cumulative age distributions.

Cumulative age distributions (Figure 7.9) reveal that, while for the most part the zircon age distributions from Surduk 2 are very similar, there are a few samples that diverge slightly. In particular, samples SER16/2/20, SER16/2/21 and SER16/2/9 attribute only a very minor percentage of their distributions (1.7-3.4%) to grains <250 Ma. On the other hand, they have larger proportion of grains older than 800 Ma (~20-24%), whereas for example for SER16/2/7 grains over 1000 Ma account only for ~7% of the age distribution.

The results of *in-situ* zircon analysis of Hf isotopes from Surduk 2 (Figure 7.10) shows the variability of grains contributing to the individual distributions. The differences, outlined below, can be seen mostly from the proportions of grains derived from juvenile crust and those incorporating hafnium from more ancient crust, especially for the dominant age populations, c. 330 Ma, 470 Ma and 630 Ma.

There is a lot of overlap between the ϵHf -age distributions of all Surduk 2 samples. The c. 330 Ma age population plots mostly just below the CHUR line, with average ϵHf values of -3. A similar ϵHf distribution is observed for the c. 470 Ma age population, with average values at c. -1.5. Finally, in the 630 Ma is a broad spectrum of ϵHf values, with a positive ϵHf (average +4) as high as +12, and negative ϵHf (average -8.5).

Samples SER16/2/1, SER16/2/4, SER16/2/6, and SER16/2/22 have a small addition of grains in the 150-250 Ma age range. In SER16/2/22 these grains represent juvenile, arc-like terrains (c. +4), while in the other samples these grains have negative ϵHf values, plotting slightly below the CHUR line.

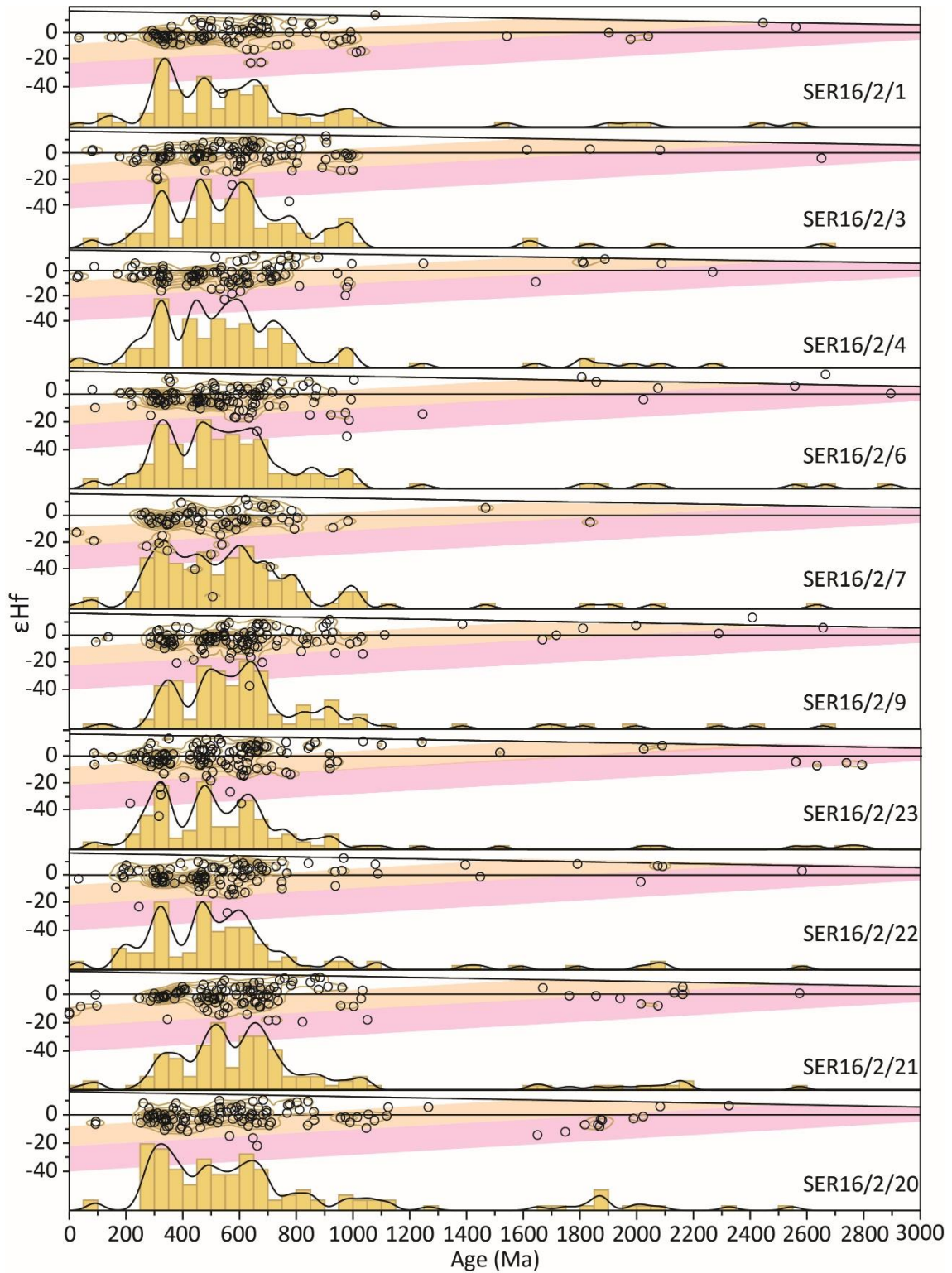


Figure 7.10 Detrital zircon U-Pb age plotted with ϵ_{Hf} vs U-Pb age for loess and palaeosol samples at Surduk 2. Areas represent the evolution of Hf in zircon through time with the Vervoort *et al.* (1999) depleted mantle model; pink between 2500 and 3330 Ma (Archean crust) and orange between 1600 and 2500 Ma (Palaeoproterozoic).

The c. 330 Ma age peak in samples SER16/2/3, SER16/2/4, SER16/2/7, and SER16/2/23, has a few grains with strongly negative values, as low as $\epsilon\text{Hf} = -20$, $\epsilon\text{Hf} = -16$, $\epsilon\text{Hf} = -26$, and $\epsilon\text{Hf} = -29$, respectively. These values indicate zircon crystallisation from melts including a component of Archean/Palaeoproterozoic crust. Distinctions can be made between grains in the 750-1150 Ma range tail described on the KDE diagram (Figure 7.8). While a few grains with negative ϵHf can be seen, grains in the range 750-900 Ma have mostly positive values (except for samples SER16/2/7 and SER16/2/9), with a number of clusters between +7 and +12. On the other hand, grains in the 900-1150 Ma range show a spread from positive ϵHf (e.g. in SER16/2/9) to negative ϵHf values (e.g. SER16/2/6), with an overall average value of -3.

The proportion of Neoproterozoic and younger grains that show contributions from Archaean crust, is significantly less than seen at Erdut.

7.2.4.2. Bulk sample geochemistry

Figure 7.11 shows selected REE and trace elements in bulk samples from Surduk 2 and are plotted normalised to UCC. There is a certain level of variability in the abundance of incompatible elements (Figure 7.11A) in between the samples, especially for Ba, Th, V, Cr, Ni, Zn and Cs. Zr and Hf are strongly depleted in the Surduk 2 samples. However they show broadly the same pattern, and therefore the concentration of these elements is likely related to the zircon minerals.

Most of the HFSE elements are depleted relative to the UCC in all the Surduk 2 samples, except for U, Eu, and La. Interesting patterns can be noted for Th, and La. Three stratigraphically adjacent samples, SER16/2/7, SER16/2/8, and SER16/2/9, show slight enrichment in Th, suggesting a potential increase in contributions from other source rocks. Samples SER16/2/1 and SER16/2/3 from the top of the loess palaeosol sequence are slightly depleted in La. The transition elements V, Cr, and Ni show a strong positive

anomaly, while Cu and Zn a negative one, though a lot of variability can be observed. Samples SER16/2/6, SER16/2/7, SER16/2/8, and SER16/2/9 have the strongest anomaly in Cr and Ni, and are the only samples with a positive anomaly in Zn.

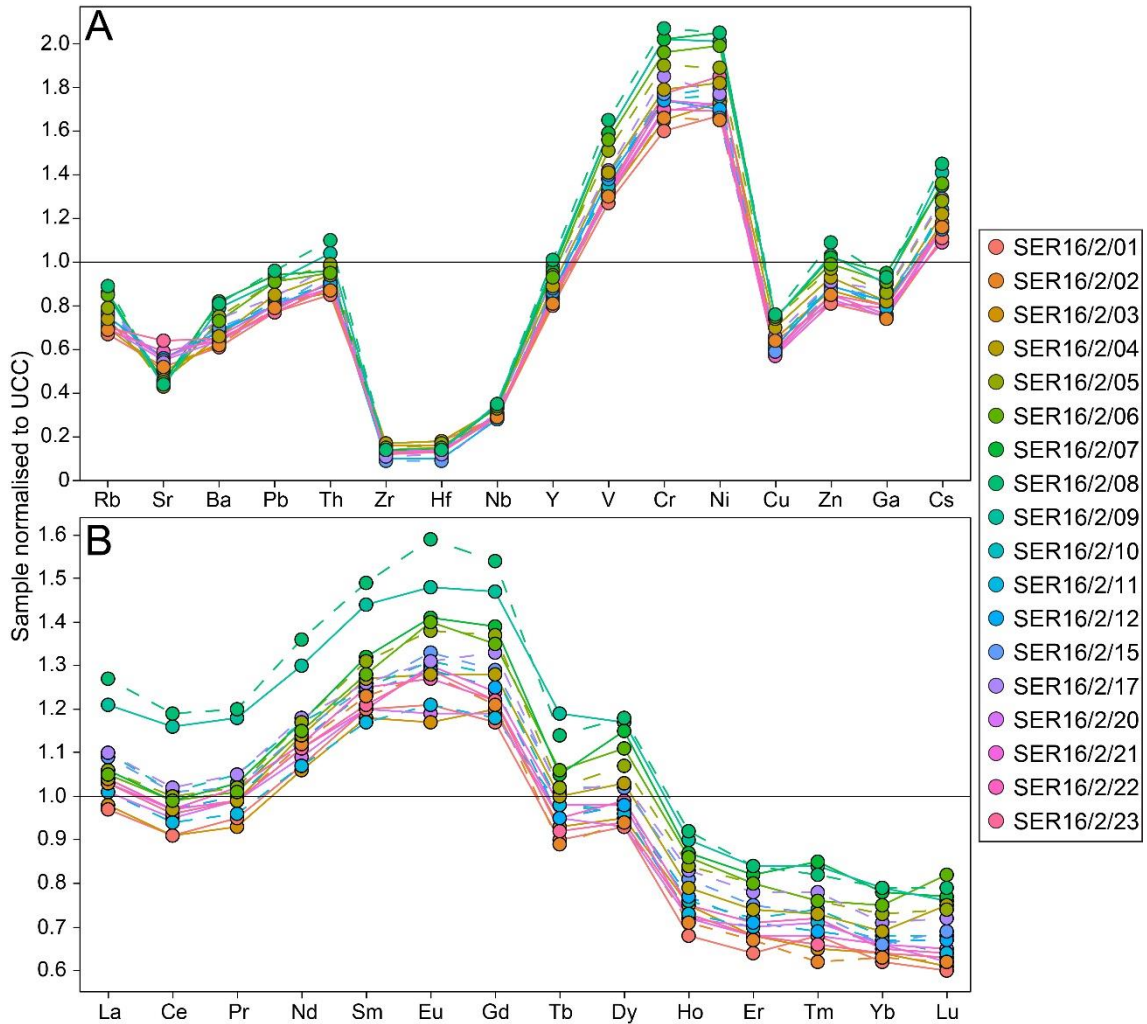


Figure 7.11 UCC-normalised bulk sample trace element diagrams for Surduk 2. A) LILE and HFSE elements B) LREE and HREE. Samples with zircon U-Pb ages and Hf data are marked as solid lines.

A negative anomaly relative to UCC can be seen for Rb, Ba, and Sr for all the Surduk 2 samples, which is related to the removal of these elements as a part of the weathering process and/or low concentration of feldspars in the samples.

The broad trend shows an enrichment in LREE (except for Ce and Pr) and a depletion in HREE, relative to UCC in the Surduk 2 bulk samples (Figure 7.11B). There is a slight

variance from that trend, especially for samples SER16/2/6, SER16/2/7, SER16/2/8, SER16/2/9, SER16/2/15, and SER16/2/17, which are enriched in Ce, Pr, Tb, and Dy. Samples SER16/2/6, SER16/2/7, SER16/2/8, and SER16/2/9 also show a very strong positive anomaly in Nd, Sm, Eu, and Gd. These stratigraphically adjacent samples show 30-50% enrichment in relation to the UCC for those LREE elements, suggesting some potential source rock changes.

7.2.5. Bulgaria

7.2.5.1. Zircon U-Pb ages and Hf isotopes

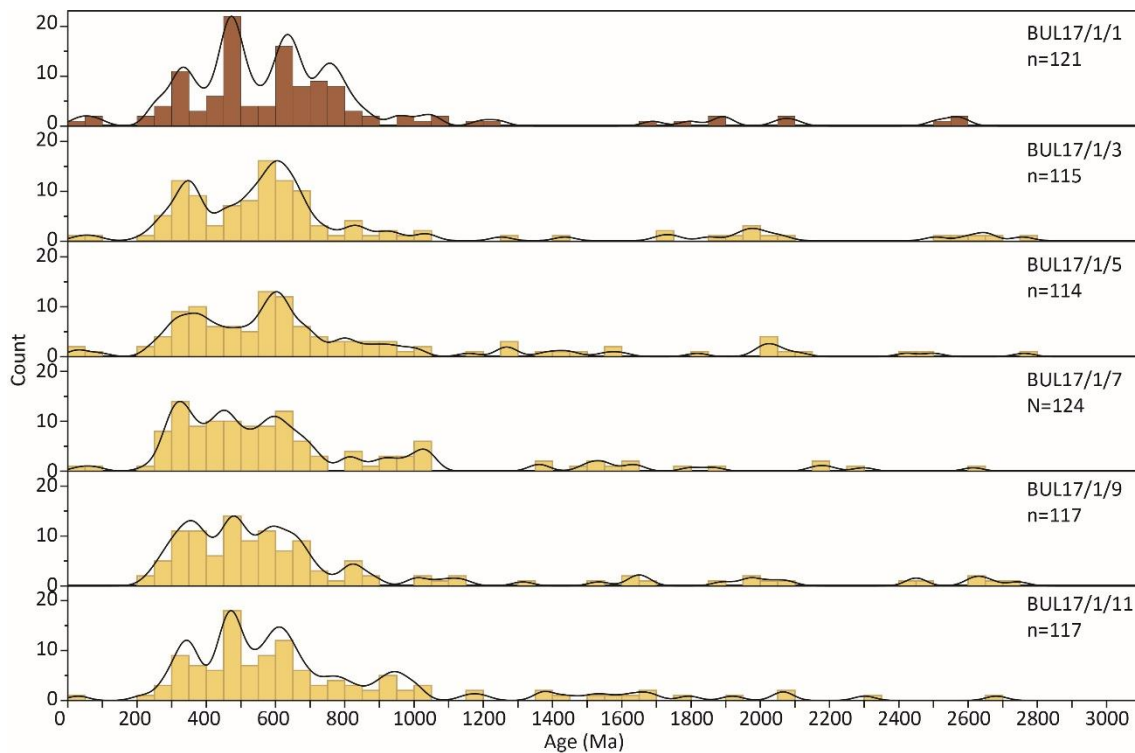


Figure 7.12 Zircon U-Pb Kernel Density Estimator (KDE) diagram at Slivata I loess-palaeosol profiles. Samples are presented in stratigraphic order and colours denote loess (yellow) vs palaeosol (brown) samples. Kernel bandwidth 30, histogram binwidth 50.

The majority of the zircon U-Pb ages at Slivata I fall in the 200-800 Ma bracket (Figure 7.12). For most samples, three distinct populations are observed at c. 330 Ma, c. 470 Ma,

and c. 620 Ma. Additionally, all samples have a distribution “tail” created by 700-1000 Ma ages, and contain sparse Palaeoproterozoic and Archaean grains.

The three distinct populations are particularly well defined in the palaeosol sample, BUL17/1/1, with the c. 470 Ma population contributing the largest number of grains. Moreover, this sample has an additional broad peak from grains in the 700-800 Ma age bracket rather than an elongated tail.

For samples BUL17/1/3 and BUL17/1/5, the Ordovician population is subordinate, making the age distribution appear bi-modal. In all other samples the c. 450 Ma population is the most abundant, whereas in the two aforementioned samples it is subdued, and the c. 620 Ma population dominates.

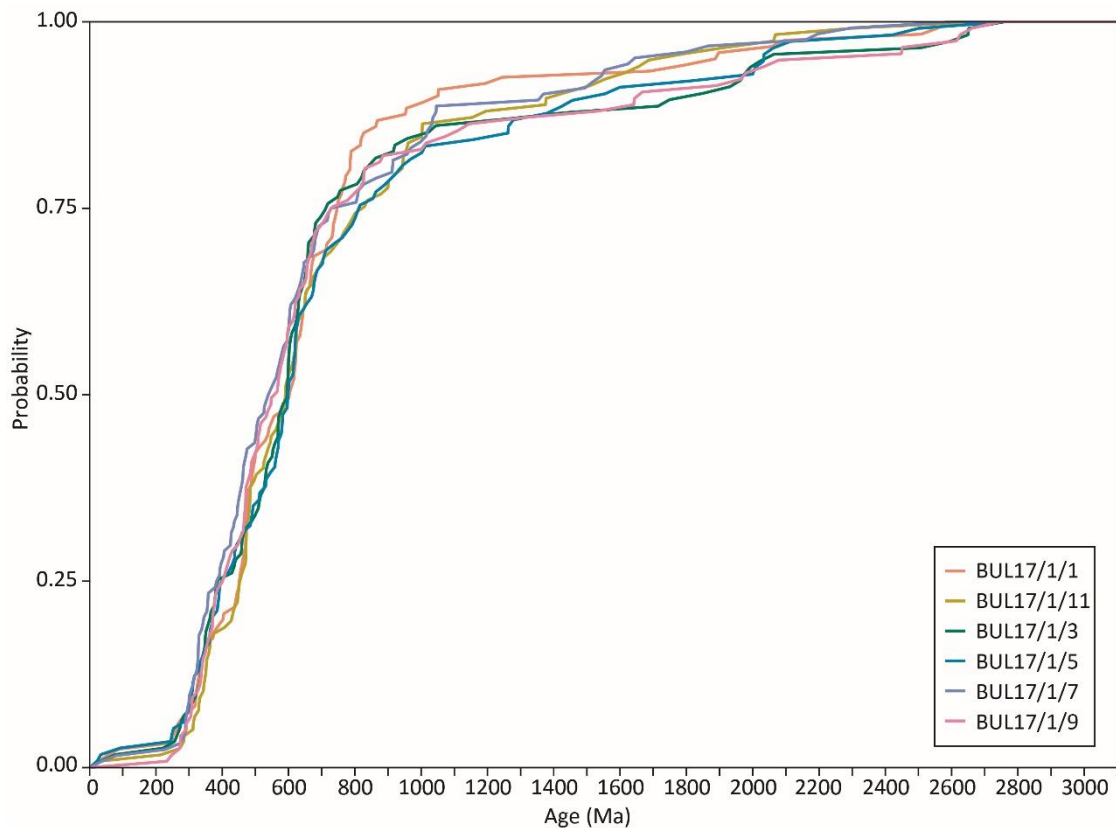


Figure 7.13 Age distributions for individual samples at Slivata 1 samples presented as a cumulative percentage.

BULI7/1/1 has a well-defined, albeit broad peak, between 700 and 800 Ma, that leads to a distinctive pattern for this sample in Figure 7.13. This sample is also dominated by grains with ages <800 Ma, with as much as ~85% of the cumulative age distribution found in this age bracket. However as in all other samples the 700-1100 Ma age range contributes relatively large proportion of grains (12-19%), in comparison to other samples. Lastly, BULI7/1/3 and BULI7/1/5 have small populations of grains of ~2000 Ma.

At the younger end of the age spectrum, all samples apart from BULI7/1/9 contain Mesozoic and younger zircon grains (< 100 Ma), centred around Oligocene (~30 Ma) and Eocene (~53 Ma) ages.

Hf analysis of zircon grains from Slivata 1 (Figure 7.14) indicates that there is limited variation between samples. Of particular interest are ϵ_{Hf} values for the three age main age populations represented on the KDE diagrams, c. 330 Ma, c. 470 Ma and c. 620 Ma, however the grains in the 700-1000 Ma “tail” are also explored. Additionally, a comparison between loess and palaeosol is discussed.

For all of the dominant age populations, corresponding distinct ϵ_{Hf} populations are seen. For the c. 330 Ma age population a slightly negative ϵ_{Hf} values are observed (>-10), while the c. 470 Ma population plots much closer to the CHUR line. In most cases 330 and 470 Ma populations can be explained by melting of Neoproterozoic mafic crust, with limited involvement of melts from older crust. The third population (c. 620 Ma) predominantly comprise a spread from positive (up to +10 in BULI7/1/1) to negative (as low as -30 in BULI7/1/3) ϵ_{Hf} grains. Finally, the 700-1000 Ma tail contains mostly grains with positive ϵ_{Hf} . BULI7/1/11 contains a population with mildly negative ϵ_{Hf} at c. 1000 Ma.

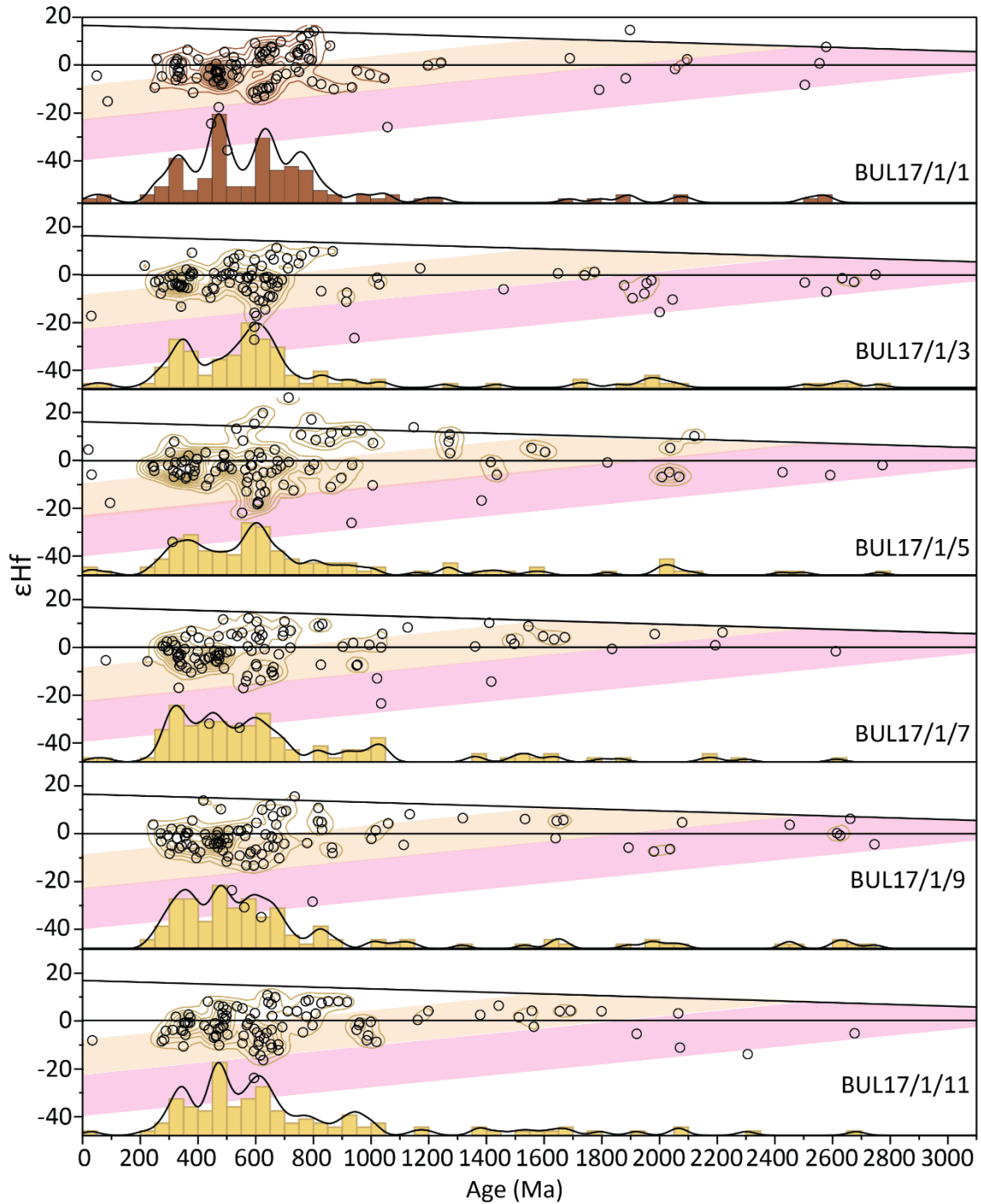


Figure 7.14 Detrital zircon U-Pb age plotted with ϵ_{Hf} vs U-Pb age for loess and palaeosol samples at Slivata 1. Pink area represents the evolution of Hf in a zircon through time with depleted mantle model between 2500 and 3330 Ma.

For the zircons from the c. 330 Ma population, in the palaeosol, BUL17/1/1, the ϵ_{Hf} values centred around the CHUR line, ranging from +0.9 to -5.5. For the c. 470 Ma population, the distribution is predominantly negative (~90%). While grains with ϵ_{Hf} values as low as

-17.4 are observed, most values are centred around c. -5. The ϵ_{Hf} values for the final major age population (c. 620 Ma) show a distinct gap between the juvenile and crust-dominated populations. The juvenile grains have ϵ_{Hf} ranging from +4 to +6, and have island arc-like signatures. On the other hand, a distinct population of zircon grains centred around $\epsilon_{\text{Hf}} = -11$ must have crystallised from a melt containing a significant amount of Palaeoproterozoic or older crust. Finally, this sample has a relatively large proportion of grains in the 700-800 Ma age bracket that is dominated (c. 85%) by juvenile, mantle derived source rocks, with values as high as 13.3 and average $\epsilon_{\text{Hf}} = 6.5$.

There is already a hint of similarity between samples BULI7/1/3 and BULI7/1/5, based on their bi-modal zircon age distribution. In BULI7/1/3 the first population (c. 330 Ma) has ϵ_{Hf} values as low as -13 and an average of -5. BULI7/1/5 also has same average, but with no strongly negative grains are seen. While in both samples the zircon grains in the c. 620 Ma population are dominated by negative ϵ_{Hf} values (70-80%), with a concentration of data between from $\epsilon_{\text{Hf}} = 0$ to $\epsilon_{\text{Hf}} = -10$, with a few of analyses as low as, -20 and -27. However, there is an interesting trend whereby the relative decrease in of the c. 450 Ma population, the more negative, and therefore ancient crust dominated, the c. 620 Ma population is (pink area in on Figure 7.13).

In the remaining three loess samples (BULI7/1/7, BULI7/1/9 and BULI7/1/11) the c. 330 Ma age population is composed primarily (70-80%) of grains with slightly negative ϵ_{Hf} values ($-10 < \epsilon_{\text{Hf}}$). Some juvenile grains can be found, however all with ϵ_{Hf} values < 2 . The c. 450 Ma population in samples BULI7/1/7 and BULI7/1/9 is dominated (80-90%) by grains with ϵ_{Hf} values c. -4.5, with some values as low as -12. However, in both samples individual juvenile grains are present with ϵ_{Hf} values as high as 11. In BULI7/1/11 ϵ_{Hf} data has a continuous spread from -10 to 6, suggesting potentially some other contributions. Finally,

in all three samples the c. 620 Ma population comprises a continuous spread of zircon grains, with most grains found within the $-14 < \epsilon_{\text{Hf}} < 12$ range.

KDEs for Slivata 2 (Figure 7.15) show that the majority of ages obtained are of Mesozoic-Palaeozoic age indicating that there are three distinct age populations. In the top three samples (BUL17/2/11, BUL/2/9, and BUL17/2/7) three dominant populations can be observed, at c. 310 Ma, c. 450 Ma, and Neoproterozoic age. However, the position of the third, population varies slightly between the samples. In BUL17/2/11, BUL/17/2/7, and BUL17/2/1 the peak can be observed at c. 600 Ma. However, in samples BUL17/2/9 and BUL17/2/3 it is found in the 550 to 600 Ma age range. Finally, almost all age distributions comprise very young grains of Miocene/Oligocene age.

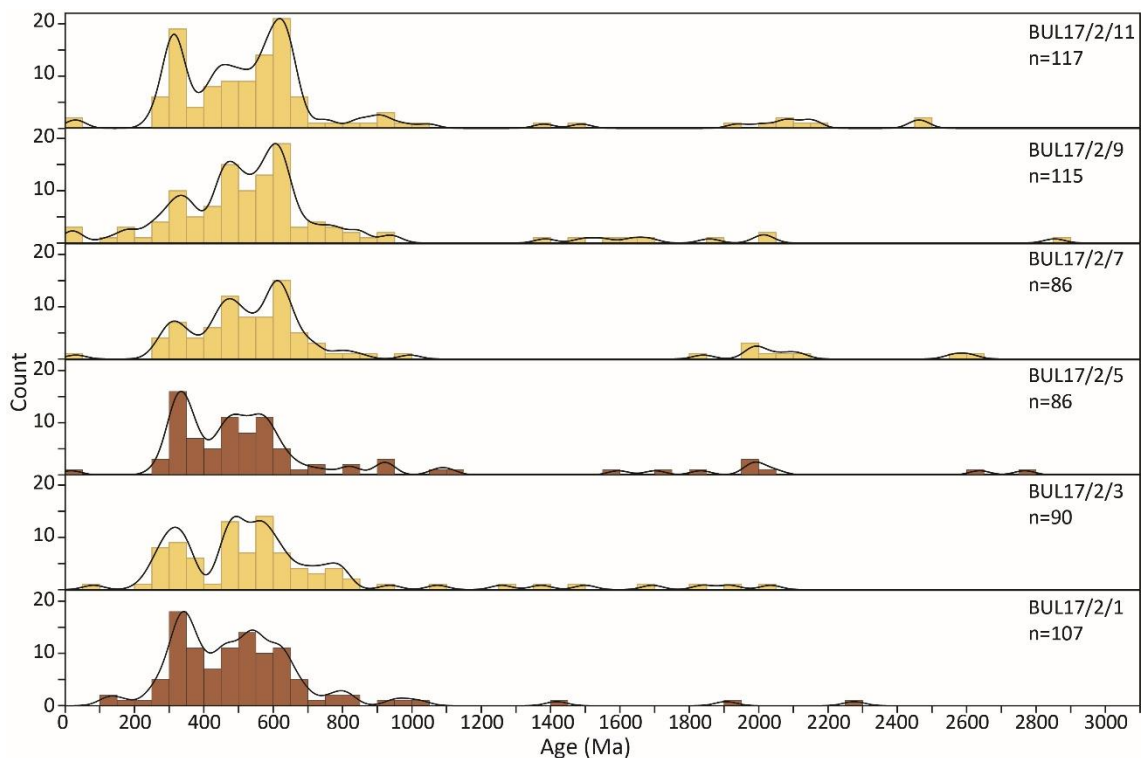


Figure 7.15 Zircon U-Pb Kernel Density Estimator (KDE) diagram at Slivata 2 loess-palaeosol profiles. Samples are presented in stratigraphic order and colours denote loess vs palaeosol samples. Kernel bandwidth 30, histogram binwidth 50.

In the bottom three samples (BUL17/2/5, BUL/2/3, and BUL17/2/1) the first (and in most cases dominant) population is centred around c. 310 Ma, with a secondary poorly-defined grouping of grains from c. 450 to 700 Ma.

Further, for sample BUL17/2/1 grains younger than 650 Ma contribute to over 85% of the age distribution (Figure 7.16), showing that the >700 Ma “tail” is somewhat subordinate. All other samples have considerable contributions of Precambrian ages, with as much as 12% of the age distribution attributable to grains older than 950 Ma, whereas for BUL17/2/1 these ages account for less than 5%. Additionally, samples BUL17/2/9 and BUL17/2/1 have sizable contributions of grains under 300 Ma; as much as 11% to their age distributions (Figure 7.16).

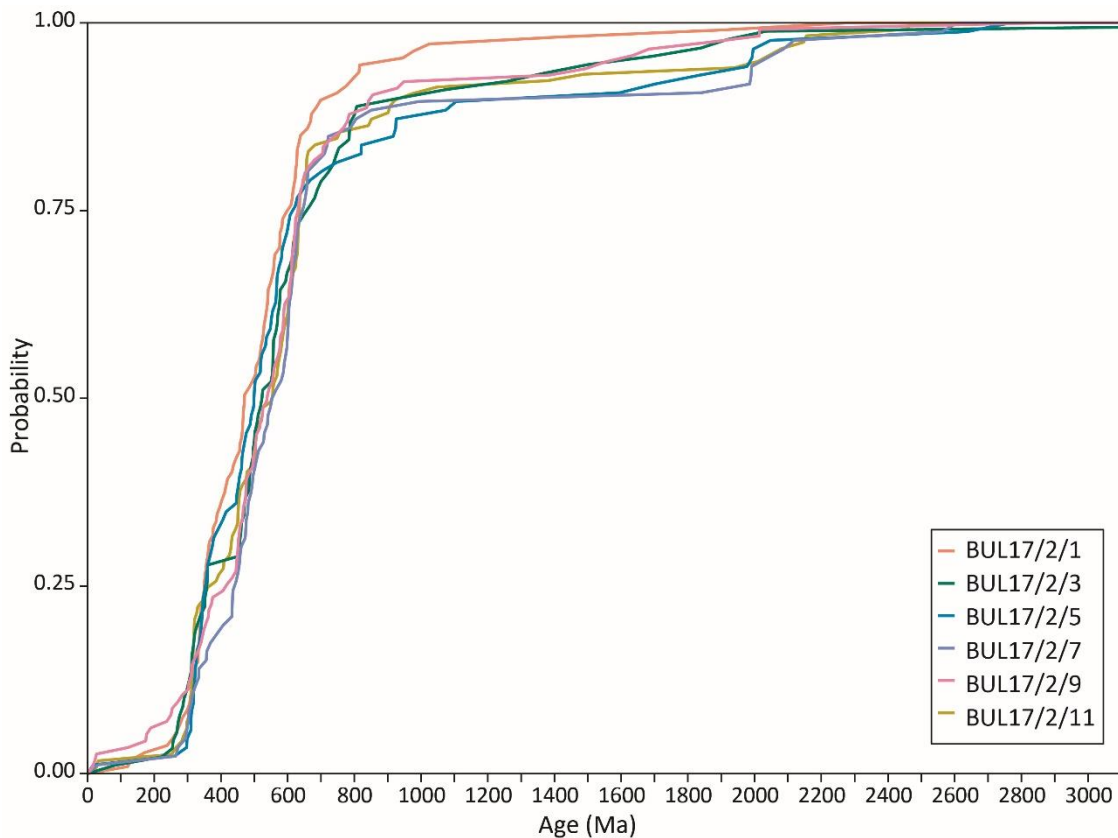


Figure 7.16 Age distributions for individual samples at Slivata 2 samples presented as a cumulative percentage.

The age populations recognised in the KDE plots (Figure 7.17) appear as discrete populations in age- ϵHf space for Slivata 2. All samples contain a c. 310 Ma population with ϵHf forming a cluster between +5 and -10). The c. 450 Ma cluster can also be seen in all samples, with predominantly negative ϵHf values averaged around -5. The older grouping appears to be more complex, made up of several components, but a population at c. 600 Ma with positive ϵHf is prominent in many samples.

In the sample BUL17/2/11 the c. 310 Ma is almost entirely clustered around the CHUR line and grains are zircons from juvenile crustal setting ($0.5 < \epsilon\text{Hf} < 4$). The c. 630 Ma age population shows two ϵHf groupings; the first, at $4 < \epsilon\text{Hf} < 11$ points to juvenile melt-derived source rocks, and the second at $-19 < \epsilon\text{Hf} < -3$. Several grains, in both c. 310 and c. 630 Ma populations are likely representing zircon growth in magmas containing a component derived from melting of Archean crust.

In both samples BUL17/2/9 and BUL17/2/7, the c. 610 Ma population is dominated (65-70%) by positive grains with average values of $\epsilon\text{Hf}=4.5$ and $\epsilon\text{Hf}=6$, respectively. However, both contain strongly negative grains with values as low as -31 in BUL17/2/9, and -24.5 in BUL17/2/7. Combined with some negative grains in the c. 310 Ma grouping, these populations likely represent a contribution from re-melting of Archean crust.

The c. 310 Ma population in sample BUL17/2/5 is predominantly composed of positive ϵHf (62%) grains, as with values as high as 8. Additionally, a cluster at c. 2000 Ma cluster, plots within the field for evolution of Archean crust.

Sample BUL17/2/3 has a large proportion of grains in the 550-850 Ma age range with relatively negative ϵHf values (< -15). Most of these grains, and older ones, plot in the Archean crustal evolution field (pink area). While some grain with this affinity are also seen in the sample BUL17/2/1, more grains appear to plot within the field for evolution of

Palaeoproterozoic crust; although of course this may reflect mixing of juvenile material with melts derived from Archaean crust.

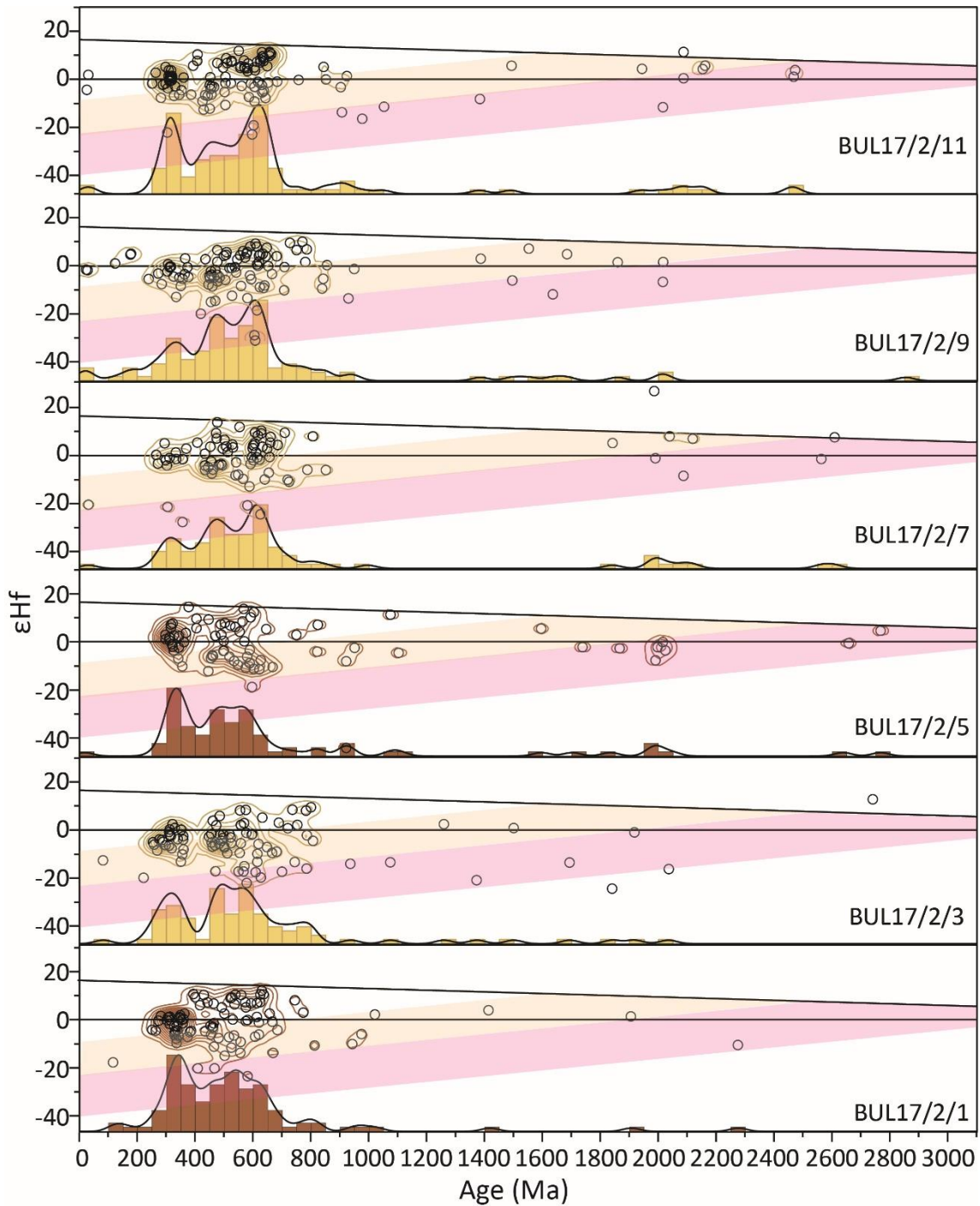


Figure 7.17 Detrital zircon U-Pb age plotted with ϵ_{Hf} vs U-Pb age for loess and palaeosol samples at Slivata 2. Areas represents the evolution of Hf in a zircon through time with depleted mantle model pink between 2500 and 3330 Ma (Archaean crust) and orange between 1600 and 2500 Ma (Palaeoproterozoic).

7.2.5.2. Bulk sample geochemistry

Selected REE and trace elements normalised to UCC, for Slivata 1 are displayed in Figure 7.18. Samples show some variability for incompatible, transitional elements, e.g. V, Cr, Ni, or Zn (Figure 7.18A). However, for most of the elements the data show there is a significant overlap and in values and trend, especially, Th, Zr, Hf, or Nb.

The transition elements V, Cr, and Ni show a very strong positive anomaly as much twice the concentration in the UCC, especially in the palaeosol (BUL17/1/1). Whereas Cu and Zn are slightly depleted but more inter-sample variability can be seen, with the most depletion seen in BUL17/1/1 and least in loess sample BUL17/1/7.

A relatively strong negative anomaly relative to UCC can be seen for the LILE, especially Pb, Rb, Ba, Cs and Sr in all Slivata 1 samples. Depletion of the mobile Sr is strongest in palaeosol (BUL17/1/1) suggesting removal as a part of the weathering process.

All heavy REE are depleted relative to UCC, Slivata 1 bulk samples (Figure 7.18B), however quite a lot of inter-sample variability can be observed. The strongest anomaly is seen in the loess sample BUL17/1/11, whereas BUL17/1/1 (palaeosol) shows the least depletion.

Light REE (Figure 7.18B) show more variable trends, with general enrichment relative to UCC, except for Ce, for which all samples show a negative anomaly. All bulk samples apart from BUL17/1/12, BUL17/1/2 and BUL17/1/3 are slightly enriched in La and Pr. In fact, samples BUL17/1/12 and BUL17/1/2 plot underneath the rest of the data, either most depleted or least enriched in the dataset. Samples BUL17/1/11, BUL17/1/7 and BUL17/1/1 also some of the strongest positive anomalies, especially in Sm.

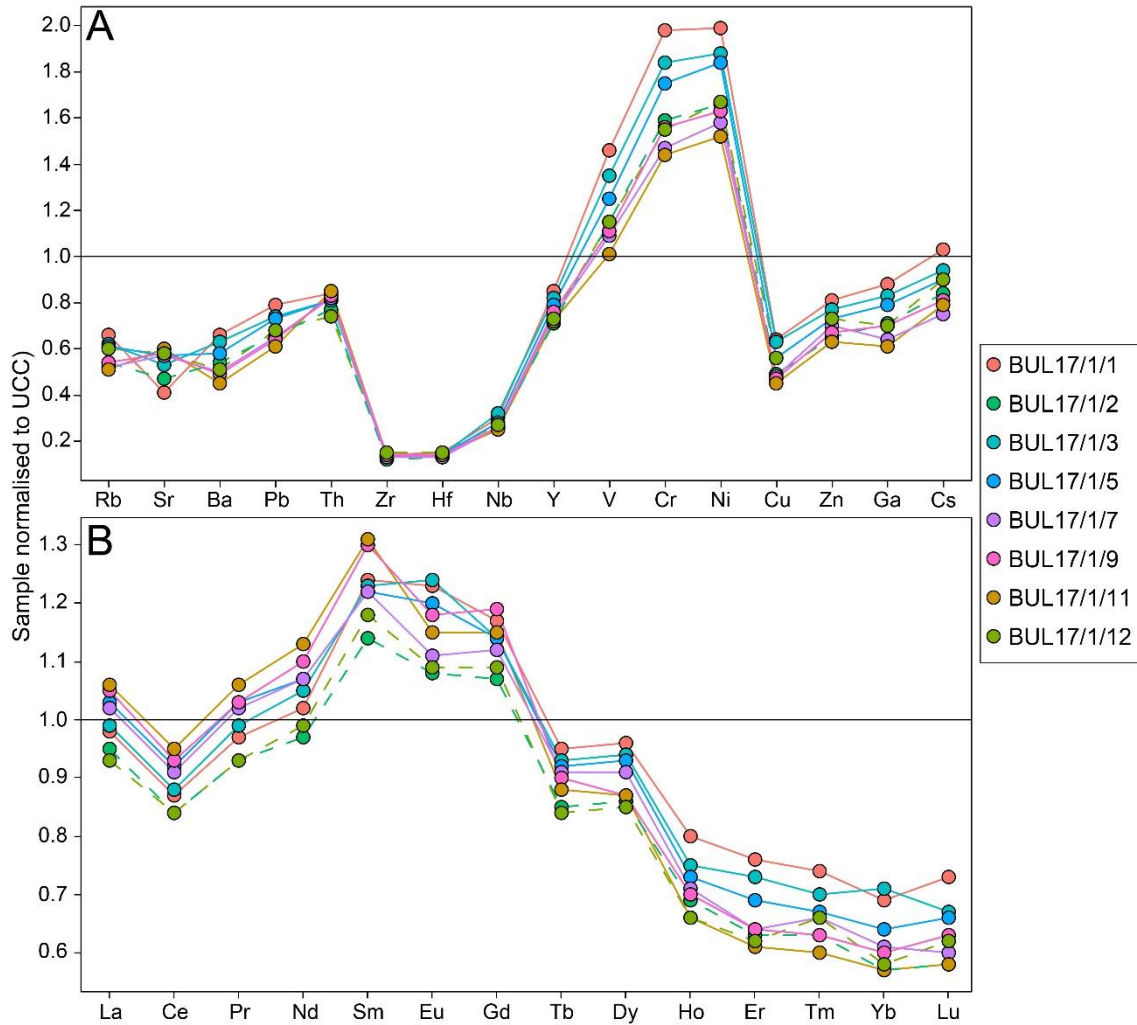


Figure 7.18 UCC-normalised bulk sample trace element diagrams for Slivata 1. A) LILE and HFSE elements B) LREE and HREE. Samples with corresponding zircon U-Pb ages and Hf data are marked as solid lines.

Figure 7.19 shows selected REE and trace elements in bulk samples from Slivata 2 normalised to UCC. A significant overlap in values and trend between the sample can be observed for some of the HFSE, e.g. Th, Zr, Hf, Nb, and Y. For the remaining HFS and LIL elements three broad “groups” can be observed. First, BUL17/2/1, BUL17/2/2, BUL17/2/3, BUL17/2/5 and BUL17/2/6, which is have a strong positive anomaly in V, Cr, and Ni (with values over twice as high as the UCC), and positive anomaly in Cs. These samples are stratigraphically sequential and come from the bottom of the Slivata 2 section covering both loess and palaeosols. The second group is formed by samples BUL17/2/7, BUL17/2/9

and BUL17/2/11, which cover the loess-palaeosol complex. These samples show the same trend as the group one by are not as strongly enriched in V, Cr, and Ni, and are slightly depleted in Cs. Lastly, BUL17/2/12 from the top of the loess plots, while it shows the same trend it plots separately from group one and two.

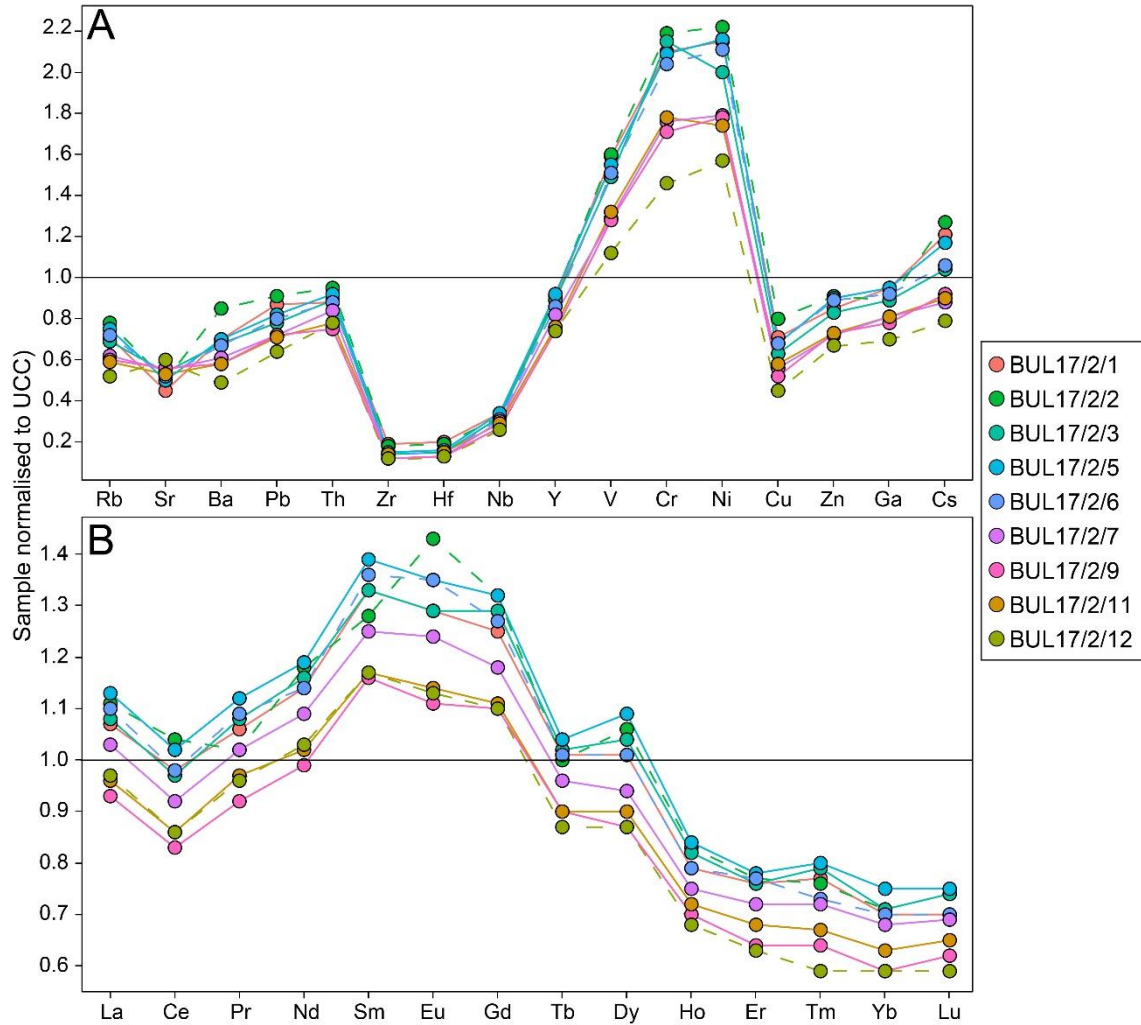


Figure 7.19 UCC-normalised bulk sample trace element diagrams for Slivata 2. A) LILE and HFSE elements B) LREE and HREE. Samples with corresponding zircon U-Pb ages and Hf data are marked as solid lines.

For bulk samples from Slivata 2 a relatively strong negative anomaly relative to UCC, can be observed for the LILE, especially Pb, Rb, Ba, Cs and Sr. Depletion of the mobile Sr is

strongest in palaeosols (BULI7/2/1, BULI7/2/2, BULI7/2/5) suggesting removal as a part of the weathering process.

In the LREE and HREE distributions from the bulk sample Slivata 2 (Figure 7.19B) three groups can be also observed. Group one comprises BULI7/2/12, BULI7/2/11 and BULI7/2/9 these samples are slightly depleted in La, Ce, and Pr (LREE), enriched in Nd, Sm, Eu, Gd (LREE), and depleted in the HREE relative to UCC. Group two is made of BULI7/2/1, BULI7/2/2, BULI7/2/3, BULI7/2/5 and BULI7/2/6. These samples show enrichment in La, very slight positive/negative (0.98-1.02) anomaly in Ce, enrichment in Pr, Nd, Sm, Eu, Gd (LREE), and some HREE (Tb and Dy), and depletion in the remaining HREE. Sample BULI7/2/7 plots in between those two groups and does not overlap much with any of the data.

SUMMARY: Geochemistry results

Chapter 7 presents the results of the multiple geochemical approaches used in this thesis, including single grain zircon U-Pb dating, single grain zircon Hf isotope signature, and bulk sample elemental composition. A total of 31 samples were analysed using single grain zircon U-Pb and Hf isotope approaches; two from rivers, seven from Erdut, ten from Surduk 2, and six for each of the Slivata loess profiles. Additionally, 49 samples were investigated for bulk sample geochemistry.

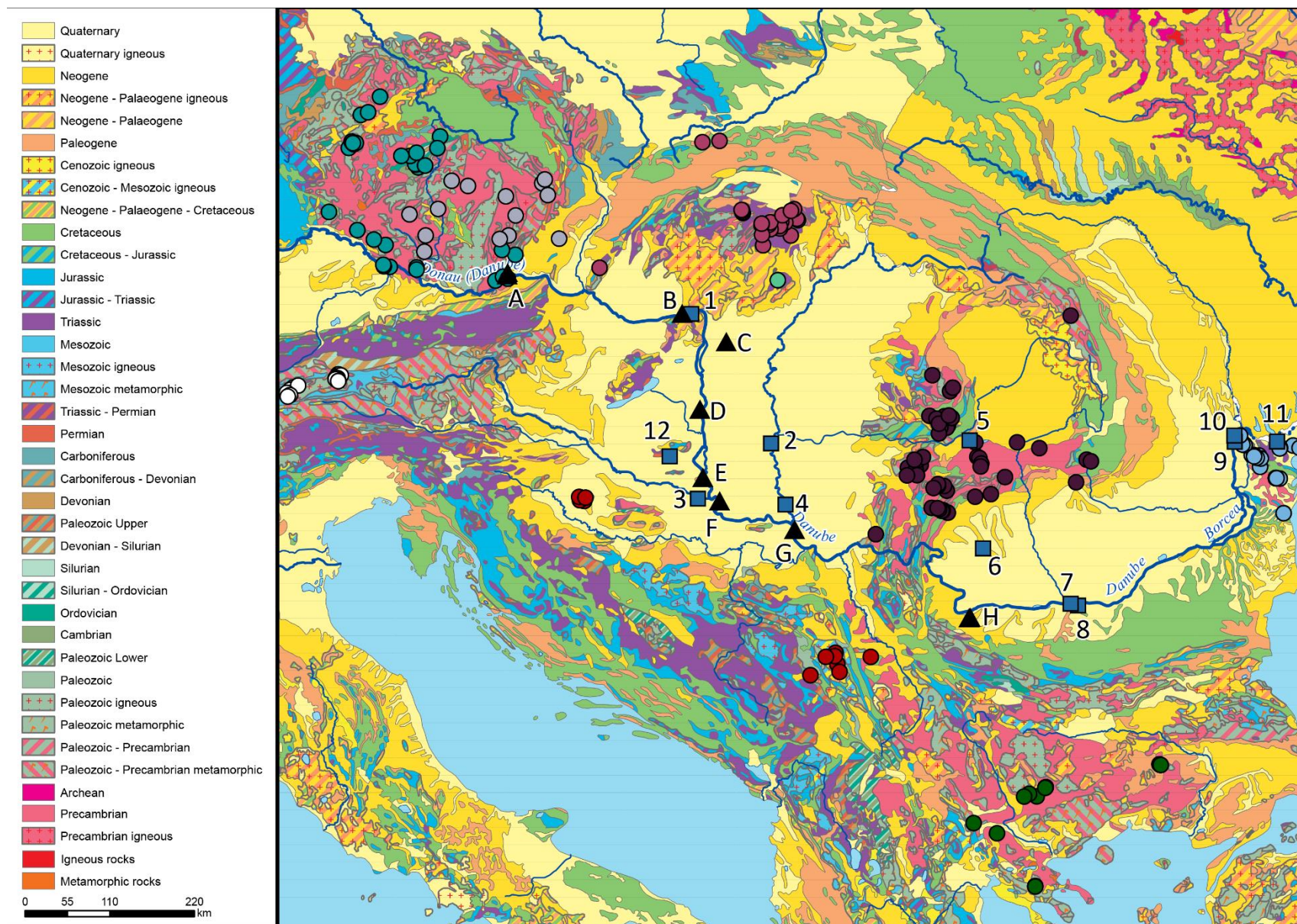
The results form the basis for the discussion of loess provenance in the Danube valley (Chapter 8), in the context of published sources, and are therefore an essential support for research Questions 1 and 2.

Chapter 8: Provenance

8.1. Introduction

This chapter interprets the provenance results presented in Chapter 7 and combines them with the geochronological results presented in Chapters 4-6 to address the source and main transport pathways of the loess-palaeosol deposits along the Danube River (Research Questions 2 and 3). This is done in three steps: firstly, through the exploration of the potential sources for the loess-palaeosol deposits along the Danube River; secondly the investigating of spatial differences between sites; and finally by examining changes over time.

Figure 8.1 Map of source and loess samples. Symbol colours correspond with colours used in Figure 8.2 and are as follows: loess (black triangles), rivers (blue squares), Alps (white circles), Balkan Mountains (green circles), Bohemian Massif (turquoise circle), Bukk Mountains (light green circle), Sahara desert (orange circle), Dinaric Alps (red circles), Dobrogea (light blue circle), Moldanubian Zone (grey circle), South Carpathians (dark purple circle), and West Carpathians (pink circle). Loess sites: A- Stratzing/Krems (Újvári and Klötzli, 2015), B- Basaharc (Újvári *et al.*, 2012), C- Mende (Újvári *et al.*, 2012), D- Paks (Újvári *et al.*, 2012), E- Erdut, F- Zmajevac (Újvári *et al.*, 2012), G- Surduk, H- Slivata (1 and 2). Rivers: 1- Basaharc fluvial sands (Újvári *et al.*, 2012), 2- Tisza (Ducea *et al.*, 2018), 3- Drava, 4- Tisza, 5- Sebeşel (Stoica *et al.*, 2016), 6- Jiu (Ducea *et al.*, 2018), 7- Olt (Ducea *et al.*, 2018), 8- Turnu (Ducea *et al.*, 2018), 9- Tulcea (Ducea *et al.*, 2018), 10- Siret (Ducea *et al.*, 2018), 11- Braila (Ducea *et al.*, 2018), 12- Danita puszta fluvial sands (Újvári *et al.*, 2012). Please note that in some locations, rock can be only determined to the nearest Era. For location, grouping details and the number of samples used for the source data, see Appendix I.



To examine the main source(s) of the loess deposits in the Carpathian Basin (step one; section 8.2), the results of zircon U-Pb analyses are combined and supplemented with published loess datasets (see Appendix I) to create an “average” Danubian loess (hereafter referred to as the ADL) sample. This has the benefit of generating a very large, statistically significant, dataset (3566 data points). This data smoothing removes any potential sources of noise (i.e. hypothetical spatial or temporal variability), thereby focusing the analysis on identifying the proto-sources. The ADL dataset is plotted against 178 published datasets from rivers, deserts, exposed geologies, and mountain belts, encompassing the variety of potential Central European source terranes (Figure 8.1).

To investigate geographical variability in source contributions (step two; section 8.3), samples were grouped by site. Each “site sample” containing data from both loess and palaeosol units. As combined datasets for the sites investigated for this research (Erdut, Surduk 2, Slivata 1, and Slivata 2), are in most cases an order of magnitude larger than other loess datasets available in Europe care must be taken when comparing the results with other sites that only have ~100 analyses. Especially when analysing an absence of the peaks, as some smaller populations might be missing due to the small number of grains analysed, in line with the suggestions of Vermeesch (2004) and Andersen (2005).

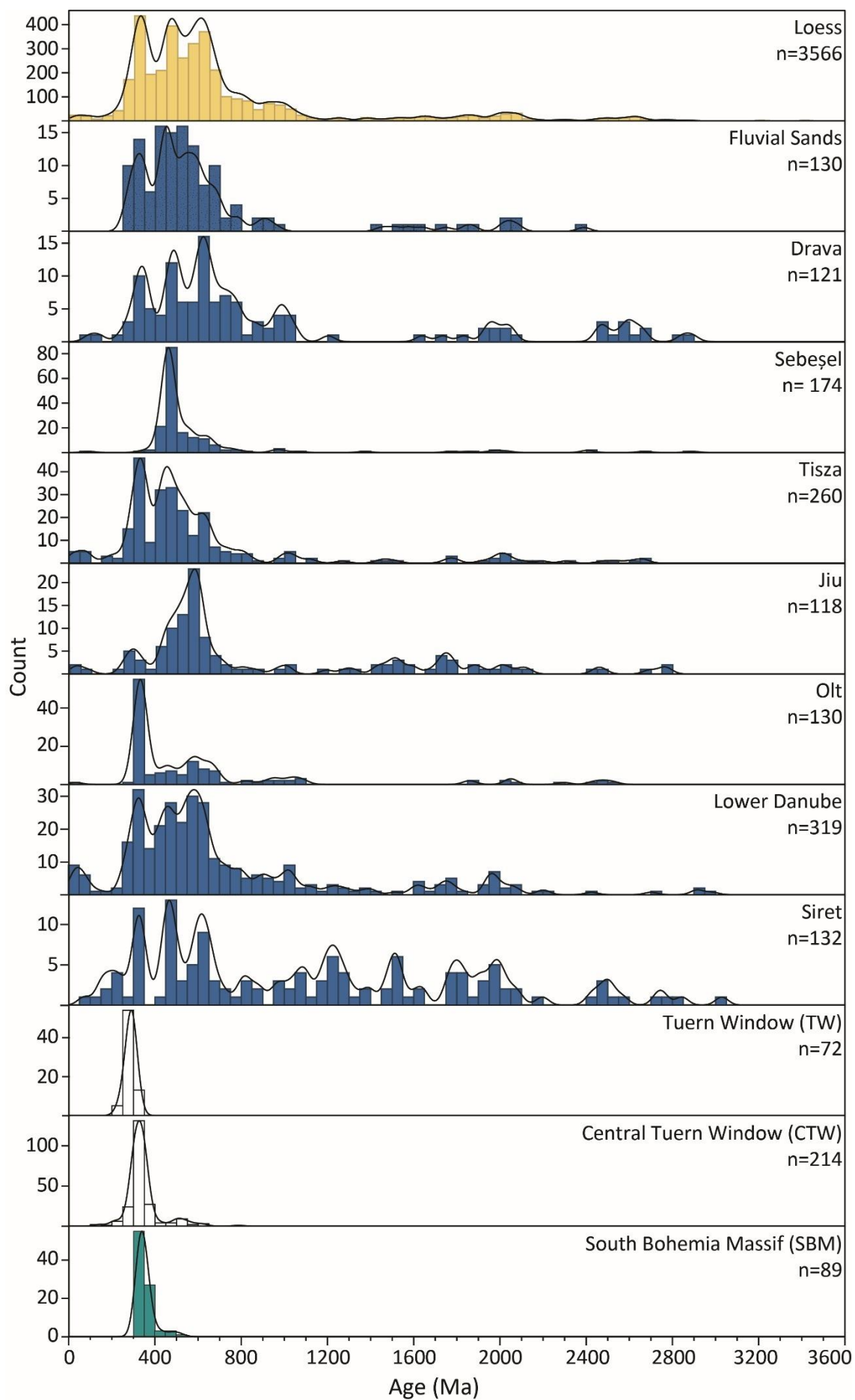
Finally, for the analysis of the temporal scale changes (step 3; section 8.4) samples were first grouped and compared from units representing glacial and interglacial periods. To date only a handful of provenance analyses have been carried out with a sufficient resolution to investigate source shifts through time. The small number of palaeosol analyses in this study precludes MDS analysis of combined palaeosol (565 samples) and loess (2518 analysis) data. Fenn *et al.* (2018) showed that any differences in this scenario are likely statistical artefacts and the individual site’s bias can be introduced based on the number of grains each site is adding to a grouping. Instead individual loess, palaeosol and

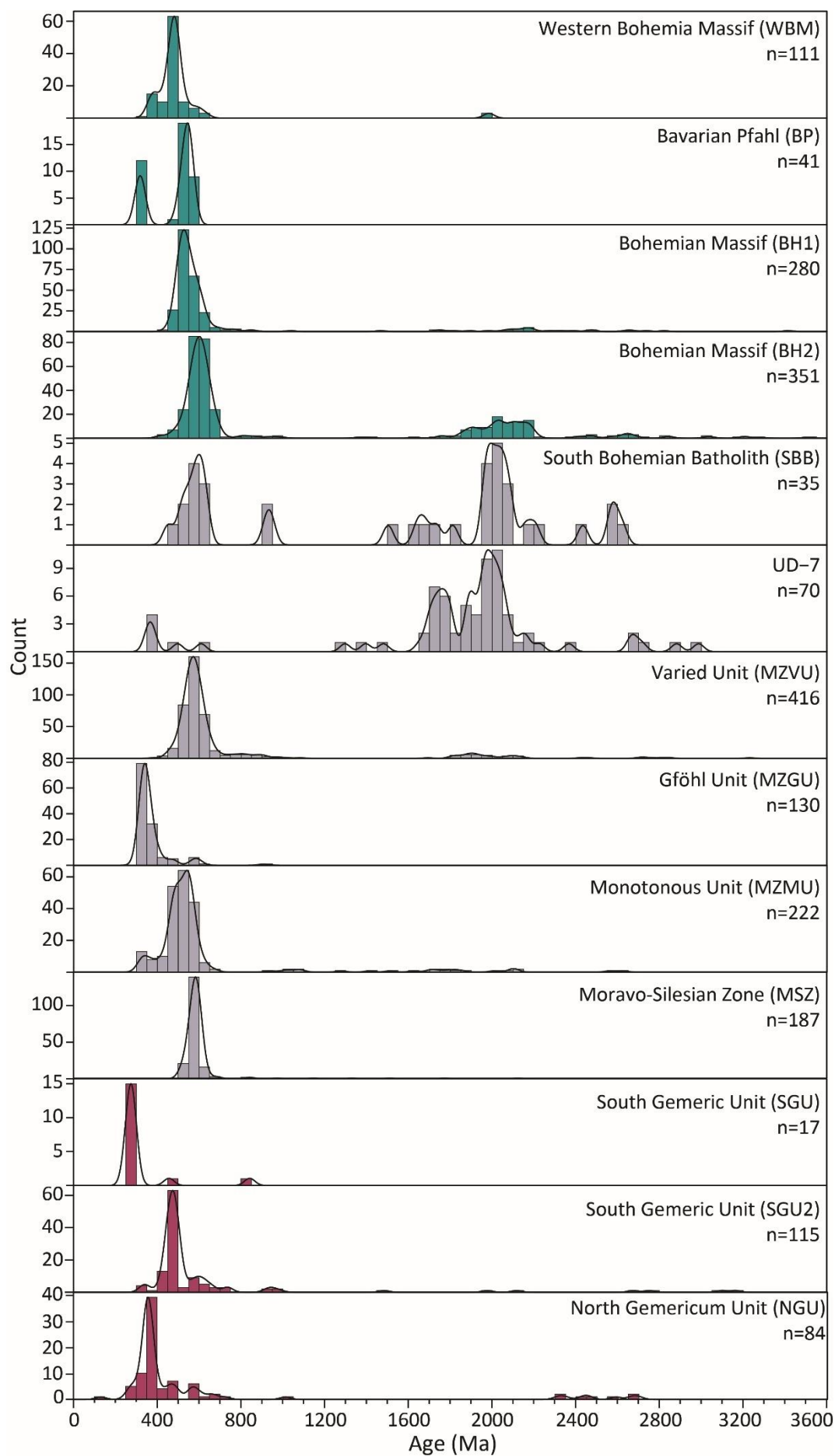
fluvial samples from all sites were compared to test if any clusters occur for the various climatic stages. In the last sub-step all individual samples from each site are compared to test for any short term abrupt source changes.

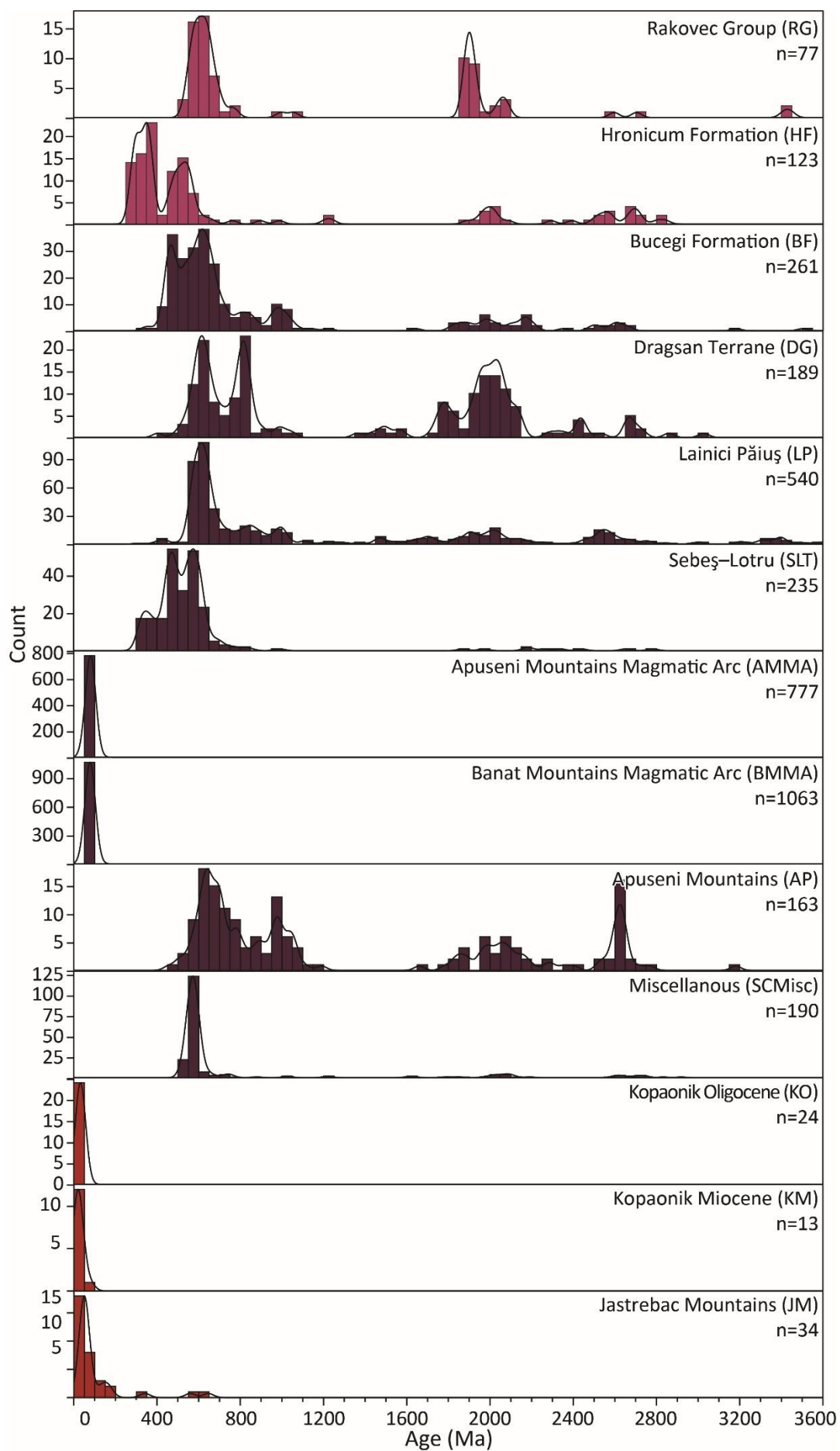
8.2. Source(s) of loess deposits in Central and Eastern Europe

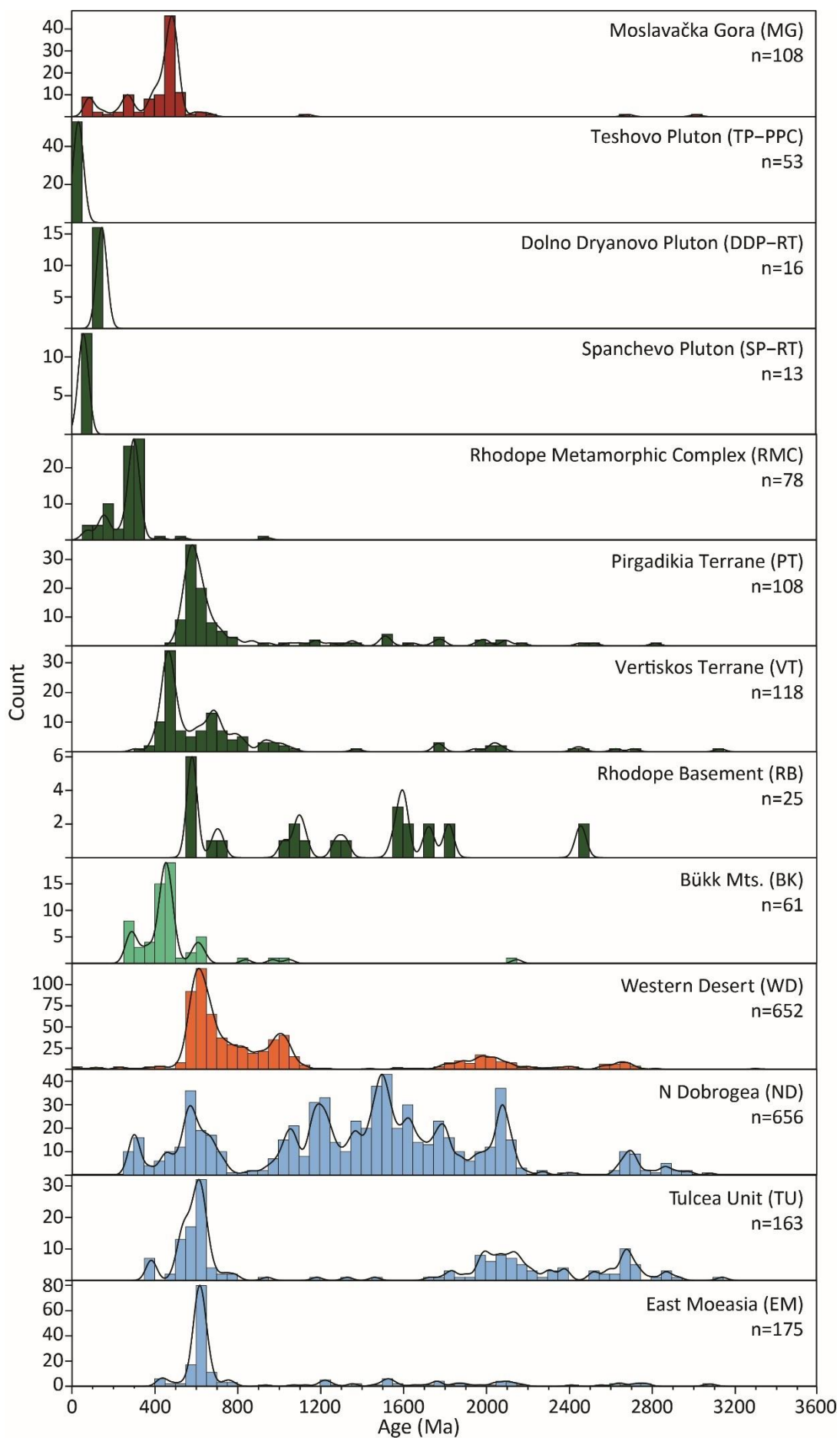
The KDE of the ADL sample shows a continuous spread of zircon U-Pb ages (Figure 8.2), with the three dominant c. 330, 450, and 600 Ma age populations previously described in Chapter 7. The Neoproterozoic tail is also apparent, as are 0-100 Ma, c. 2000 Ma, and c. 2500 Ma populations, albeit they are much smaller. To a greater or lesser degree, all or some of these populations are seen in all of the source samples, emphasising again the geological complexity of this region (discussed in the section 2.6). To investigate the statistical similarity between the various datasets, samples were analysed using multidimensional scaling plots (see section 3.7.4.2), in which samples with the greatest similarity between their age distributions plot close together. The MDS plot (Figure 8.3) is based on the zircon age distribution data presented in the Figure 8.2 and shows that the average loess sample plots in the centre of the source cluster.

Figure 8.2 Zircon U-Pb Kernel Density Estimator (KDE) diagram for potential dust sources and the loess-palaeosol sequences. All samples were grouped into one “Loess Average”, see Appendix I for source data. Same source colours are used across all of the KDE and MDS diagrams, and maps: loess (beige), rivers (blue), the Alps (white), Balkan Mountains (dark green), Bohemian Massif (turquoise), Bukk Mountains (light green), Sahara desert (orange), Dinaric Alps (red), Dobrogea (light blue), Moldanubian Zone (grey), South Carpathians (dark purple), and West Carpathians (pink).









Rivers are an important source proxy, especially when published zircon datasets from the region might be missing, as their zircon distributions approximates the geology of the catchment. In the KDE plots (Figure 8.2) the ADL sample has a very similar age distribution (with the three populations represented) to the Drava, and Lower Danube samples. The Lower Danube distribution, shown in Figures 8.2 and 8.3, incorporates three samples collected downstream from the Olt River. It represents the most averaged Danube's signal, having received sediment from its largest tributaries. The Lower Danube shows a very similar age distribution with three dominant age peaks at c. 300, 450, 600 Ma, with smaller populations also replicated. This is the likely reason why such similarity is seen between the ADL and the Lower Danube distribution.

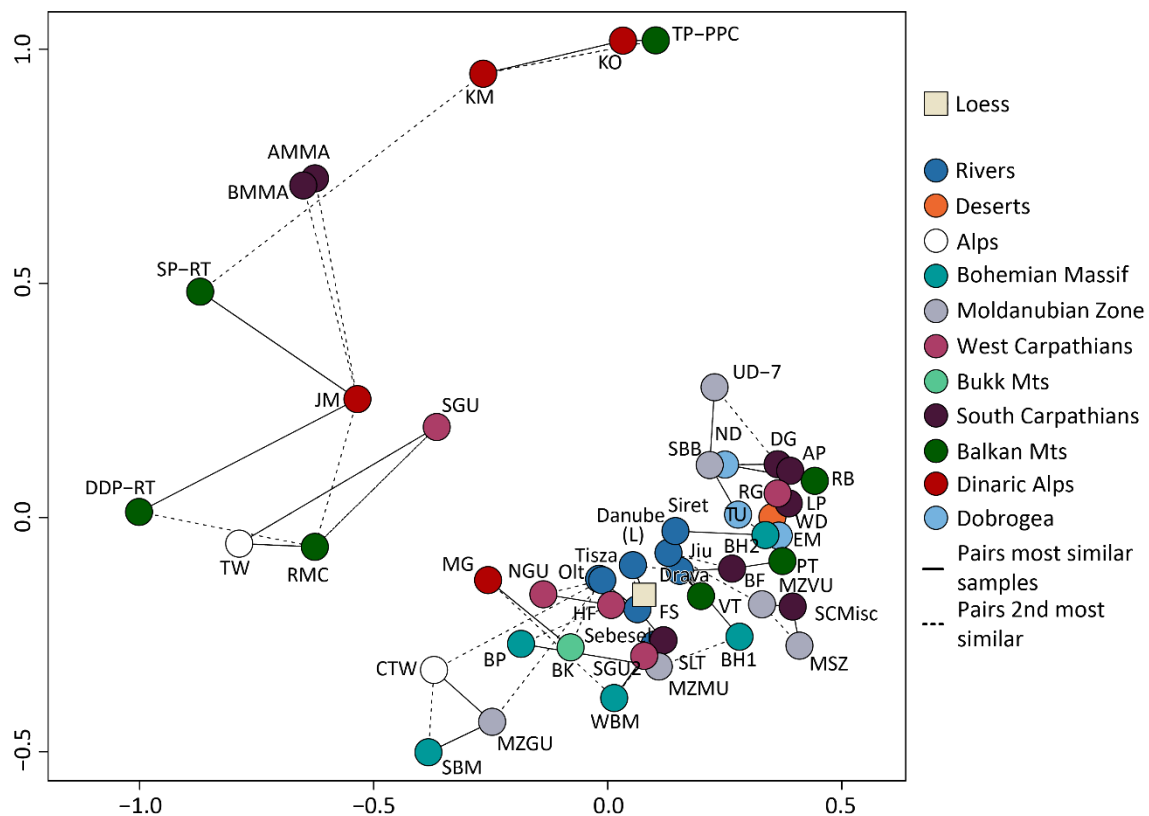


Figure 8.3 Multi-dimensional scaling (MDS) diagram for zircon data in Figure 8.1, showing the average loess-palaeosol sample and potential dust sources. Note that the Lower Danube is shortened to Danube (L). See Appendix I for source data.

The Danube's tributaries, instead, show only some components of the distributions seen in the loess and the Danube's samples, e.g. the Drava shows a typical three-peak pattern, but with the c. 600 Ma peak dominating. The Tisza displays all three populations but has a relatively small 600 Ma population. While Jiu and the Olt samples have at least some of the elements seen in the ADL sample, 600 and 300 Ma respectively. On the MDS diagram the ADL is almost entirely surrounded by river samples (Lower Danube, Tisza, Olt, Jiu, and Drava), which shows the similarity between the samples and strongly suggests a source link between them. Moreover the Miocene/Pleistocene fluvial sand sample from Hungary (Újvári *et al.*, 2012), also plots very closely (Figure 8.3) and given the older age suggest that the sample likely share a source or that the fluvial sand at least in some part contribute to the ADL.

Source lithological samples on the MDS map (Figure 8.3) show a big cluster surrounding the ADL. However, most of them plot slightly further away from loess, having closer connections with rivers than loess. This special clustering suggests that fluvial is critical in the sediment delivery. While discussion over the silt production mechanisms and the various loess modes still persists in the literature, river transport is now an integral element of loess source-to-sink models (e.g. Lehmkuhl *et al.*, 2016; Li *et al.*, 2020). These results support the previous work of Smalley *et al.* (2009) who argued for the importance of fluvial transport in the genesis of loess deposits. Whilst this has already been shown in the genesis of loess deposits in the Chinese Loess Plateau (Licht *et al.*, 2016; Nie *et al.*, 2015; Stevens *et al.*, 2013b), the importance of the Danube River system to loess deposits in the Carpathians has not been fully explored to date. Figures 8.2 and 8.3 strongly suggest that the most immediate geomorphological source of loess deposits along the Danube River is the Danube's alluvium. The alluvium source has been hinted at based on: grain size and XRF analysis for Balkan loess (Basarin *et al.*, 2011; Obreht *et al.*, 2014, 2016)); theoretical and bulk sample geochemistry for Romanian and Bulgarian loess (Bugge *et al.*,

2008; Jipa, 2014); and bulk sample geochemistry and zircon analysis for loess in the Carpathian Basin (Bugge *et al.*, 2008; Újvári *et al.*, 2012).

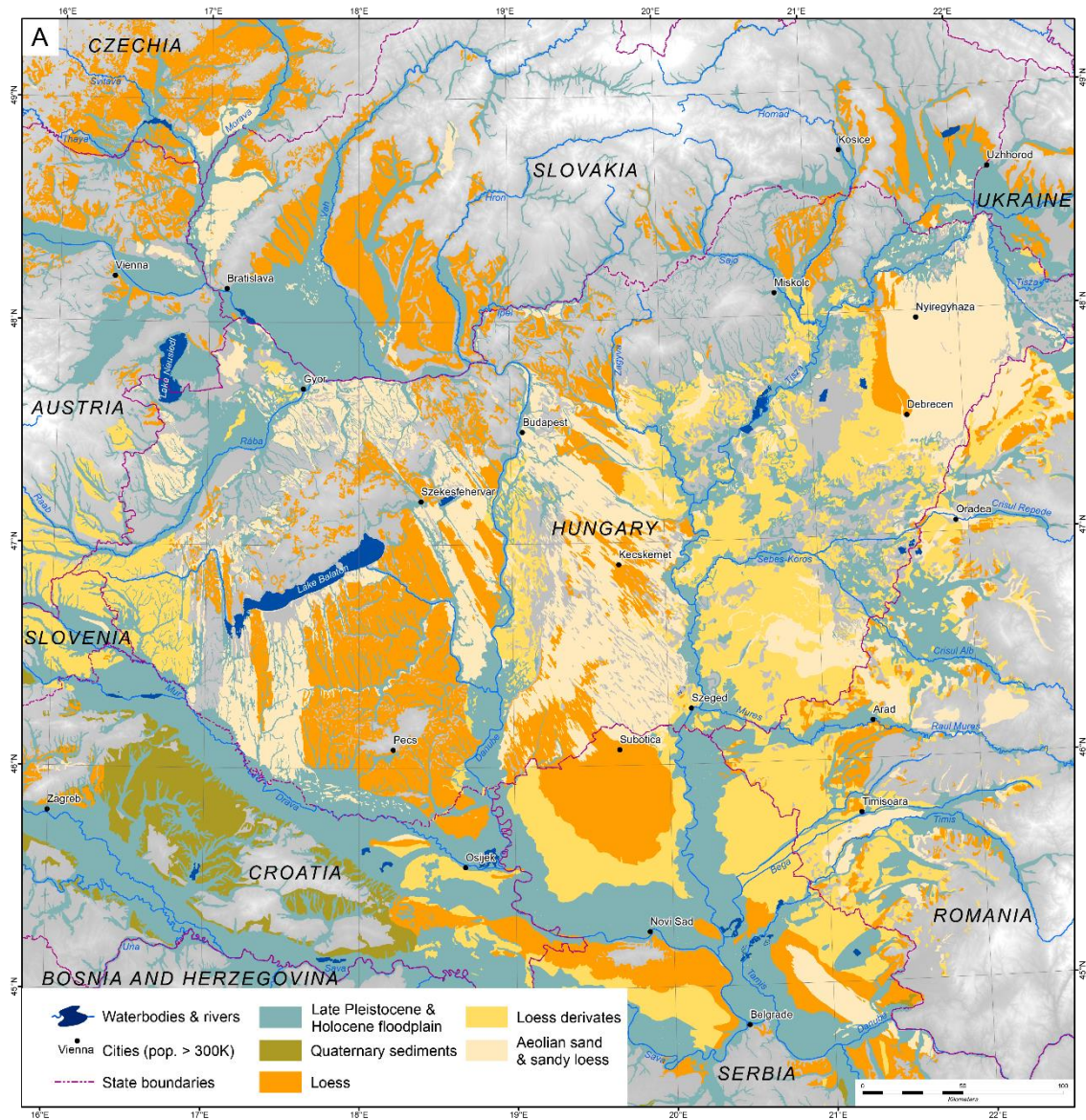


Figure 8.4. Map of the Quaternary deposits in the Carpathian Basin (Lehmkuhl *et al.*, 2018).

If alluvium is the primary and intermediate source for loess deposits then the often suggested long distance transport (1000's km) of silt particles (Lehmkuhl *et al.*, 2016; Obreht *et al.*, 2015, 2019; Rousseau *et al.*, 2011; Varga *et al.*, 2013, 2016), should be revisited. Figure 8.4 shows the distribution of loess deposits in the Carpathian Basin along with the

floodplains. The distance of alluvium to most loess sections is in the order of tens of kilometres, with most of the loess sections sandwiched between the Danube and its tributaries. The geomorphology (Figure 8.4) combined with the zircon pattern on the MDS diagram (Figure 8.3) show that it is far more likely that the fluvial processes mix the sediment from the proto-sources prior to the final aeolian distribution from the floodplains, rather than transporting sediment directly from the proto-sources with mixing in the air or via various multi step processes along the way.

This next section considers over 200 source datasets and explores the potential proto-sources contributing to each of the main three age populations in more detail to try and identify the main source(s) of sediment in the Danubian sedimentary system.

8.2.1. Gondwana Sources

The Danube catchment lies in a complex tectonic setting incorporating fragments of peri-Gondwanan terranes (Figure 2.7) that docked with Eurasia as a result of subduction-accommodating convergence since the Jurassic (Schmid *et al.*, 2008; van Hinsbergen *et al.*, 2020). In addition, these fragments may carry reworked Gondwana-derived sedimentary rocks with zircons of a distinctive Gondwanian age and Hf-isotope distributions. Sources within Gondwana include Neoproterozoic arc terranes, syncollisional granites at 600 and 1000 Ma (Da Silva *et al.*, 2005; Küster and Harms, 1998; Meira *et al.*, 2015), and relicts of the Archaean and Palaeoproterozoic orogenies (Gasquet *et al.*, 2008; Kouamelan *et al.*, 2018; Meert, 2012; Piper, 2010).

Zeh and Gerdes (2010) have demonstrated the presence of Gondwana-derived sedimentary rocks as far north as the Mid-German crystalline rise. They describe the likely distribution of zircons in Gondwana-derived sediments as dominated by grains with ages from 550-750 Ma, with minor peaks at c. 1000 Ma, 1750 and 2000 Ma, and sparse

Archaean grains. A dominant 600 Ma population in their sample from northern Germany was characterised by a broad range in ϵHf , as low as -18, indicating a contribution from melts of Palaeoproterozoic or older crust.

Fielding *et al.* (2017) studied the distribution of detrital zircon sources available to the Nile catchment in NE Africa and found a similar pattern to Zeh and Gerdes (2010). These zircon distributions are dominated by populations in the 550–800 Ma age range, and predominantly positive ϵHf , which are interpreted as having formed in oceanic island arcs that were incorporated into Gondwana during the Pan-African orogeny at c. 550–600 Ma. However, at 1000 and 600 Ma, zircon populations with strongly negative ϵHf are also present, indicating melting of Archaean crust during collisional orogenesis. Palaeoproterozoic and Archaean zircons are also present, with Hf-isotope characteristics indicating a mantle-extraction age of c. 3500 Ma.

The age and Hf-isotope characteristics of 550 Ma and older zircon grains seen in the Danubian loess are similar to that which would be expected from sediment derived from Gondwana (Fielding *et al.*, 2017; Zeh and Gerdes, 2010). The oldest of the three dominant peaks observed in the average Danubian loess distribution comprise Neoproterozoic (550–650 Ma) age zircon grains. These grains are also seen in the majority of the source datasets collected from the literature (Figure 8.2), sedimentary and igneous rocks, rivers, and deserts. The proto source for these sediments, in a geological sense, are rocks originating from Gondwana and peri-Gondwana terranes, that have been incorporated into what is modern Europe through multiple orogenic cycles over the last 600 Ma. For the purpose of the discussion, sources of >550 Ma Precambrian zircons will be considered as a single ‘Gondwanan’ source.

The upper reaches of the Drava flow almost entirely through the Precambrian and Palaeozoic-Precambrian rocks (Figure 8.5). This is corroborated by Drava’s zircon KDE

distribution (Figure 8.2), which contains the highest relative proportion of the c. 600 Ma grains. While these signatures are also seen in the Tisza, they are subordinate, likely explained by only few outcrops within the Tisza's drainage (Figure 8.5). On the other side of the South Carpathians, the Jiu flows almost entirely through Precambrian rocks reflected in almost a single c. 600 Ma population (Figure 8.2). A sample from the upper reaches of the Danube is absent, though it is expected that the Danube carries a large contribution of the 600 Ma age grains delivered by the Inn (from the Alps) and smaller tributaries that have their headways in the Bohemian Massif. The drainage area of the Danube's tributaries suggests a constant contribution of the recycled Gondwanian material, confirmed by the c. 600 Ma population, the second most dominant in the Lower Danube sample.

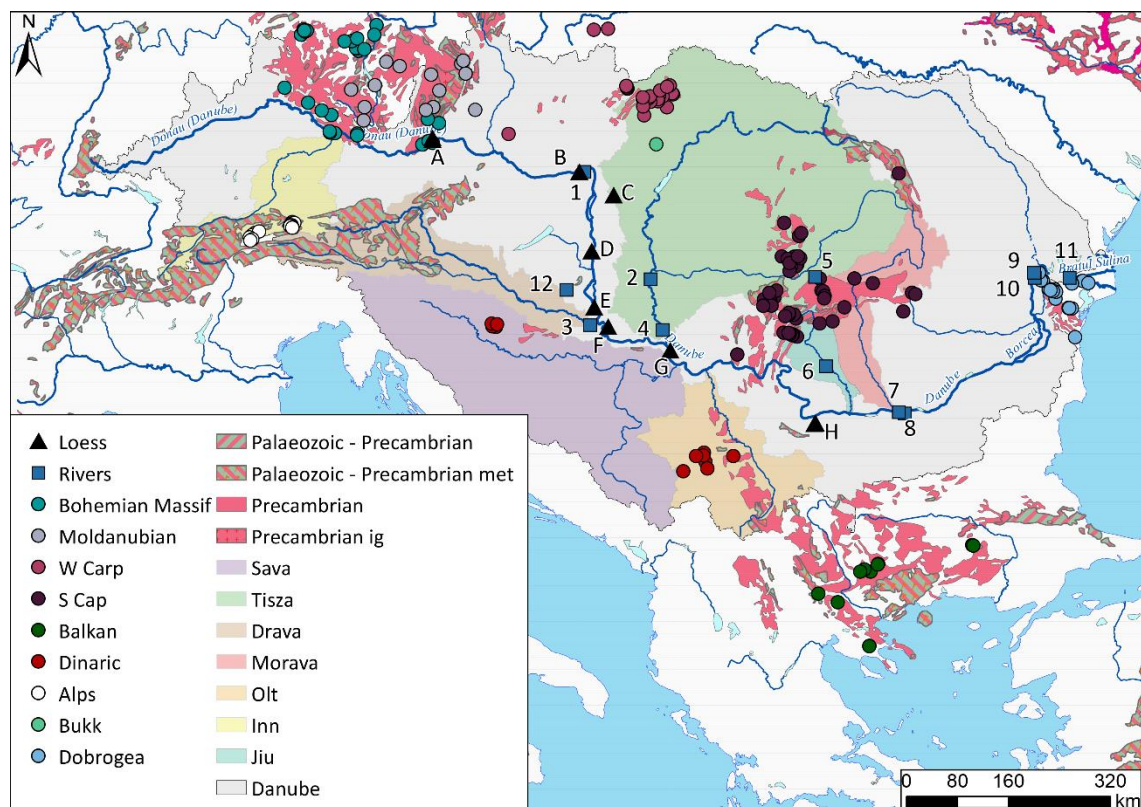


Figure 8.5 Map of Proterozoic (550-650 Ma population) source rocks, with the zircon U-Pb loess and source locations in the context of the Danube River basin, and its tributaries. Sites and references are outlined in the caption of Figure 8.1.

Highlighted are watersheds for the main tributaries Inn, Drava, Tisza, Sava Morava and Olt. Please note that in some locations the age of the rocks can only be determined to the Era level (Sources: WWF (Lehner *et al.*, 2008) and USGS).

The Gondwana signatures seen in the Western Saharan Desert sample (WD), are likely the reason for the presence of the sample within the main data cluster on the MDS map (Figure 8.3). While this source cannot be excluded, the strong evidence for predominantly, short distance transport from the alluvial sources suggests that the far-travelled North African sources are unlikely or at least contributing only minor quantities of the sediment to the Danubian loess.

The MDS analysis (Figure 8.3) also shows the profusion of the Precambrian signatures. All samples that do not contain them (except for UD-7 and SBM), plot in the second data “cluster” (AMMA, BMMA, KO, KM, TP-PPC, SP-RT, DDP-RT, RMC). Therefore, it is likely that a number of these Gondwanian source rocks contribute sediment to the loess sequences along the Danube.

This emphasise the limitation of using a single proxy to determine source of sediments in sedimentary studies, even though zircons provide remarkable information about sedimentary sources. This was the major obstacle encountered in the provenance research on the Chinese Loess Plateau (Licht *et al.*, 2016; Nie *et al.*, 2015; Stevens *et al.*, 2013b; Xiao *et al.*, 2012; Zhang *et al.*, 2016), where the source cannot be identified beyond the North Tibetan Plateau. In the European case, due to the direction and rotation of the proto-European blocks, rocks of similar ages are surrounding Carpathian Basin showing a need for additional provenancing tools.

Hf isotope–time evolution for the ADL (in this instance ADL includes only samples analysed during this research) was plotted as a probability density plot with potential source data superimposed on it (Figure 8.6). Most notably, ϵHf data for the Tauern

Window shows a positive to negative spread of values in the 600 Ma population and negative values 1000 Ma age population, producing a convincing overlap with the Danubian loess data.

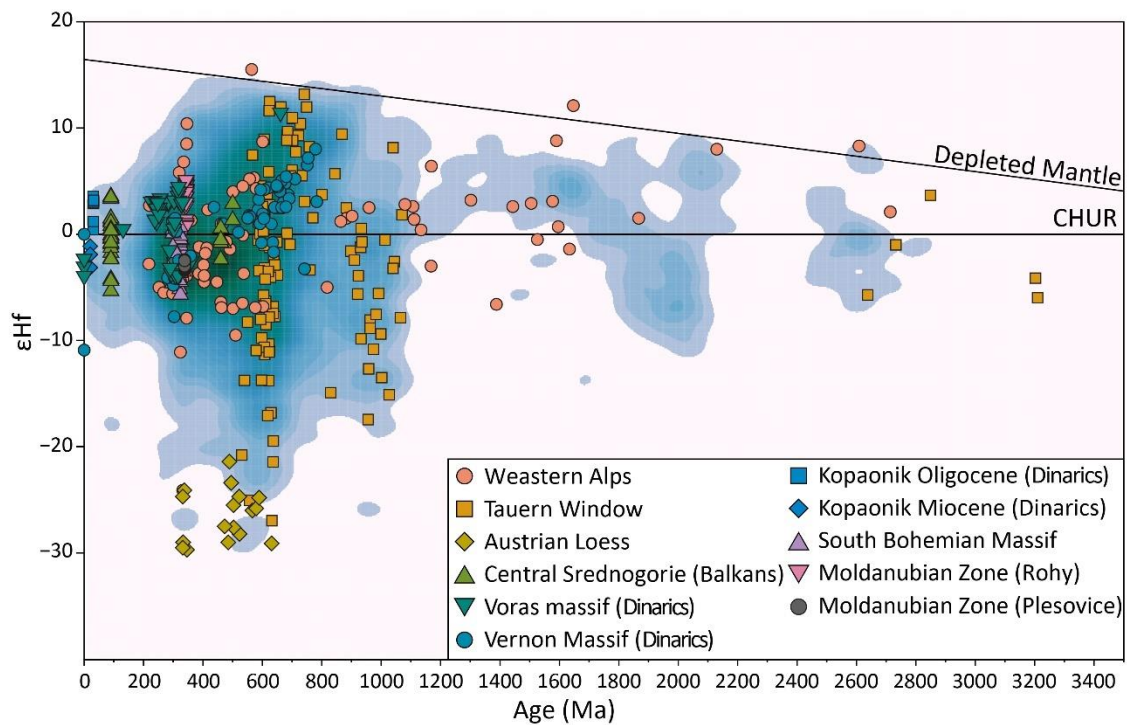


Figure 8.6 Probability density plot showing Hf isotope–time evolution of the averaged Danubian loess. The density of the data distribution is calculated using a modified version of the Kernel Density Estimation (Botev *et al.*, 2010) analysis modified for R. The source Hf are superimposed, see Appendix J for the Hf metadata.

Therefore, it is suggested that metamorphic rocks in the East Alps are a large contributor of sediment to the Danubian loess profiles. A majority of these rocks lie within the drainage of the River Inn (Figure 8.5), showing that vast quantities of the source sediment carried by the Danube before it even enters the Carpathian Basin. Other source contributions (e.g. the Dinarics or other Alpine data) cannot be excluded as they also plot within the 600 and 1000 Ma age ranges, however these can be considered as minor.

8.2.2. Cambrian-Ordovician Sources

The middle of the age peaks in the ADL is of Cambrian-Ordovician age (450-500 Ma) and it is the second most abundant age population. Lithologically, the majority of the source sediments across Central Europe contain these age populations. In the Alps some gains are seen at the Tauern Window (CWT), delivering sediment into the Danube, via the Inn and Drava river systems (Figure 8.7). While Palaeozoic igneous and sedimentary rocks are exposed in the Bohemian Massif (WBM, BP and SBB) and Moldanubian Zone (MZVU, MZMU, and MZGU), many of these localities belong to the Elbe drainage rather than the Danube's. Only small exposures of the igneous rocks of that age are found in the Western Carpathians (SGU2), suggesting that this region is not contributing large quantities of the 450-500 Ma grains into the Danubian loess sequences. Relatively large Cambrian-Ordovician zircon contributions can be expected from the Southern Carpathians, where numerous terranes of that age are represented in source sample; SLT (plotting particularly close on the Figure 8.3 to the loess sample), LP and DG.

Contributions from the Dinaric Alps (MG) and the Balkan Mountains (PT, VT, RB) can be seen. Though, these regions are not considered large sediment contributors in the literature, but the geographical distribution of the rocks as well as the in proximity to the e.g. Morava River could suggest otherwise. The Vertiskos Terrane (VT) forms a southern part of the Serbo-Macedonia Massif, which does not have a direct connection into the Danube River system. This could, however, be taken as a representation of rocks found in the Balkan region (Figure 8.7), and indicate minor contributions from that region. Given the source rock distribution, it is likely that it is the Alps, the Bohemian Massif, the Dinaric Alps and the Balkan Mountains that are the main sediment supplier to the Danubian river-loess system.

Finally, grains of Cambro-Ordovician age are abundant in the Miocene-Pleistocene fluvial sand (FS) samples (Figure 8.2). Numerous exposures of that age are seen in the drainage area of the Drava, especially south-east Alps and therefore explain large contributions of zircons of that age in Drava's sediment. In Tisza's sediment, the 450-500 Ma age grains are subordinate to the 300-350 Ma age population but nonetheless abundant, and likely delivered by Mures, Tisza's tributary.

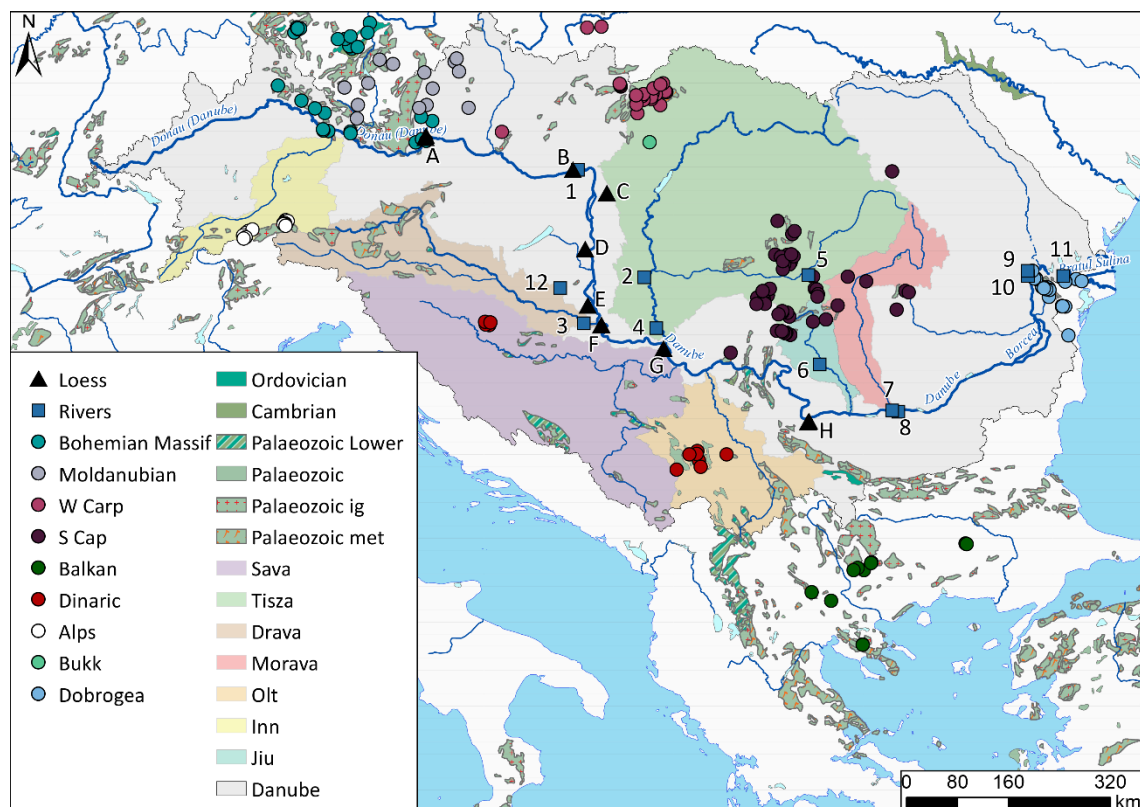


Figure 8.7 Map of Ordovician and Cambrian (450-500 Ma population) source rocks, with the zircon U-Pb loess and source locations in the context of the Danube River basin, and its tributaries. Sites and references are outlined in the caption of Figure 8.1.

8.2.3. Carboniferous Sources

The youngest of the three main peaks, the Carboniferous (300-350 Ma) is the most abundant population in the ADL sample, and some of the fluvial samples e.g. Tisza and Olt (Figure 8.2). While again no one sample is a single source of grains in the 300-350 Ma

age range, there are numerous granitic, rhyolitic, orthogneiss and gneiss bearing rocks across Central Europe (Figure 8.8) that could yield zircons of this age.

The 300-350 Ma signal predominantly reflects the Variscan orogeny and associated magmatism, and is abundant in source rocks along the whole course of the Danube River. The wide ranging distribution reflects the modelled evolution of the Peri-Gondwana (Figures 2.7 and 2.9), which saw formation of multiple arcs at the front of the Gondwana, progressive closure and subduction of the Rheic Ocean. Thus these Carboniferous populations are seen in the KDE diagrams, in the Alps (Tauern Window; CTW and TW), the Bohemian Massif (Western Bohemia Massif (WBM), South Bohemia Massif (SBM), and Bavarian Pfahl (BP)), in the Moldanubian Zone (MZVU and MZMU), the West Carpathians (South Gemeric Unit (SGU2)), the South Carpathians (Sebeş–Lotru terrane (SLT), Lainici Păiuş (LP)), the Dinaric Alps (Moslavačka Gora (MG) and Jastrebac Mountains (JM)) and the Balkan Mountains (Vertiskos Terrane (VT) and Rhodope Metamorphic Complex (RMC)). All of these sources plot relatively near the ADL on the MDS diagram (Figure 8.3), and are found relatively near the main course of the Danube itself or quite abundant within the watershed of Danube's tributaries (Figure 8.8). Therefore, any of these terrains could be a source of these grains.

The 300-350 Ma peak is also recorded in sedimentary rocks across the Carpathian Basin, e.g. the Hronicum Formation sandstones (HF), the North Gemericum Unit alluvial and deep water sediments (NGU), the Bucegi Formation sandstones (BF), or the Bükk Mountains limestones (BK). Therefore, these could contribute grains to the peak seen in the loess population and represent sediment recycling. Finally, Figure 2.7 also shows additional mixing of sediments on the margins and shelf of Gondwana, from Western and Eastern African provinces (Stephan *et al.*, 2019), which ultimately ends within the Carpathian Basin and surrounding mountainous regions, in the form of nappes. This

highlights the reason for the widespread 600 Ma and older ‘Gondwanian’ populations in the all source rocks for loess deposits.

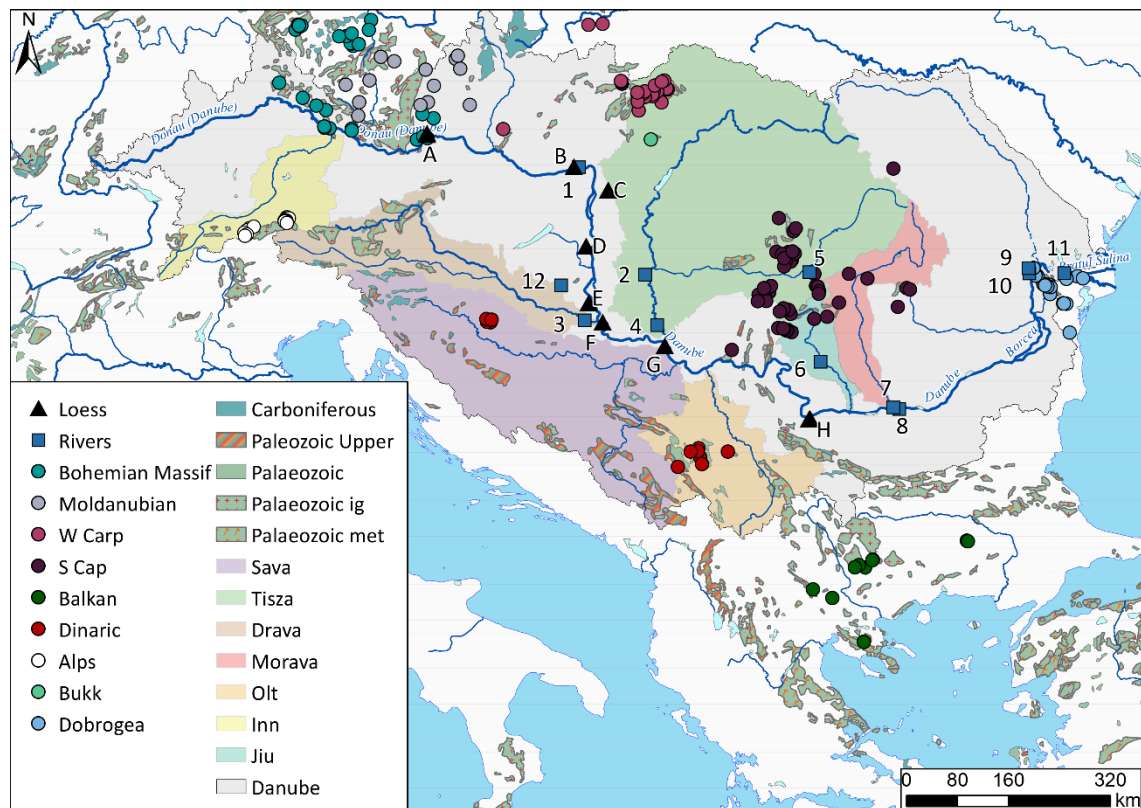


Figure 8.8 Map of Carboniferous (300-350 Ma population) source rocks, with the zircon U-Pb loess and source locations in the context of the Danube River basin, and its tributaries. Sites and references are outlined in the caption of Figure 8.1.

Hf source data (Figure 8.6) helps to disentangle these signals, as while a spread of Hf signatures are seen for the c. 300 Ma population, the highest density is seen in the slightly negative ($-5 < \epsilon_{\text{Hf}}$ values < 0) part of the diagram. The source data indicates strong contributions from the Eastern Alps, the Moldanubian Zone (Plešovice) and South Bohemia Massif and the Dinarics. The Plešovice source sample lies outside of the Danube’s watershed, however the southern Bohemia Massif samples come from the region draining directly into the early reaches of the Danube (above the Inn confluence). The overlap with the igneous rocks from the W Alps also suggest that a significant quantity of sediment

could be already contributed into the Danube's sediment before the river enters the Carpathian Basin.

8.2.4. Interpretation issues

The KDS (Figure 8.2), MDS plot (Figure 8.3) and geological map of the region (Figure 8.1) emphasise the difficulty in determining the specific contributions to the loess-palaeosol sequences from individual mountain belts, as many of them contain outcrops of varied ages across relatively short geographic distances. For example, samples AMMA and AP are separated by ~50km, yet they have completely different zircon age distributions. AMMA has a distinct singular peak (Figure 8.2), representing Upper Cretaceous volcanic activity in the Apuseni Mountains (Gallhofer *et al.*, 2015), while AP shows a Precambrian age distribution for metamorphosed quartzite from the same region (Balintoni *et al.*, 2009). The complicated geology of Central Europe, which experienced multiple periods of re-activation during numerous tectonic cycles, was summarised in section 2.6 and these results further highlight the problems encountered when trying to identify primary sources of sediments from the Carpathian Basin using just zircon ages as proxies.

Further even those potentially “distant” samples on the MDS diagram (Figure 8.3), such as Dinaric Alps (red, e.g. KO, KM, JM) or Balkan Mountains (green, e.g. SP-RT, DDP-RT) cannot be excluded as potential sources solely based on the MDS diagram. While the KDE shapes for those samples may also appear very different, these samples could be contributing to some of the smaller peaks observed in loess or river samples.

There is also an issue of relying purely on the source datasets. For example, there are relatively large additions of Oligocene grains in the Tisza, which are absent in the Drava sample. Source datasets are only available for the outcrops of Oligocene granodiorites in the Dinaric (KO) and Balkan Mountains (TP-PPC). However, additional exposures within

the drainage area of the Tisza can be seen (Figure 8.9), even though datasets are absent. It is therefore likely that most of the Oligocene grains contributing to loess deposits are delivered by the Tisza or Sava rivers, even though the datasets for rock in Tisza's watershed and Sava are missing. There are also parts of the Carpathians, Dinarides, and Balkan Mountains that have not been investigated. Therefore, there might be regions which are big contributors but lack zircon data for comparison and are not identified as such.

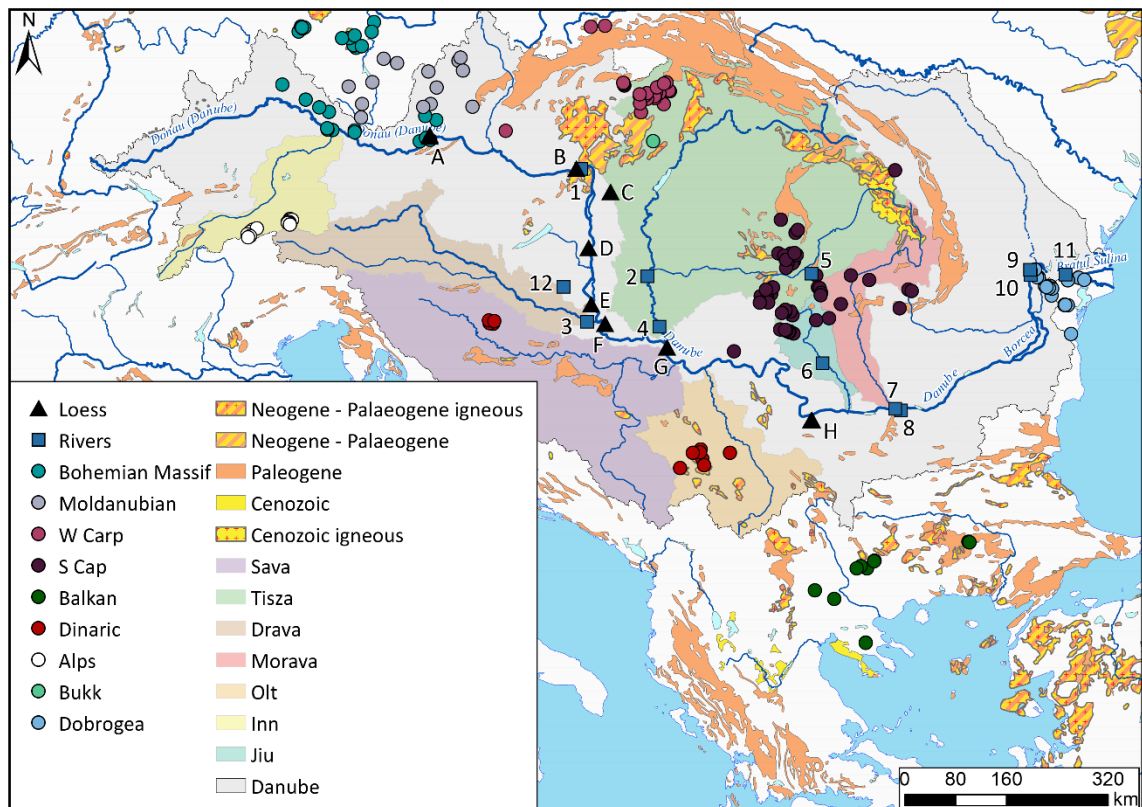


Figure 8.9 Map of Palaeogene (Oligocene) source rocks, with the zircon U-Pb loess and source locations in the context of the Danube River basin, and its tributaries. Sites and references are outlined in the caption of Figure 8.1.

LOESS SOURCE SUMMARY

Section 8.2 discussed the results presented in Chapter 7 in the context of source of loess deposits in the Danube valley (**Objective 4**).

The provenance analysis above suggests that Danubian loess deposits do not have a single lithological source. In terms the immediate, geomorphological source, river load and therefore alluvium is the most likely sediment source for the loess sequences along the Danube River, supporting previous suggestions (e.g. Buggle *et al.*, 2008; Jipa, 2014; Újvári *et al.*, 2012). Loess deposits are often interpreted as an archive of long distance aeolian transport (Lehmkuhl *et al.*, 2016; Obreht *et al.*, 2015, 2019; Rousseau *et al.*, 2011), however the results presented in Figure 8.3 suggest the opposite. It is the short-distance transport from the Danube alluvium (tens rather than hundreds of kilometres) that makes the predominant contribution to the loess deposits in the Danube valley. These “shortened” transport pathways reinforce a loess generation and transport model proposed by Smalley *et al.* (2009) and the importance of rivers in the process.

This research shows that the primary rock sources for the Danubian loess deposits are those “surrounding” the course of the river, including the Alps, the Bohemian Massif, all of the Carpathians, the Dinaric Alps, and the Balkan Mountains; most of which have been proposed as a source in the past (Jipa, 2014; Schatz *et al.*, 2015; Thamó-Bozsó *et al.*, 2014; Újvári *et al.*, 2010b, 2013, 2014b; Újvári and Klötzli, 2015). However, based on the Hf isotope analysis, there is a strong argument for significant Alpine and Bohemian Massif contributions.

Previously it has been argued that strong glacial activity is required to produce large quantities of silt size sediment (Mahaney and Andres, 1991; Wright, 2001). Although an ice-cap has have been reconstructed in the Alps, there is no evidence for a series of

large, connected glaciers across the Carpathians, the Dinaric, or the Balkan Mountains (Ehlers and Gibbard, 2007; Hughes and Woodward, 2017; Urdea, 2004; Urdea *et al.*, 2011). Material production by large glaciers may still be valid for the Alpine region. However, this analysis suggests that in the other mountainous regions either small glaciers may be sufficient to produce large quantities of sediment, or another mechanism, e.g. colluvial, fluvial or permafrost may have to be considered supporting analysis of Buggle *et al.* (2008) and Smalley *et al.* (2009).

8.3. Spatial variability of provenance signals in loess deposits

The KDE diagram constructed for each of the loess sites (Figure 8.10) shows that while three peaks can be observed in the averaged loess sites, the relative proportion of grains represented by each peak varies, showing some inter-site variability. For sites with few analysed grains, this could be an artefact of the small sample size. As all sites are in close proximity to the Danube River (Figure 8.11) the characteristic 3-peak pattern seen in Danube sediments is expected.

Averaged loess site data for each site plotted together with potential sources, using an MDS map (Figure 8.12), shows that the individual sites form a cluster surrounded by the river data. Any variability noted between sites is much smaller than the variability seen between sources, suggesting no significant variation between sites based on the U-Pb ages. Data for rivers plots closer to all loess sites than any source lithological data, except for the West Carpathian Carboniferous-Permian sandstones (HF). The close proximity of the loess data on the MDS plot to the Danube and tributary data further supports the conclusion that the loess sites have inherited the U-Pb age signatures of the river-borne material, and preserve a strong Danubian signal.

Although still plotting in the cluster, sites located outside confines of the Carpathian Basin, plot away from the centre of the cluster, e.g. Stratzing which is found in the foothills of the Bohemian Massif. The c. 600 Ma age population is not as dominant in this sample, despite the proximity to Precambrian aged rocks, suggesting that either the age distribution for this site is not fully captured, as the Bohemian Massif was not shown to contribute large quantities of Precambrian grains in the section 8.2.

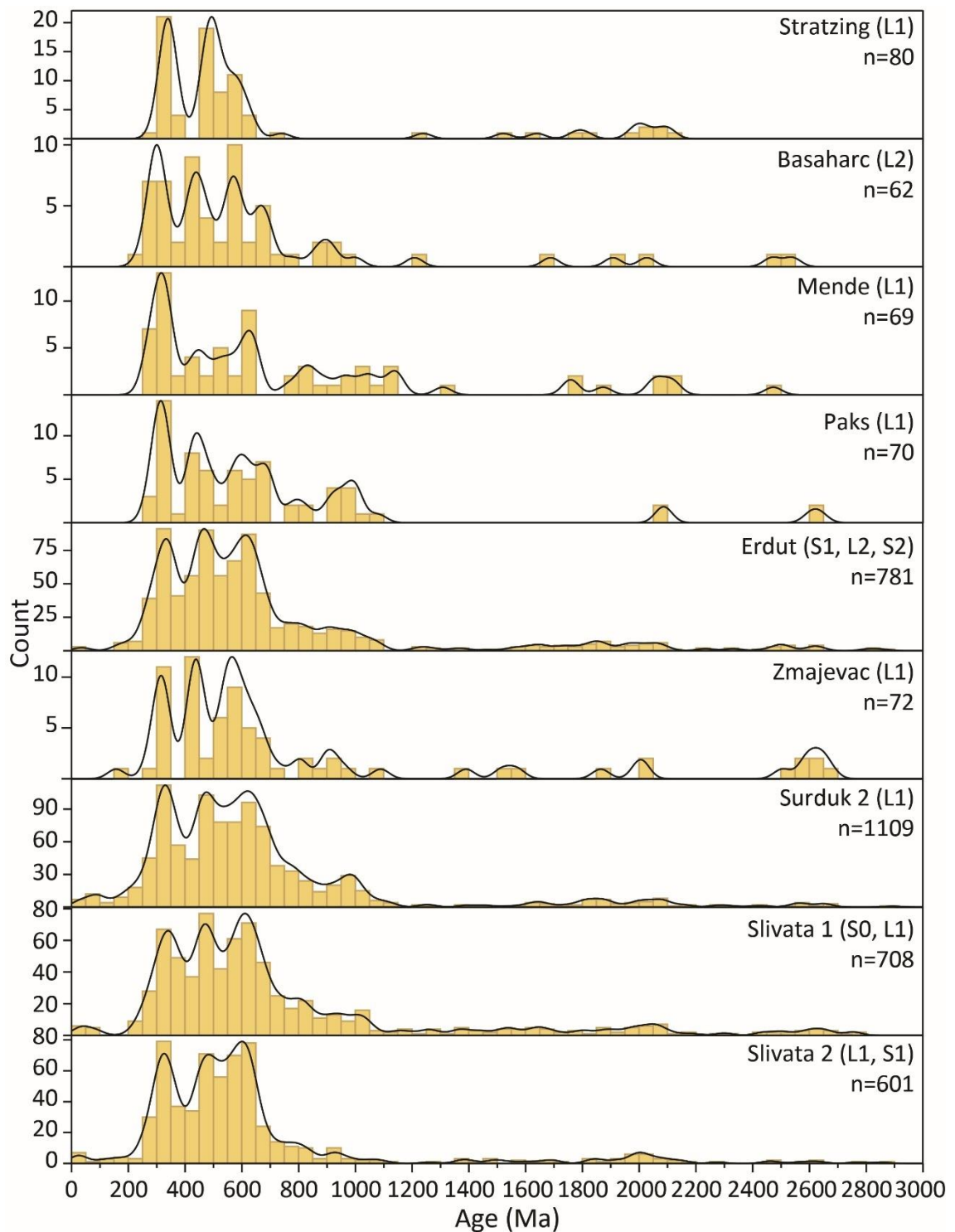


Figure 8.10 Zircon U-Pb Kernel Density Estimator (KDE) for each loess site. Erdut, Surduk 2 and both Slivata sites, represent grouped datasets. The approximated chronostratigraphic position of each unit is indicated in brackets. Paks, Mende, Basaharc, Zmajevac (Újvári *et al.*, 2012). Stratzing combines Stratzing and Krems datasets (Újvári and Klötzli, 2015).

Slivata 1 notably plots away from Slivata 2 on the MDS plot (Figure 8.12), a feature already highlighted in Chapter 5 (section 5.4.4), and maintained despite of inclusion of other datasets. When plotted as a cumulative distribution plot (Figure 8.13) Slivata 1 lies closer to the Drava, while Slivata 2 is close to the Tisza. This is likely driven by the increased contributions to the 300-350 Ma population and the drop in proportion of the c. 450 Ma grains at the Slivata 2, instead larger contributions of 1000-2000 Ma grains are seen at Slivata 1.

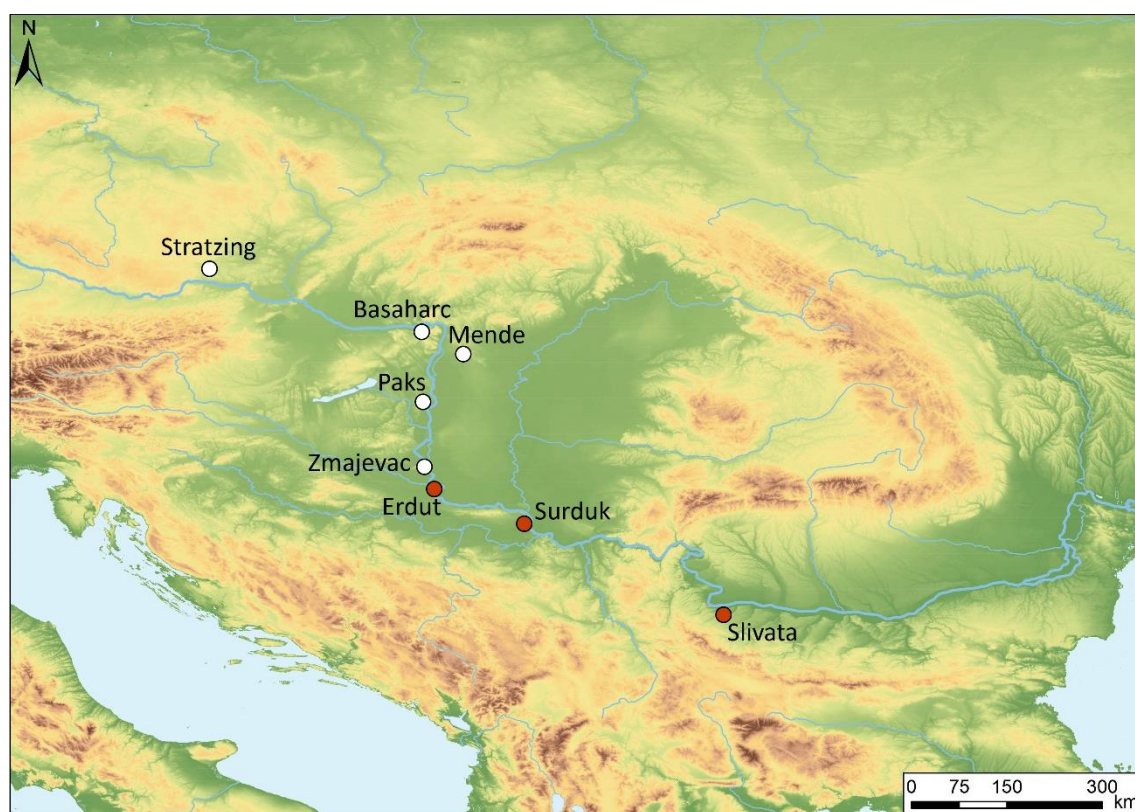


Figure 8.11 Location of sites shown in Figure 8.9. Orange dots show the location of the sites sampled as part of this research.

The strong similarity between the Drava dataset and Slivata 1 (Figure 8.12), is likely due to the shape of c. 450 Ma peak as well as the older Proterozoic grains. This could suggest that more sediment was delivered to the Danube by the Drava at certain points in time and therefore the Danube had a slightly more “Drava like” signature. This however is not seen

at Surduk 2, which covers the same time period and lies downstream from the Drava. Both VT and MG samples have a strong c. 450 Ma peak, and even though these samples are sourced outside of the drainage system of the Danube it suggests potential signatures derived from the Dinaric Alps and the Balkan Mountains. A closer investigation of the 450-500 Ma geological time slice (Figure 8.7), reveals abundance of Cambrian-Ordovician age rocks in both mountainous regions. The 450 Ma zircons could be delivered to the Danube by the Great Morava before it enters the Iron Gate, explaining their absence in Surduk 2. Alternatively, both Slivata profiles are found on the foothill of the Balkan Mountains where Cambrian-Ordovician rocks are common and there are number of small tributaries that could deliver it almost directly to the site.

Slivata 2, in contrast, does not have such strong c. 450 Ma signature, suggesting that the contribution from the Dinaric and Balkan sources was not as strong (discussed in more detail in section 8.4). Moreover, Slivata 2 also has a more dominant c. 300 Ma signature which is likely a reason behind the proximity to the Tisza sample on the MDS plot. This is likely reflecting the Carboniferous rocks eroded in South Carpathians by the Tisza, the Dinaric Alps by the Sava and Morava (for which there is no source dataset), and the more direct, “local” inputs from the Balkan Mountains.

Despite the geographical proximity of the Tisza and Surduk 2, a resemblance between the two samples is not seen on the MDS plot (Figure 8.12). Tisza reflects a dominance of the c. 330 Ma and 450 Ma peaks, and a paucity of the ‘Gondwana’ peak, but including smaller and older 1000 Ma, 1800 Ma, and 2000 Ma populations. These lithologies are abundant within the drainage area of the Drava (Figure 8.5), and seen within its KDE distribution (Figure 8.2). While these Precambrian signatures contribute to the Erdut’s distribution they are slightly smaller, which this could be explained by 300 grain difference between the samples. It is therefore proposed that the Southern Alps and other terranes within

drainage of the Drava River are the primary source of the Precambrian aged grains, although small contributions from the Bohemian Massif are also likely.

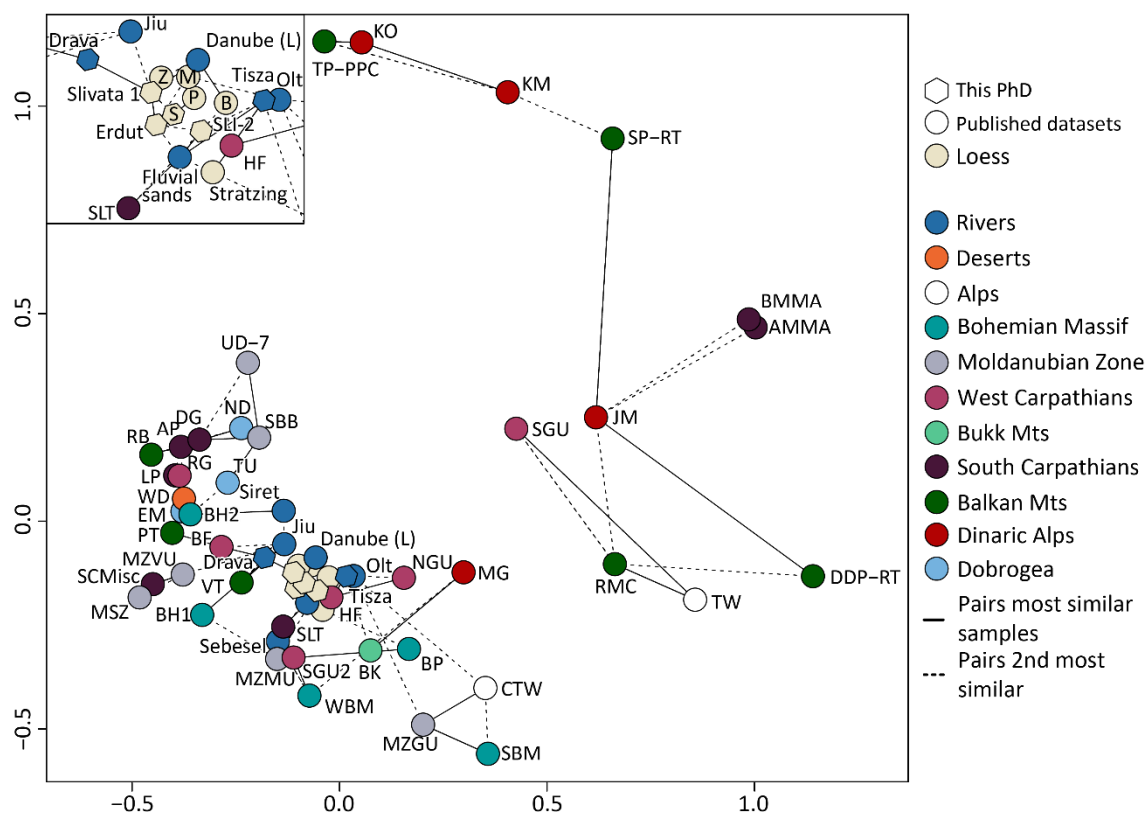


Figure 8.12 Multi-dimensional scaling (MDS) map for grouped Erdut, Surduk 2, and Slivata samples based on zircon U-Pb ages presented alongside potential sediment sources. Full lines connect the two most similar samples, whereas dotted lines show the second closest data matches. Inset, the enlarged loess data cluster. Abbreviations: B- Basaharc, M-Mende, P-Paks, S- Surduk-, SLI-2 – Slivata 2, Z- Zmajevac, Danube (L) – Lower Danube.

Lastly, there is a notable population of young Jurassic-Triassic grains (150-250 Ma) seen in the Surduk sample, which is subordinate in samples from Erdut, Zmajevac, Slivata 1, and Slivata 2, and absent in all other samples. The absence of the 150-250 Ma grains in other sites, could be an artefact of small number of grains analysed, especially in the previously published loess datasets (Stratzing, Basaharc, Mends, and Paks). However, not

many 150-250 Ma grains have been captured in the river datasets either (Figure 8.2); only some individual grains were measured in the Drava and Tisza datasets. A handful of source samples contain these grains (the Dinarics (MG and JM) and the Alps (CTW and TW)), therefore more source data on these terranes is needed. The largest areas of Triassic and Jurassic rocks are present in the Alps, the Transdanubian Mountains, the Dinaric Alps and the Balkan Mountains (Figure 8.14), though small pockets are seen in the Carpathians. Based on the spatial analysis, there is no obvious dominant Jurassic-Triassic source within the Tisza's drainage basin or locally to the site, that could explain the abundance of these zircon grain at Surduk 2. It is likely that these grains are either carried via the Danube from its upper reaches and the small number of analysis is missing these populations in at Stratzing, Basaharc, Mends, and Paks. Alternatively, Jurassic-Triassic grains are absent in the aforementioned samples, and the Drava and Sava are delivering the majority of these grains to the Danube. This could be revealed by increasing the number of analysis at Erdut, Zmajevac, and both Slivata sites to a comparable levels between these sites.

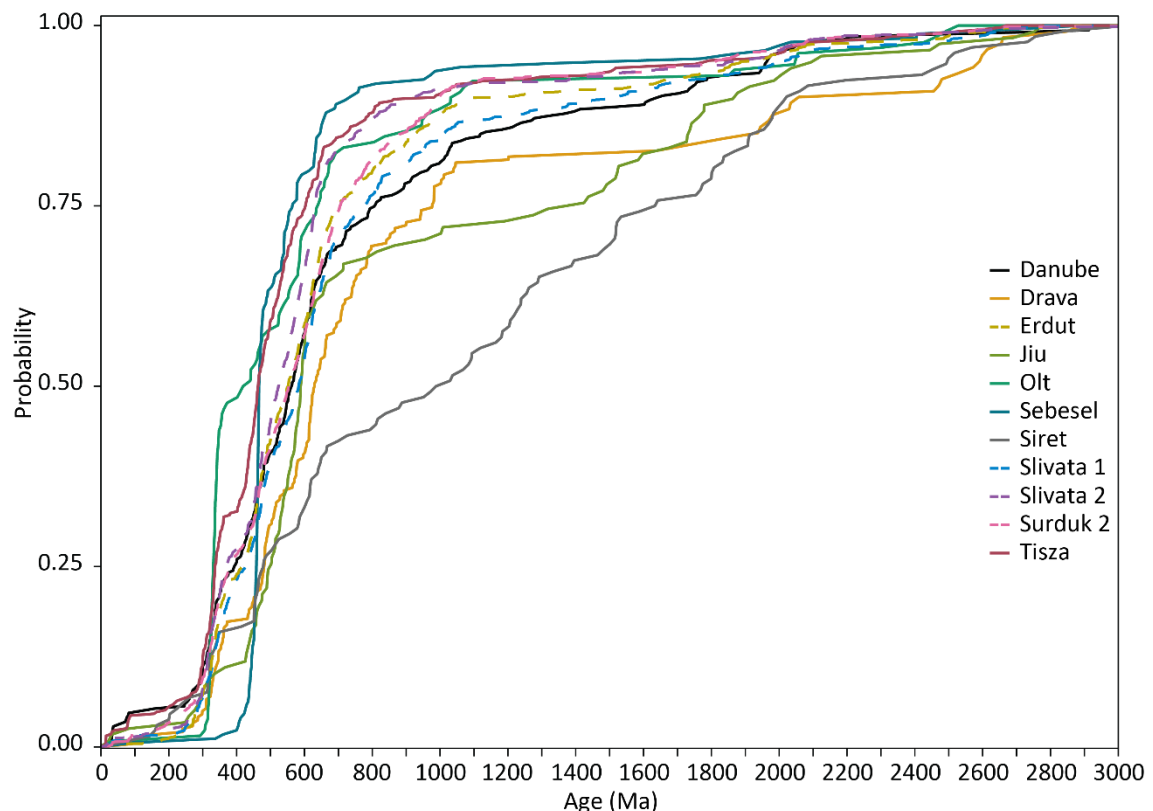


Figure 8.13 Cumulative age distributions for KDEs (Figure 8.9) of the loess sites analysed as a part of this study (Erdut, Surduk 2, Slivata 1 and Slivata 2), presented alongside the rivers dataset (Figure 8.2).

To investigate the spatial variability between sites, all U-Pb ages have been plotted in combination with Hf-isotope results for each site. Due to the small number of analyses of U-Pb ages from Austria (<20 per sample) (Újvári and Klötzli, 2015), these datasets were not used in the Hf comparison.

Figure 8.15 shows similar dominant features in U-Pb age spectra across the three sites, with three fairly well-defined peaks and three maxima in ϵHf – age space. For all sites, except Slivata 1, zircons in the c. 330 Ma age population is the most abundant. This is also observed in the ϵHf density maps showing the highest concentration of grains in that population, centred slightly below CHUR line. Moreover a c. 450 Ma peak is observed in all samples, with another cluster of slightly negative ϵHf values (0 to -5). The 600 Ma population shows a wide range in hafnium isotope composition, including a strongly positive grouping (ϵHf c. +10), extending as low as -35, and so the signatures on the density map are somewhat diffuse.

Plotting the site's ϵHf isotopic results with source data (Figure 8.16) indicates that metamorphic and igneous Alpine rocks (the Tauern Window and the Western Alps), have strong contribution to the loess deposits at Erdut. There is overlap between Austrian loess samples and Erdut at c. 500 Ma suggesting, a common source. While it is likely that the Dinarics are contributing the younger Palaeogene-aged zircons, their ϵHf values are not explained by the source datasets and suggests rocks that had larger crustal melt contributions. At present there is insufficient source data to determine the sources of the 450 Ma and Palaeoproterozoic populations.

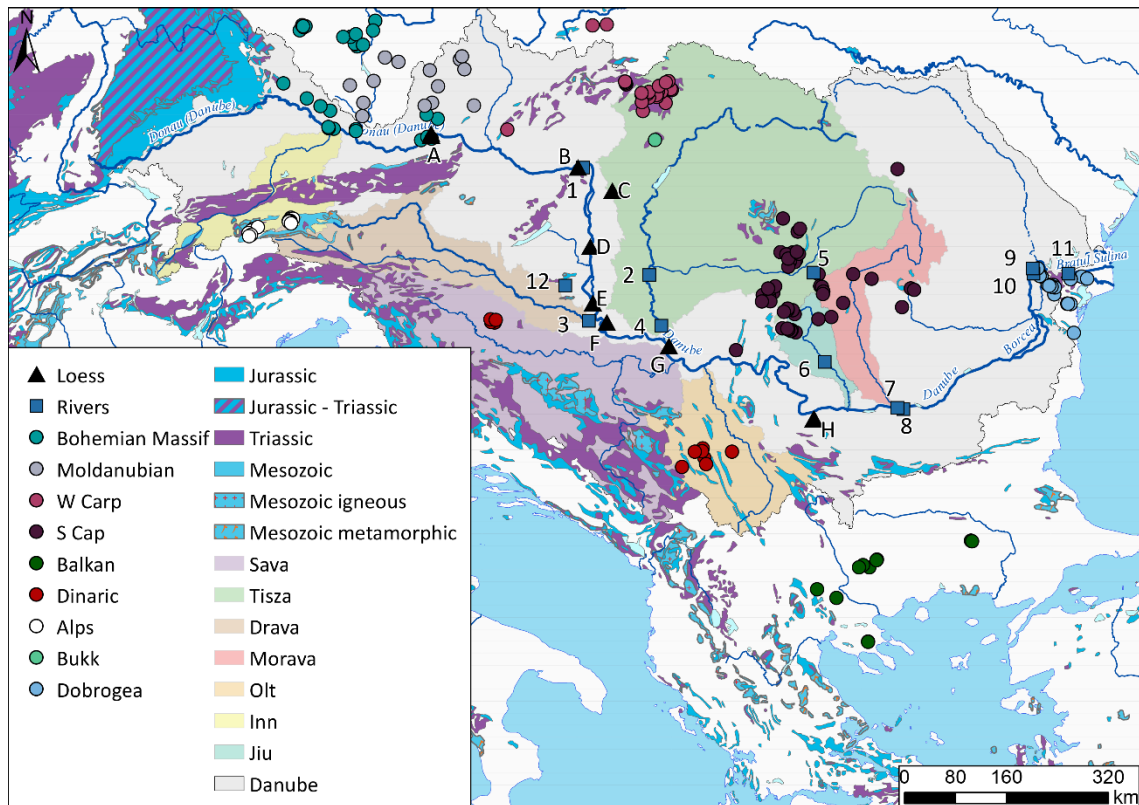


Figure 8.14 Map of Jurassic-Triassic (150-250 Ma population) source rocks, with the zircon U-Pb loess and source locations in the context of the Danube River basin, and its tributaries. Sites and references are outlined in the caption of Figure 8.4.

Surduk 2 has the largest proportion of grains younger than 250 Ma (Figures 8.10 and 8.13) and a continuous spread of ϵ_{Hf} from +5 to -10, indicating mixing between depleted mantle-derived and more mature crustal hafnium. The data also shows a slight discontinuity between density “hotspots” for the c. 600 Ma age grouping, with both juvenile ϵ_{Hf} (+3-4) as well as crustal contributions (<-5), suggesting at least two different sources contributing to the 600 Ma age peak.

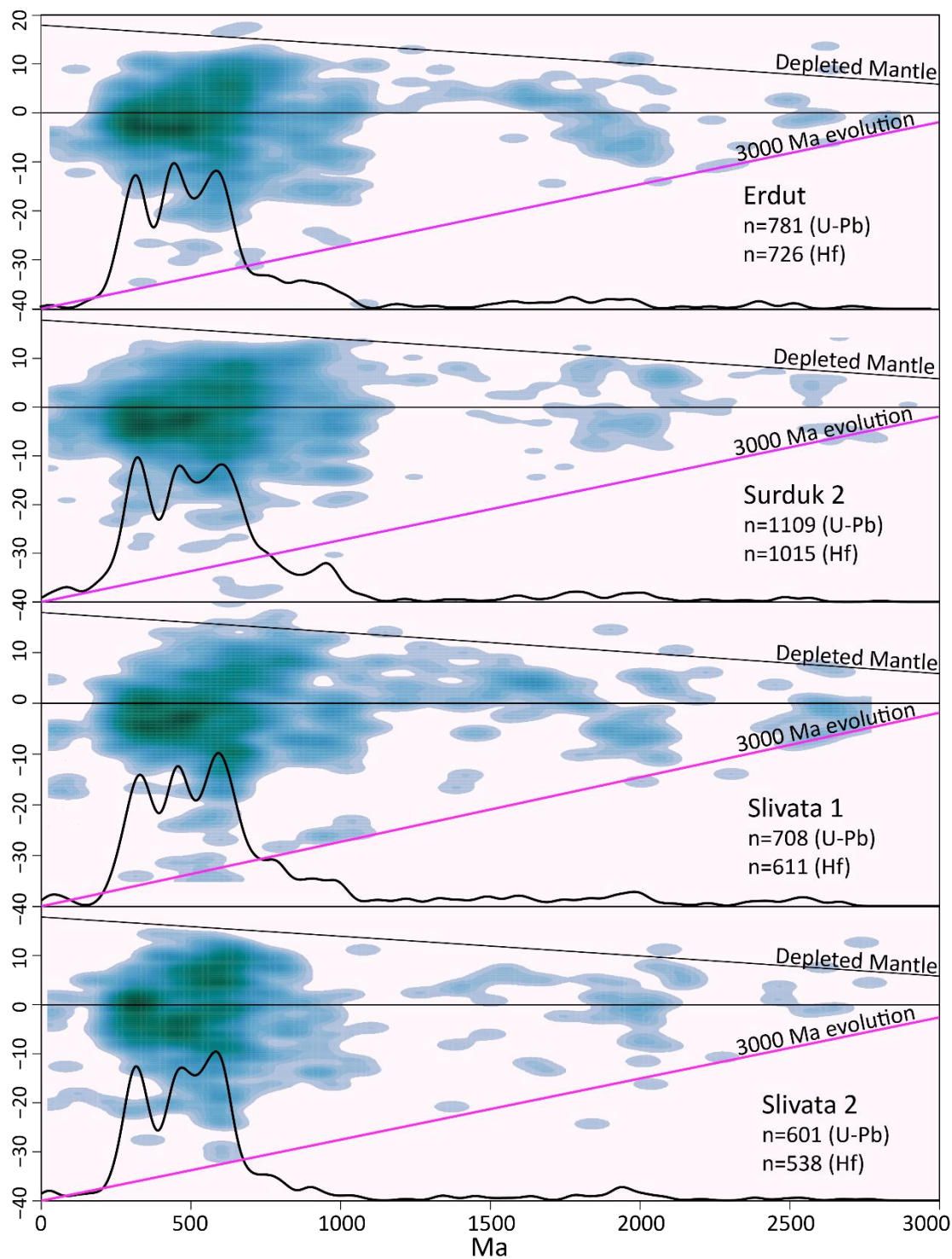


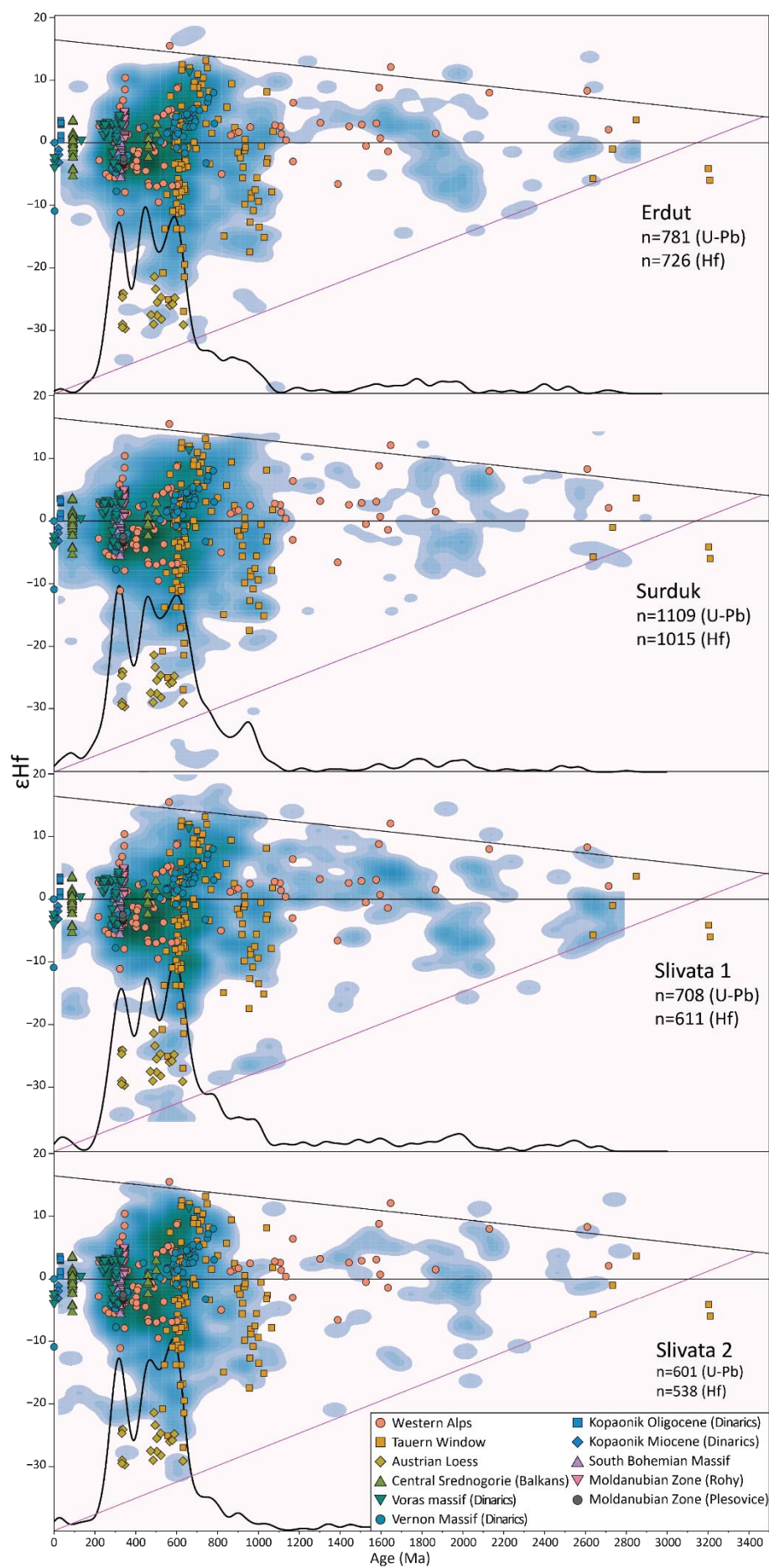
Figure 8.15 Probability density plot showing Hf isotope-time evolution of three sites investigated in this study. The density of the data distribution is calculated using a modified version of the Kernel Density Estimation (Botev *et al.*, 2010) analysis amended for R.

Plotting Surduk's 2 ϵHf isotopic results with source data (Figure 8.16) still shows a strong Tauern Window correlation, however the Western Alps data does not fit that well with the Mesoproterozoic rocks and older rocks, suggesting that source is not well characterised yet. Austrian loess still shows an overlapping source, even though this primary source is not captured.

The Upper Cretaceous and Palaeogene Balkan data (Srednogorie) fits perfectly with the Surduk 2 Hf data. Srednogorie cannot be the source of sediment for Surduk due to its geographical location. However, it was a part of the magmatic arc that encompasses Apuseni, Banat, Timok and Srednogorie Mountains, and which developed during closure of Neotethys (Gallhofer *et al.*, 2015). While the Hf data is not available for the whole arc, this strong correlation suggests that Apuseni and Banat Mountains are the source of these young zircon grains.

Slivata 1 has a very consistent and relatively abundant spread of Proterozoic U-Pb zircon ages, from 1100-1850 Ma (Figure 8.10 and 8.13), with a spread of data in ϵHf -age space. It shows that these grains have almost entirely juvenile crust influence (i.e. $\epsilon\text{Hf} > 0$). Slivata 1 also shows the lowest ϵHf (i.e. most cratonic) grains for the c. 600 Ma population, as well as grains plotting along the evolution line for the 3000 Ma North African crust (Fielding *et al.*, 2017).

Figure 8.16 Probability density plot showing Hf isotope–time evolution for each site. The density of the data distribution is calculated using a modified version of the Kernel Density Estimation (Botev *et al.*, 2010) analysis amended for R. The source Hf are superimposed, see Appendix J for the Hf metadata.



The lithological Hf data for Slivata 1 (Figure 8.16) shows that the captured Upper Cretaceous and Palaeogene datapoints are not the main source (small overlap with a few Balkan points). Instead Slivata 1 has more negative ϵ_{Hf} values pointing to more crustal melt additions. This shows different source rocks for the loess of Slivata 1 and Surduk 2, though at present it is not possible to pinpoint the source of these grains for Slivata 1. Similarity in source is seen between the Slivata 1 and Austrian loess samples in the 500-600 Ma age is also seen. However, the source for the c. 300 Ma grains is different and likely constrained by the Danubian signatures (i.e. all the zircon suggested above as being carried by the Danube) as well as those of the Dinaric Alps. The c. 300 Ma ϵ_{Hf} values cluster at Slivata 2, is less negative than seen in the other samples, averaging just above CHUR line (+1). While presenting a spread of ϵ_{Hf} values in the c. 600 Ma age population, the dominant cluster is actually positive (+5) unlike at all other sites, suggesting a different contribution from a depleted source such as oceanic-arc rocks. This validates the use of the ϵ_{Hf} as a provenancing tool in loess, showing the where U-Pb ages are indicating similarity (i.e. 600 Ma age peak), the ϵ_{Hf} is able to improve the results by separating source contributions.

The difference between Hf signatures at Slivata 1 and Slivata 2 for the Upper Cretaceous and Palaeogene grains is really notable (Figure 8.16), with both Dinaric and Balkan shown as a likely contributor. The source for the c. 500 Ma population in the Austrian loess does not appear to be contributing greatly to Slivata 2. While there are some Tauern Window and Western Alps grains plotting near the c. 600 Ma positive “hotspot”, there is an absence of source grains that contribute to it, suggesting there is another source of grains to that age range at Slivata 2.

SPATIAL VARIABILITY SUMMARY

Geographical variability in sediment source for loess deposits along the Middle and Lower reaches was investigated in Section 8.3 (**Objective 3**).

The U-Pb and Hf-isotope data analysed as part of this study in combination with published data shows that for the most part there is no spatial variability between loess-palaeosol sites along the Danube River, supporting the suggestion of a mixture of lithological sources providing sediment to the wider Carpathian Basin. Moreover, for the most part, the dominant sources remain the same along the Danube River, and therefore support a homogeneous source across the Carpathian Basin model in line with results from studies of bulk sample elemental composition (Bugge *et al.*, 2008; Újvári *et al.*, 2008) and isotopic variation (Schatz *et al.*, 2015). This suggests that the dominant sources remained consistently active during the late Quaternary.

Small but distinct deviations can be noted in both proxies that point to variations in source lithologies, as previously observed by Újvári and Klötzli (2015) in Austria and by Újvári *et al.* (2010) in Hungary and Serbia. However, any small variability seen does not change along the course of the Danube River. If a new dominant source was added with each tributary, a progressive change in the dominant age peak should be observed, along with step changes in age peaks between sites. Also, on the MDS diagram, sites would plot near the source's closest tributary. The opposite is observed, with little similarity between sites and tributaries downstream. Therefore, the loess sequences along the Danube are not influenced by gradual additions from its tributaries (Figures 8.2 and 8.12). It follows that the variability seen between sites is most likely a result of changes in contributions from smaller sources and local geologies that may not be fully captured by the collected datasets or generalised geological maps.

8.4. Implications of multiple sources and homogeneous sediment source across the region.

For the most part KDEs and MDS (Figures 8.2 and 8.3) show a combination of relatively similar source signatures, suggesting that there is no single dominant source supplying sediment to the loess-palaeosol profiles along the Danube. Instead an amalgamation of sources from the lithologies along the Danube and surrounding the Carpathian Basin likely provide the sediment to loess deposits along the Danube River. A lack of a single source requires an exploration of sediment generating mechanisms in the region, as only the Alps were covered by an ice-cap during the last glacial period (Hughes *et al.*, 2006; Hughes and Woodward, 2017). The Carpathians, the Dinaric Alps, and the Balkan Mountains supported only smaller, often unconnected, glacier lobes (Hughes *et al.*, 2007, 2011; Hughes and Woodward, 2008), yet there are a number of populations seen in the loess KDEs that are likely sourced from these regions. This has implications for understanding the genesis of the sediment for loess deposits. It is strongly argued that strong glacial activity, often associated with the Fennoscandian Ice Sheet or Alpine ice-cap, is critical for the generation of large quantities of silt (Mahaney and Andres, 1991; Wright, 2001), and the debate on the production mechanism and genesis of loess has long persisted in the literature (Li *et al.*, 2020; Muhs and Bettis, 2003; Obruchev, 1945; Smalley, 1966; Smalley *et al.*, 2011; Smalley and Krinsley, 1978; Smith *et al.*, 1991; Wright, 2001; Wright and Smith, 1993). Typically, loess in terms of its origin has been divided into “glacial” or “cold” loess, and “desert” or “warm” loess (Obruchev, 1945; Smalley, 1966; Smalley and Krinsley, 1978; Wright, 2001), a division that has persisted in the literature for years. The glacial grinding of bedrock to produce glacial flour, deposited, eroded, and suspended by fluvial action prior to the final aeolian transport are shown to be critical for the genesis of glacial loess. The proximity of reconstructed ice-sheets and glacial margins

to loess deposits are thought to support this conclusion. The desert loess applies to loess deposits bordering arid zones not linked to glaciated regions. It is argued not to be “true loess” as no desert processes are seen as capable of silt generation on a large scale (Smalley and Vita-Finzi, 1968). Instead deserts are proposed as sediment storage areas, prior to aeolian transport (Smalley and Krinsley, 1978). In recent years this division has been argued to be too simplistic, with researchers arguing that silt size sediment is likely to be produced and transported by various mechanisms simultaneously (Muhs, 2014; Muhs and Bettis, 2003) and attempts at new classifications have been made e.g. continental glacier provenance-river transport, mountain provenance-river transport, and mountain provenance-river transport-desert transition (Li *et al.*, 2020).

The identification the Carpathians, the Dinaric Alps, and the Balkan Mountains as sources further weakens this simplistic division. The mechanisms relating to physical weathering such as frost shattering (Wright *et al.*, 1998), or colluvial processes and fluvial transport especially in sediment filled rivers (Wright, 1995; Wright and Smith, 1993), in combination with some glacial and permafrost action can be sufficient to generate silt size particles. Most of these processes can operate in desert regions, therefore showing the separation of the “desert” loess to be unnecessary.

8.5. Provenance changes over time

8.5.1. Variability between large units

To investigate provenance changes on an orbital scale the goal was to group and compare samples from units representing glacial and interglacial periods. However, to date only a handful of provenance analyses have been carried out with sufficient resolution to investigate source shifts through time. The small number of palaeosol analyses in this study precludes MDS analysis of combined palaeosol (565 samples) and loess (2518

analysis) data. Fenn *et al.* (2018) showed that any differences in this scenario are likely statistical artefacts and the individual site's bias can be introduced based on the number of grains each site is adding to a grouping. Instead individual loess, palaeosol and fluvial samples from all sites were compared to test if any clusters occur for the various climatic stages.

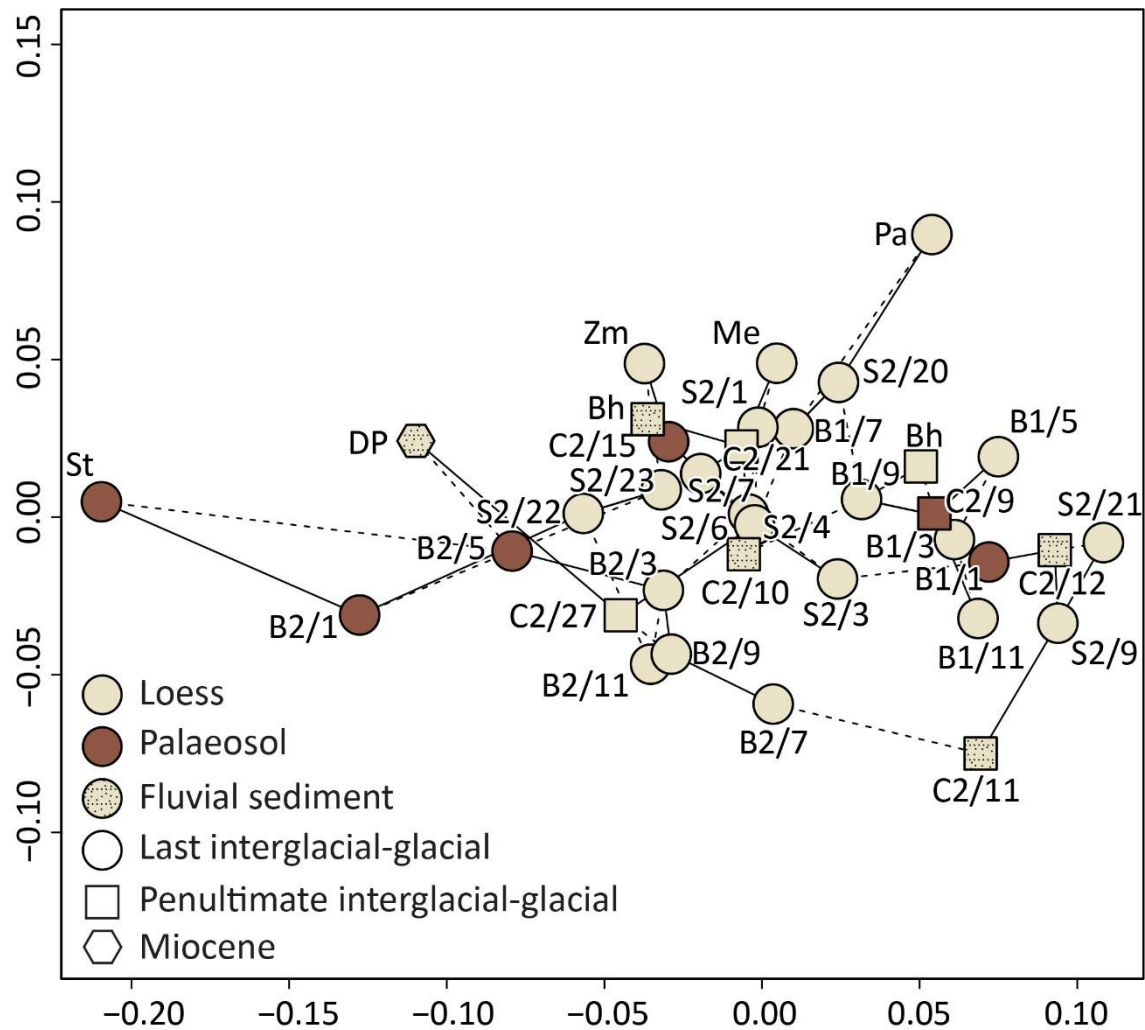


Figure 8.17 Multi-dimensional scaling (MDS) map based on the U-Pb ages for individual samples from Erdut (C2/*), Surduk 2(S2/*), Slivata (B1/* and B2/*), Zmajevac (Zm), Paks (Pa), Basaharc (Bh), Mende (Me), Stratzing (St), and Danitzpuszta (DP) based on zircon U-Pb ages. Full lines connect the two most similar samples, whereas dotted lines show the second closest data matches. For clarity, sample codes for samples analysed in this study are shortened (e.g., BULI7/2/1 is B2/1).

The graph shows (Figure 8.17) samples from loess from the last glacial (L1) and previous glacial (L3) periods, and palaeosols of Holocene (S0), last interglacial (S1) and penultimate interglacial (S2) ages, as well as samples from pedogenic horizons developed during the last glacial period. Fluvial samples from Basaharc (Late Pleistocene and Miocene) and Erdut (MIS 6 fluvial horizon) were also added. The MDS analysis, shows no obvious or consistent grouping of palaeosol samples versus loess samples. This suggests that the source remains the same between glacial and interglacial periods. The visual comparison of ϵ_{Hf} isotopes and bulk sample geochemistry results (Chapter 7) show no consistent patterns of glacial-interglacial change either.

A comparison between the last glacial (L1) and penultimate loess (L2) units across all sites (Austria, Croatia, Hungary, Serbia and Bulgaria) also does not show a consistent grouping in the MDS plot (Figure 8.17). Not only is there no separation seen between loess samples from the Weichselian or Saalian periods, but also there are no separate clusters for palaeosols of Eemian and Holsteinian. In fact, there are no patterns emerging at all based on the zircon U-Pb ages, with loess, palaeosol, and fluvial samples of various ages plotting in one big cluster. These results support the bulk sample Nd-Sr results from a loess-palaeosol profile section in Tokaj (Schatz *et al.*, 2015) which showed low variability in isotopic values between the loess and palaeosol units. The lack of large scale temporal variability was also argued by Újvári *et al.* (2012) in Hungarian loess. Here the analysis shows that this is true for all analysed sites i.e. Austria, Croatia, Hungary, Serbia, and Bulgaria (Figure 8.10). The large number of samples and spatial coverage of sites suggest that across the Carpathian Basin there are no source changes on the orbital timescale. These results imply the sediment transport pathways (fluvial or atmospheric) and/or source did not shift between different glacial and interglacial periods, or did not shift sufficiently to generate changes on the MDS plot. Alternatively, if the transport pathways changed, they still passed over the same source lithologies.

The data, therefore, suggests that the main sediment sources and transport mechanisms in the Carpathian Basin operated in the same way over not only a long Quaternary timescale, but also beyond that as there is no difference between the fluvial Miocene samples and Quaternary fluvial and loess samples indicated. Firstly, this strongly suggests that major climatic reorganisations, including changes from glacial to the interglacial periods, bore no effect on the sediment production mechanism for the Carpathian Basin. Secondly, it highlights the importance of the Carpathian Basin element of the Danube Basin–Black Sea (Matenco *et al.*, 2013) system as a sedimentary sink.

8.5.2. Variability within individual units

To test any potential provenance shifts at individual sites, results of U-Pb and Hf analysis for the individual samples were plotted alongside each site's stratigraphy and luminescence chronology, as presented in Chapters 4-6.

Croatia

Results of zircon U-Pb dating and Hf isotopes combined with sedimentary logs and the results of luminescence dating in Erdut are presented in Figure 8.17. Data presented here covers ~100 ka of sediment deposition, over parts of the last two glacial-interglacial cycles. Sediment deposition for the uppermost palaeosol was dated to 75.01 ± 5.44 ka, while the top of the bottom palaeosol was dated to 231.29 ± 40.63 ka.

For the most part the loess and palaeosols at Erdut show a lot of similarity in zircon U-Pb age distributions, ϵ_{Hf} values and bulk sample geochemistry (Figure 8.18). Therefore, it is likely that the contributions from source(s) of sediment for Erdut remained mostly unchanged over time during the penultimate glacial-interglacial cycle.

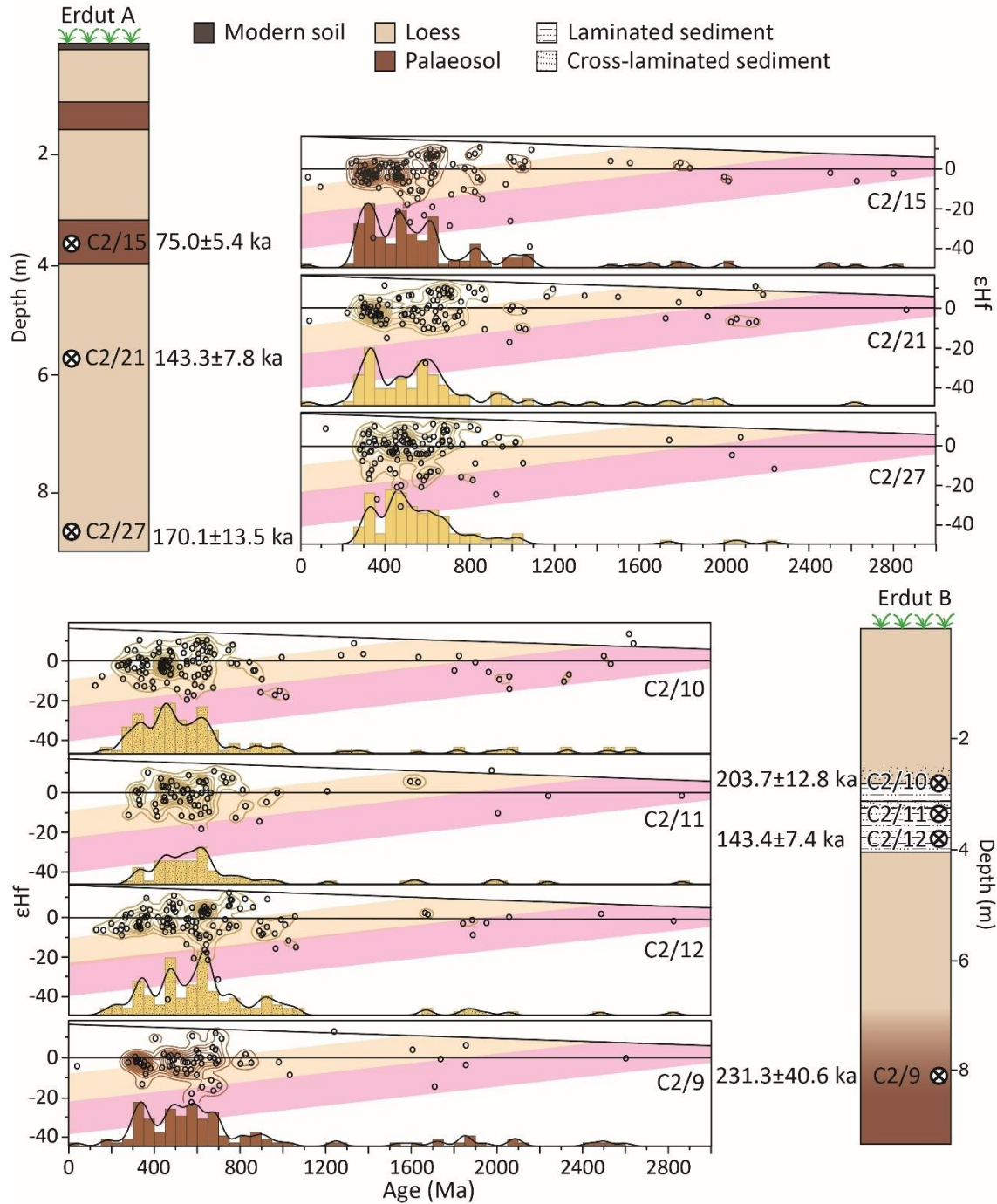


Figure 8.18 A summary of zircon U-Pb dating and Hf isotopes for Erdut. Stratigraphy of each profile is shown, along with luminescence chronology for each provenance sample (*ROI6/ removed). Areas represents the evolution of Hf in crust through time for 2500-3330 Ma Archean crust (pink), and 1600-2500 Ma Palaeoproterozoic crust (orange).

However, there are hints of variability, coinciding with the fluvial episode which commenced between 148.69 ± 6.98 and 143.36 ± 7.43 ka. Zircon U-Pb age distributions in

the samples above the fluvial unit (CRO16/2/15, CRO16/2/21 and CRO16/2/10) have a relatively large contribution from a c. 280 Ma age population, which is minor or non-existent in the samples below the fluvial sediments. Additionally, samples above the fluvial unit have a dominant c. 340 Ma age population, while in samples CRO16/2/27 and CRO16/2/9 (below fluvial sediments) grains of that age are as abundant as grains in other peaks.

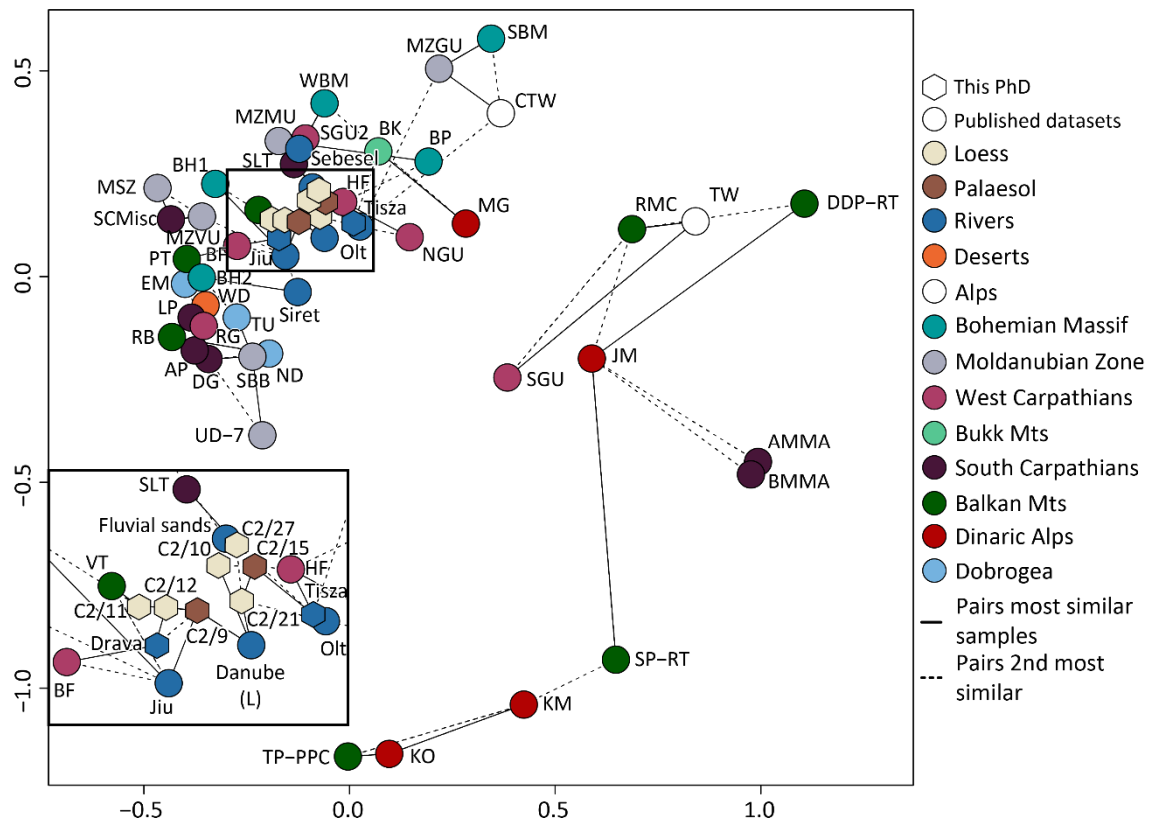


Figure 8.19 Multi-dimensional scaling (MDS) map for Erdut samples based on zircon U-Pb ages presented alongside potential sediment sources. Full lines connect the two most similar samples, whereas dotted lines show the second closest data matches. Note that the Lower Danube is shortened to Danube (L).

Grains with negative and especially strongly negative ϵ_{Hf} values (< -10) are particularly abundant in the c. 340 Ma and c. 450-500 Ma age populations in samples below the fluvial event (CRO16/2/27). Other samples record negative anomalies in these peaks (most found

at $\epsilon\text{Hf} < -10$), however none are as strong ($\epsilon\text{Hf} = -30$) as the one seen in CRO16/2/27. These zircon grains plot along the evolution line for Archaean crust (pink area on Figure 7.20), with 2500-3300 Ma depleted mantle model ages, although there are also grains of that affinity seen in the CRO15/2/15 (palaeosol) and CRO16/2/10 (sandy loess sediment). The presence of the grains plotted along the Archean and Palaeoproterozoic depleted mantle age model, in the c. 340 Ma and c. 450-500 age populations in CRO16/2/27 and CRO16/2/9, further supports the difference.

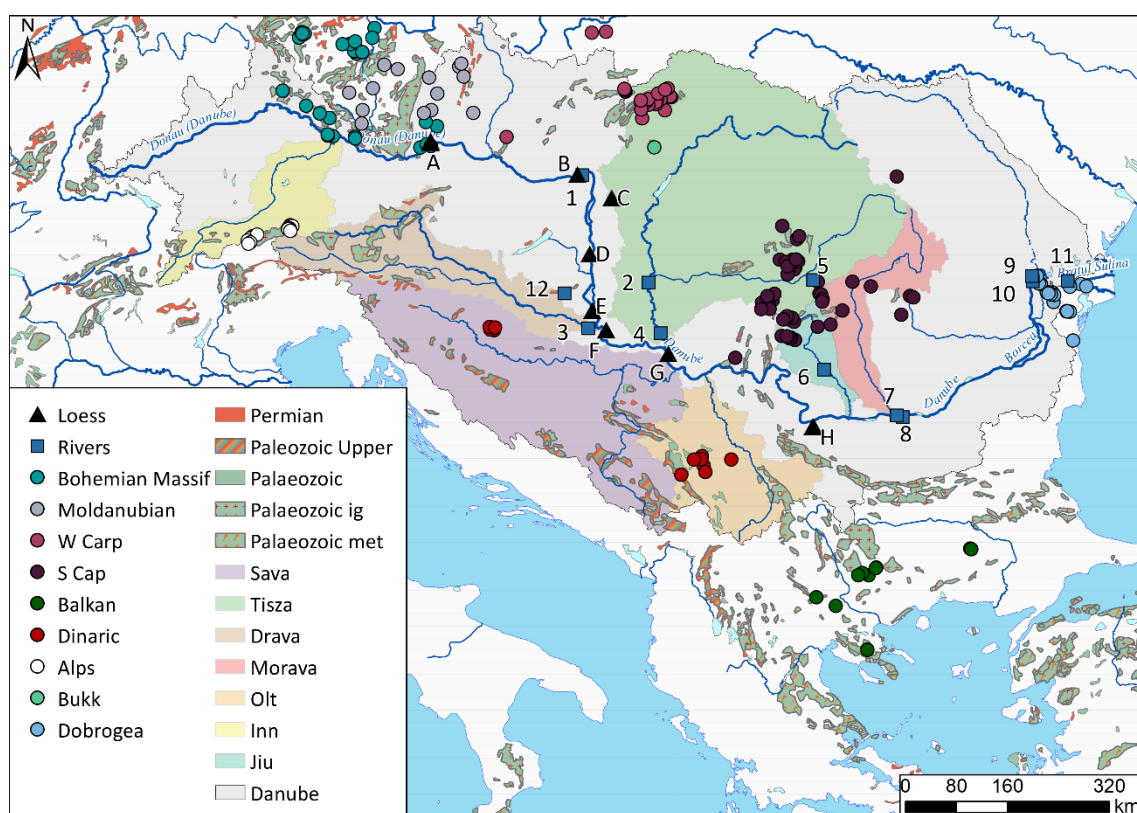


Figure 8.20 Map of Permian (250-300 Ma population) source rocks, with the zircon U-Pb loess and source locations in the context of the Danube River basin, and its tributaries. Sites and references are outlined in the caption of Figure 8.4.

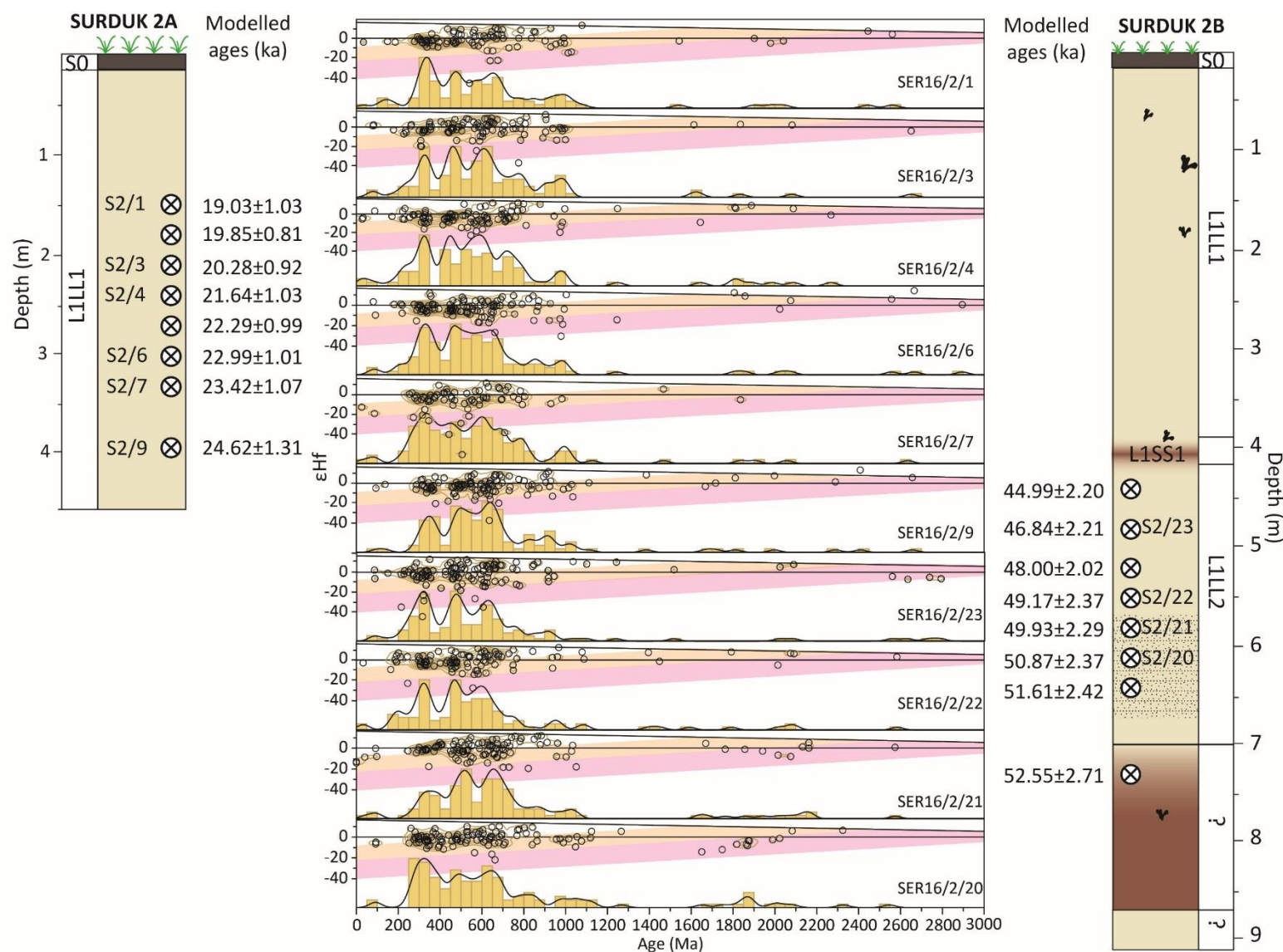
Results of the analysis presented in Chapter 4 suggested a fluvial event, potentially basin wide, occurred during the penultimate glacial period. Figure 8.19 shows an MDS map for Erdut samples plotted with the source data. The fluvial-influenced samples (CRO16/2/11 and CRO16/2/12) plot very close to the Drava sample. Additionally, CRO16/2/10 and

CRO16/2/27 overlap with a fluvial sands (Miocene/Pleistocene), which also has a strong c. 280 Ma population (Figure 8.2), indicating strong fluvial influence on this group of samples. The outcrops of Permian rocks within the drainage of the Drava River as well as on the border between Drava and Sava (Figure 8.20). It is possible that after 148.69 ± 6.98 and 143.36 ± 7.43 ka a hydrological and geomorphological reorganisation occurred, e.g. a shift in the watersheds of the Drava drainage. This introduced new source rocks, with zircon ages c. 280 Ma, that begun contributing to the sediment delivered and deposited at Erdut. This reorganisation was either caused by or caused the flooding event.

Serbia

Figure 8.21 shows combined results of luminescence dating, zircon U-Pb dating and Hf isotopes presented alongside of the sedimentary logs for two profiles (A and B) at Surduk 2. The investigated loess-palaeosol profile covers the ~40 ka of sediment deposition during the last glacial-interglacial cycle. After a period of soil development, the primary loess deposition at Surduk 2B begun at 52.55 ± 2.71 ka and was likely interrupted by an erosional event at some point after 44.99 ± 2.20 ka. Surduk 2A represents deposition during the final stages of the LGM, and covers the period of rapid sediment deposition between 24.62 ± 1.31 and 19.03 ± 1.03 ka.

There is an overlap between the U-Pb age distributions and Hf isotope data across all samples at Surduk 2 (Figure 8.21), with three main populations represented in the age- ϵ_{Hf} space, at c. 330 Ma, 470 Ma and 630 Ma. The similarities are very evident in the distributions of the top four samples, especially SER16/2/1, SER16/2/4, and SER16/2/6, that represent sediment deposition between 22.99 ± 1.01 and 19.03 ± 1.03 ka. All have a dominant c. 330 Ma peak with slightly negative ϵ_{Hf} values, and smaller but relatively equal contributions in the c. 470 and 630 Ma populations with ϵ_{Hf} values just below the CHUR line. Their bulk sample geochemical signatures (Figure 7.11) are also very similar.



However, a small shift can be seen in the loess sample SER16/2/3, which has equal contributions in all three dominant zircon age peaks. The difference is not really seen on the MDS map (Figure 8.22), likely due to the similarity of the age distributions between the samples. However, in comparison to the surrounding loess this sample has more negative ϵ_{Hf} values in the c. 330 Ma population. Moreover, a change in the bulk sample chemistry is seen with a strong depletion in the LREE (Figure 7.11B) noted, e.g. one of the two negative anomalies in the La, the lowest Eu values and the strongest negative Eu/Eu* anomaly (0.69; Appendix G). In some magmatic processes, Eu^{2+} substitutes in for Ca^{2+} in plagioclase, leading to a positive Eu anomaly in its REE distribution (also described as Eu/Eu*). Lower Eu/Eu* values represent lower concentration of plagioclase in the sediment (McLennan *et al.*, 1990) and potentially larger contributions of felsic source rocks (Cullers, 1994).

These combined zircon U-Pb and Hf, and bulk sample geochemistry results suggest that for the most part of the LGM the sediment source remained unchanged, however some potential source additions likely occurred between 21.64 ± 1.03 and 19.03 ± 1.03 ka. Figure 6.11 shows that period of the deposition of sample SER16/2/3 also corresponds to a shift in a mass accumulation rates from the lowest ($318 \text{ g m}^{-2} \text{ a}^{-1}$) to the second highest ($938 \text{ g m}^{-2} \text{ a}^{-1}$) values at the Surduk 2A profile. Rocks of Ordovician to Precambrian age are fairly abundant in the drainage of area of Tisza (Figure 8.5 and 8.7), therefore it could suggest a increased fluvial activity delivering more material, increased erosion during this time, and/or heterogeneous source rocks.

Many other sites in the region lack high-resolution chronologies that would support the comparison of this potential change or its cause. Nonetheless, high resolution luminescence dating from the near by Titel Loess Plateau (Perić *et al.*, 2019) shows multiple age inversions, and a substantial variability in the dose rates around that time

period, which could indicate changes in the geochemical composition (Stevens *et al.*, 2013a), and support a temporary change in provenance around the LGM. Additionally, modelling results show that Carpathian Basin is likely to have been on average drier and -6 to -9°C colder during the LGM (Strandberg *et al.*, 2011), which would also facilitate sediment availability and transport.

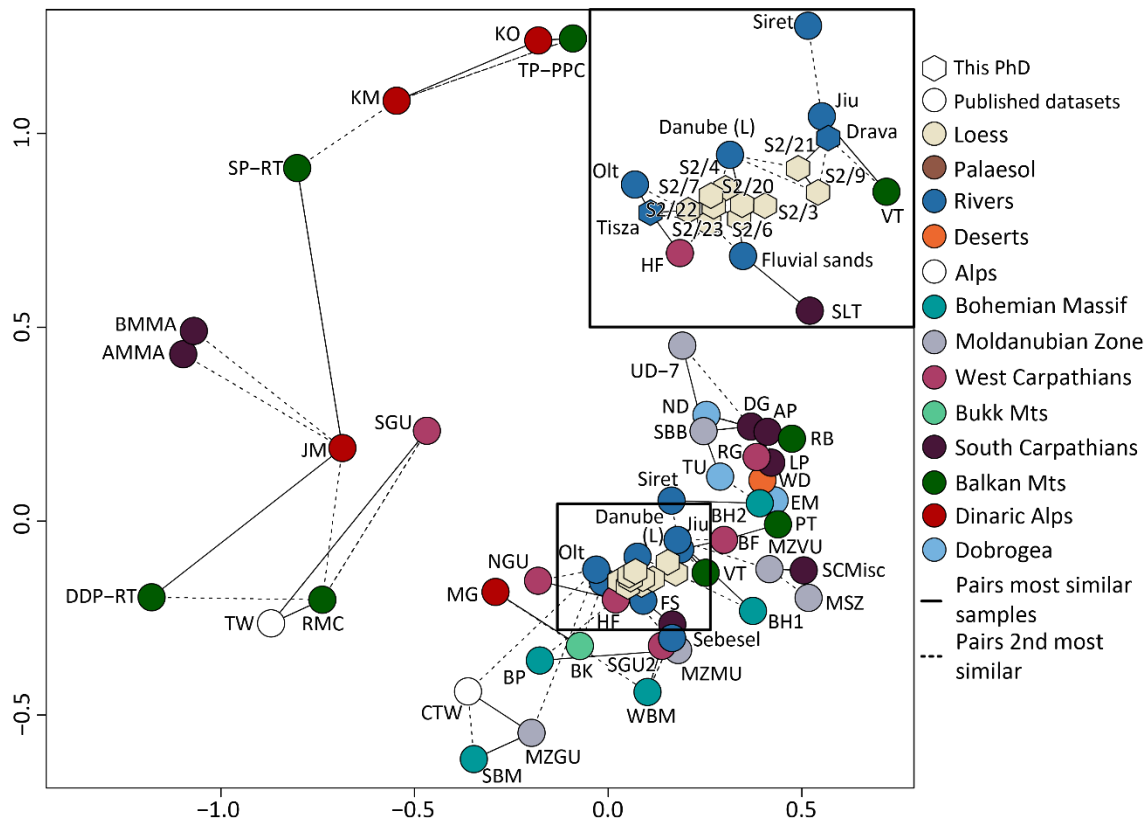


Figure 8.22 Multi-dimensional scaling (MDS) map for individual samples from Surduk 2 based on zircon U-Pb ages presented alongside of potential sediment sources. Full lines connect the two most similar samples, whereas dotted lines show the second closest data matches. Note that the Lower Danube is shortened to Danube (L).

There are also some similarities in the distribution of loess samples SERI6/2/9 and SERI6/2/21, with a subordinate 330 Ma age population in comparison to the the c. 450 and 630 Ma populations, counlikeother Surduk 2 samples. In both cases c. 330 Ma, εHf have a well constrained clusters of very slightly negative data points. An absence of zircon

grains younger than 250 Ma and 400-450 Ma, which are otherwise seen in almost every sample (Figure 8.21). However, these trends are not repeated in the bulk sample geochemical data (Figure 7.11), as SER16/2/9 plots closely with samples SER16/2/7 and SER16/2/8. These samples have been highlighted in Chapter 6, due to their anomalous luminescence behaviour. Bulk sample chemistry for sample SER16/2/21 plots in the “average” group, transitional between the two more “extreme” groups. Plotted on the MDS diagram (Figure 8.22), these two samples also plot away from the main Surduk 2 sample cluster and close to Drava and Jiu. While this could suggest that Ordovician and “Gondwana” material was more readily available or stronger Drava inputs into the Danubian system, at this stage the data is considered inconclusive and requires further investigation.

Finally, sample SER16/2/20 represents a period of high sediment accumulation at Surduk 2B, at 51.61 ± 2.42 - 49.93 ± 2.29 ka (Figure 8.21). The most distinct feature is the largest contributions of young grains in the 250-300 Ma age bracket, that merge into the 330 Ma peak. Additionally, it has a relatively large fraction of U-Pb ages in the 1650-2000 Ma range, with the ϵ_{Hf} values that likely correspond to remelting and crystallisation of Archaean crust, and therefore reflecting Palaeoproterozoic orogenic and continental processes (Hawkesworth *et al.*, 2010; Zhao *et al.*, 2002). For the most part the distribution of U-Pb ages and ϵ_{Hf} in SER16/2/20 has a very similar pattern to the rest of the samples at Surduk 2, and the changes are likely representing a contribution from one of the smaller, additional sources. The absence of young grains (<250 Ma) could suggest that the source rocks for these grains were temporarily “shut off” around 53.96 ± 1.82 ka. The source for 250-350 Ma zircons in SER16/2/20 was also only a temporary contributor, which diminished within 10.9-5.6 ka (Figure 8.21). Permian rock sources are not well captured in the source dataset (Figure 8.2), with majority of the samples containing this peak of sedimentary nature (e.g. sandstone), except for the Alpine samples (CTW and TW). The

distribution Permian age rocks (Figure 8.20), may suggest increased Drava contributions as only small Permian outcrops are seen in Tisza's drainage area. These large additions are likely explained by an increased erosion or the high zircon fertility in the source rock.

Bulgaria – Slivata 2

Zircon U-Pb dating and Hf isotopes combined with sedimentary logs and results of luminescence dating for Slivata 2 are presented in Figure 8.23. Data presented here covers ~73 ka of sediment deposition, encapsulating the period of climatic deterioration following the previous interglacial until the LGM. The bottom palaeosol sample has a 95.55 ± 6.29 ka age while the top chronological marker is provided by the Cape Riva/Y-2 tephra, 21.92 ± 0.63 ka.

As with all other sites, there are a lot of similarities in the zircon age KDE distributions, showing that loess source is mostly homogenous. In all sample populations at c. 310 Ma, c. 450 Ma, and in the 600-630 Ma range are present, indicating that rocks of those ages contributed the majority of the sediment to this site over the last ~95 ka, irrespective of changing climatic and environmental conditions. However, a change in the shape of the distribution can be observed between samples BULI7/2/7 and BULI7/2/5.

While the c. 630 Ma population is the most abundant in the top three samples (BULI7/2/11, BULI7/2/9, and BULI7/2/7), it is subordinate in the bottom three samples (BULI7/2/5, BULI7/2/3, and BULI7/2/1) and replaced by a 500-550 Ma population which is as abundant as the c. 450 Ma. The c. 310 Ma (Carboniferous) population contributes in the bottom samples before there is a switch too. The trace elements from bulk sediment (Figure 7.19) also show this grouping with some transitional samples. This trend can somewhat also be seen on the MDS plot (Figure 8.24), with BULI7/2/5, BULI7/2/3, and BULI7/2/1 plotting closer to Tisza, Olt, Miocene-Pleistocene fluvial sands, and the South Carpathian sample (HF), all of which show a dominant Carboniferous population (Figure

8.2). Instead the top three samples (BUL17/2/11, BUL17/2/9, and BUL17/2/7), coalesce in the centre between all the surrounding fluvial samples.

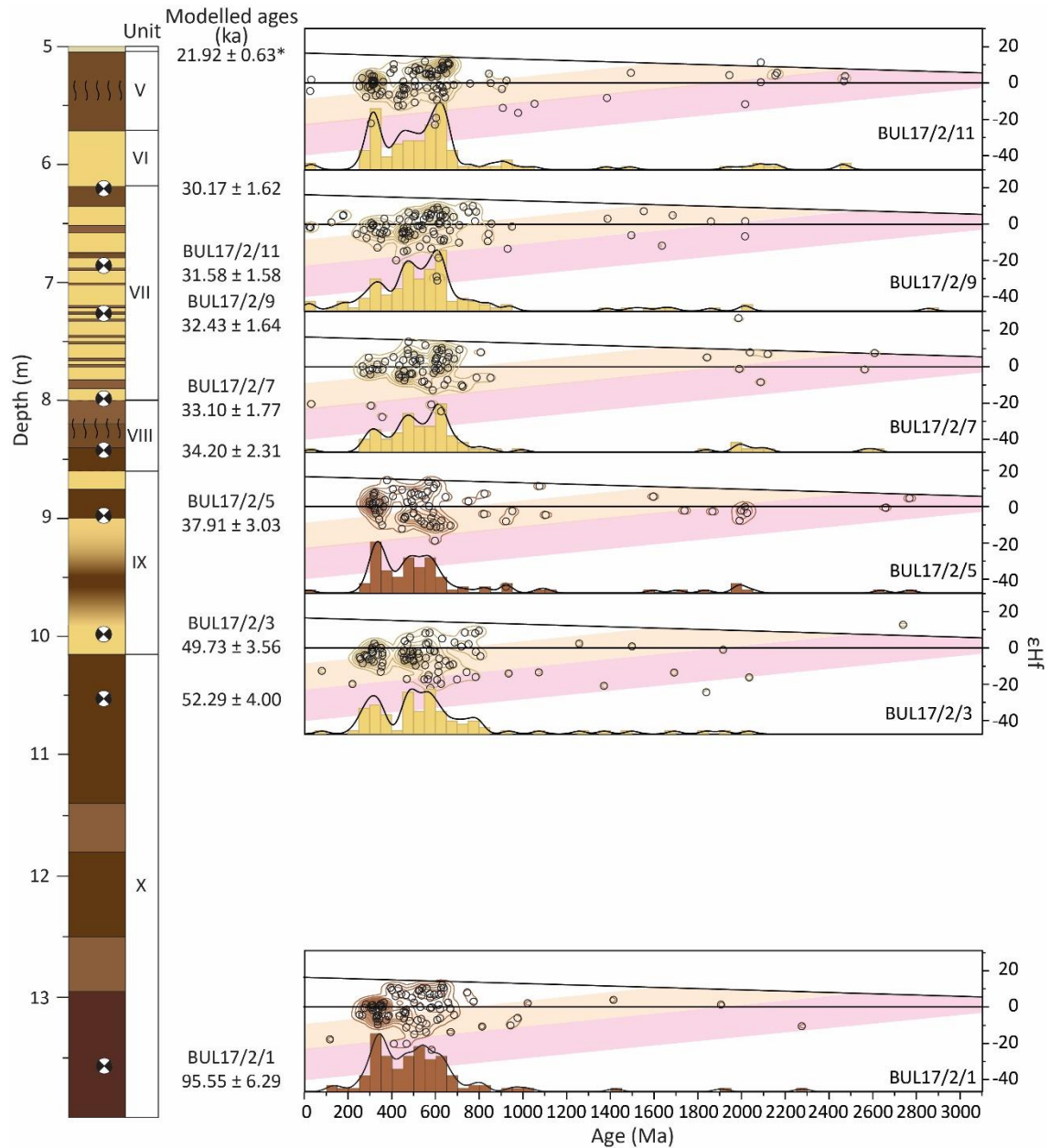


Figure 8.23 A summary of zircon U-Pb dating and Hf isotopes for Slivata 2. Stratigraphy of the profile is presented along with luminescence chronology for each provenance sample (shown inside of the diagram underneath of each sample code). Areas represents the evolution of Hf in crust through time for 2500 - 3330 Ma Archean crust (pink), and 1600 - 2500 Ma Palaeoproterozoic crust (orange).

Loess and palaeosol deposited prior to 37.91 ± 3.03 ka show a strong affinity to Carboniferous sources, with only small proportion of “Gondwanian” sediments. This Tisza-like KDE structure could suggest that the South Carpathians were a large contributor of sediment during that time, because either glaciers were able to build up already in that area or another mechanism of sediment production was active, while the Dinaric and Balkans were still relatively stable in terms of sediment production. Also a smaller sediment contributor (sources rocks of ~500-550 Ma) was potentially active at that time, delivered by the Danube from sources in the Alps, the Bohemian Massif and the South Carpathians (Figure 8.2).

Therefore a switch occurred after 37.91 ± 3.03 ka, broadly coincident with a shift in accumulation rates, U-ratio values, and a drop in magnetic susceptibility (Figure 5.7). While the proportion of the 450-500 and 600 Ma populations increases, suggesting a new source activation, or hydrological re-organisation, i.e. new tributary, or small course change. The top three samples come from the unit that contain these numerous “soil-like” feature that are interpreted as in-washed, colluvial soil material. Figures 8.7 and 8.8 show a relative proximity of rocks of that age to the Slivata profiles. The combined sedimentological interpretation also points to a highly active and unstable sedimentary system. The period after ~34 ka was suggested to experience stronger seasonality and therefore likely lead to increased periodic ice-melting (Rostek and Bard, 2013; Wegwerth *et al.*, 2016). The vegetation cover was thought to be reduced and the climate continued to deteriorate (Connor *et al.*, 2013; Feurdean *et al.*, 2014) which could lead to increased run-off and therefore erosion. Therefore it is hypothesised that the extra contributions could be delivered from the local Balkan Mountains source rocks, via in-wash of “soil-like” material.

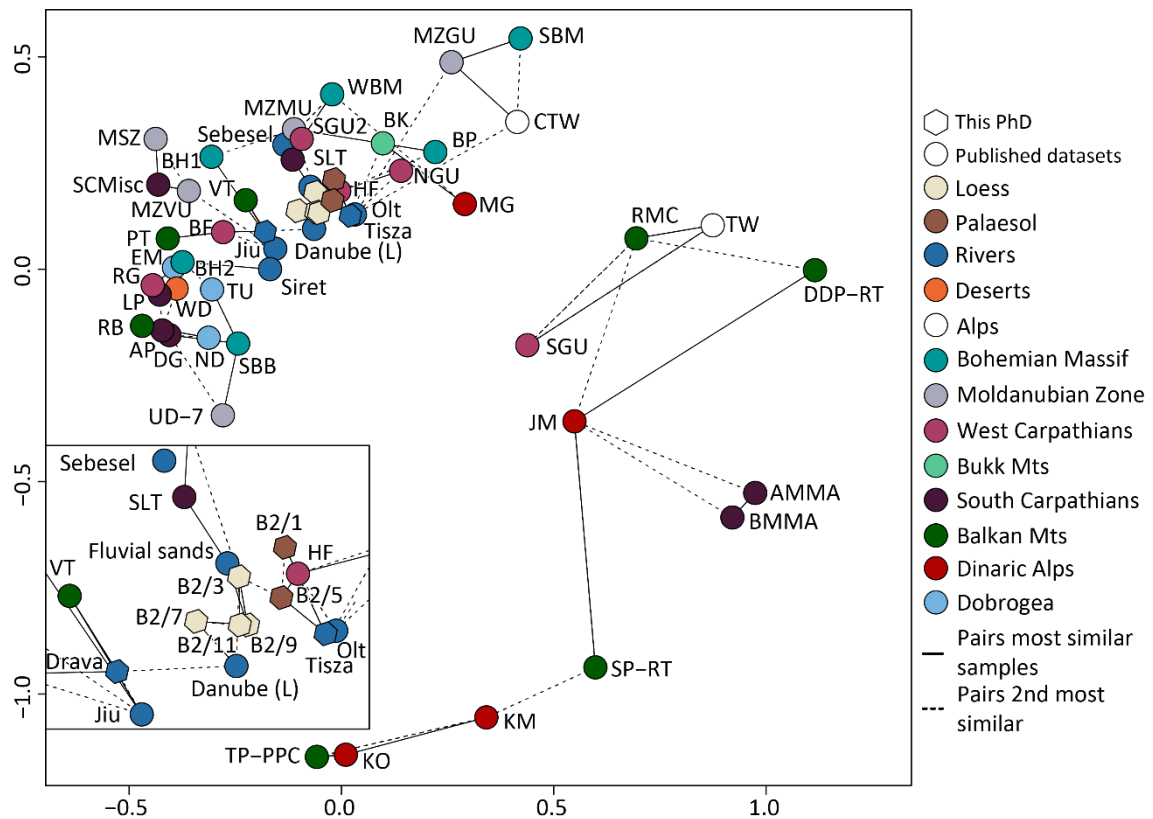


Figure 8.24 Multi-dimensional scaling (MDS) map for individual samples from Slivata 2 based on zircon U-Pb ages presented alongside of potential sediment sources. Full lines connect the two most similar samples, whereas dotted lines show the second closest data matches. Note that the Lower Danube is shortened to Danube (L).

Bulgaria – Slivata 1

Zircon U-Pb dating and Hf isotopes combined with sedimentary logs and results of luminescence dating for Slivata I are presented in Figure 8.25. Data presented here covers ~23 ka of sediment deposition, over the LGM and into the Holocene (Feurdean *et al.*, 2014). Sediment deposition for the bottom of the palaeosol was dated to 14.11 ± 1.07 ka, while the bottom of the loess to 23.30 ± 1.50 ka. This section contains a record of a rapid sediment accumulation, and therefore changes in sediment sources could be indicative of climatic or geomorphological reorganisation during the LGM and the deglaciation that followed.

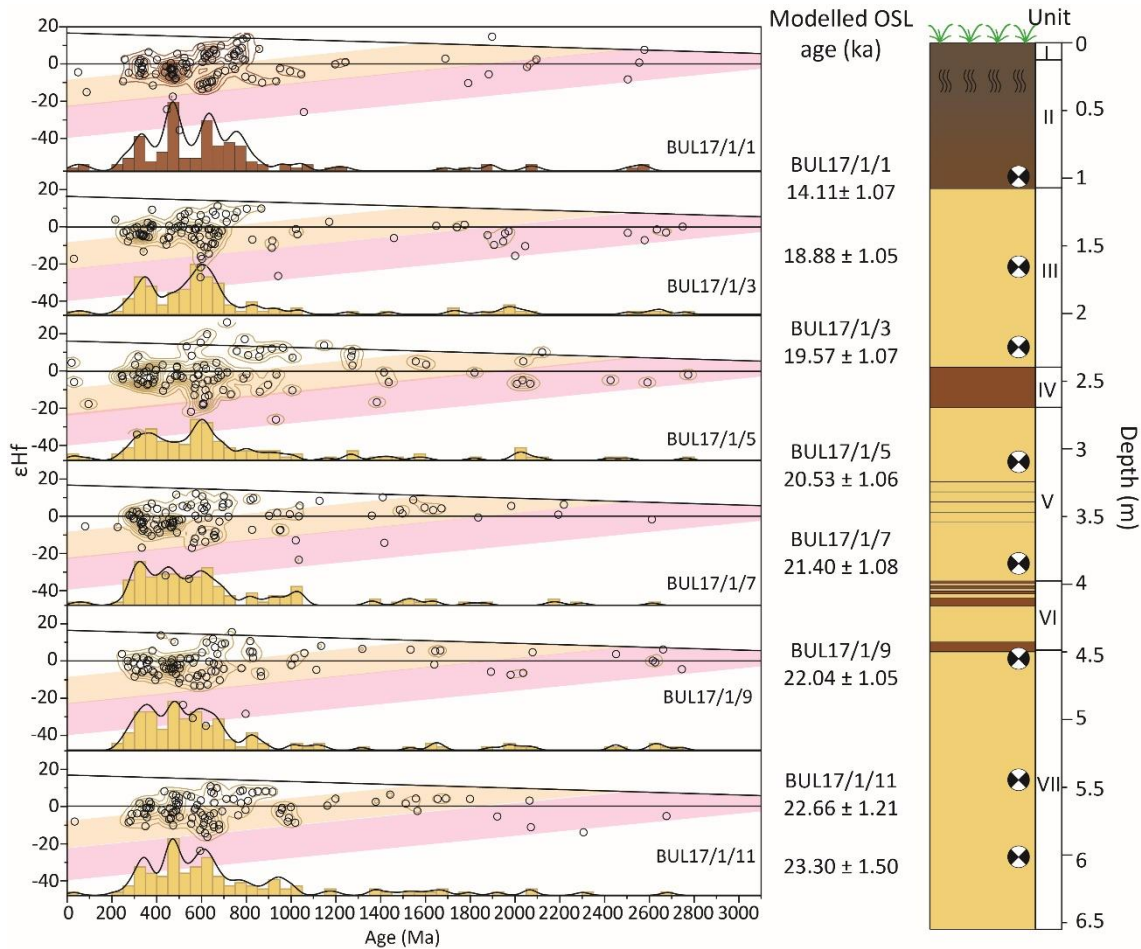


Figure 8.25 A summary of zircon U-Pb dating and Hf isotopes for Slivata I.

Stratigraphy of the profile is presented along with luminescence chronology for each provenance sample (shown inside of the diagram underneath of each sample code). Areas represents the evolution of Hf in crust through time for 2500 - 3330 Ma Archean crust (pink), and 1600 - 2500 Ma Palaeoproterozoic crust (orange).

Zircon U-Pb ages and Hf isotopes (Figure 8.25) indicate there is little variation in loess source in Slivata I, with three dominant populations at c. 330 Ma, 470 Ma and 620 Ma and replicable ϵHf populations for each peak. However, a small variation be also observed for loess samples BUL17/1/3 and BUL17/1/5, which have almost a bi-modal age distribution as the 450 Ma Ordovician age population is relatively muted. At the same time ϵHf values for the c. 650 Ma population become strongly negative (indicating involvement of recycled crust). They are the only two samples with grains plotting along an Archaean crustal

evolution trend. While bulk samples are not showing major anomalies for those samples, they do plot closely together for all trace elements (Figure 7.18). The MDS plot (Figure 8.26), does not clearly separate these loess samples out, however it plots them much closer with the Drava and the Jiu rivers, which likely is induced by a large proportion of “Gondwana derivatives” and subdued Carboniferous contributions in both rivers (Figure 8.2).

These samples were deposited between 20.53 ± 1.06 ka and 19.57 ± 1.07 ka, which coincides with a temporary drop in MARs (Figure 5.6), from 1381 to $1165 \text{ gm}^{-2}\text{a}^{-1}$, indicating a dynamic aeolian deposition and increased sediment supply, with potentially increased meltwater volumes entering the system. The relative muted 450 Ma population, also compares with the relative muted zircon signal from the bottom part of Slivata 2 (Figure 8.23). Kuhlemann *et al.* (2013) showed that in the Balkan Mountains two local glacial advances occurred at 25-23 ka and 18-16 ka. In the Southern Carpathians, the advances are dated to ~21 ka and ~19.5 ka (Ruszkiczay-Rüdiger *et al.*, 2016). This provides a mechanism by which some sediment could be “locked up” or “triggered” out of sync. If the Balkan Mountains are taken as a source of the 450 Ma age zircons, then during the period of loess and palaeosol deposition Balkan Mountains were in the phase of the deglaciation. Instead short periods of glacial re-advanced were noted around that period for in South Carpathians which could be bringing a lot of Carboniferous and “Gondwana-derived” signatures down the Danube.

Note the presence of three similar-sized peaks in the sample SER16/2/3 (Figure 8.21), showing that at that time in Serbia all three populations were evenly distributed. The temporary lack of dominance of “Gondwana-derived” zircons could also be explained by the meltwater draining South Carpathians directly to the Lower Danube around the area of Iron Gate where many Precambrian exposures are noted (Figure 8.5).

Despite these small excursions, the results indicated that for the most part sediment sources over the last ~23 ka remained constant, regardless of the glacials reaching their maximum extent and the deglaciation that followed. This suggests that the broad scale sediment delivery and deposition system has remained unchanged. It appears however, that any changes are driven by the local geomorphological, or micro-climatic factors.

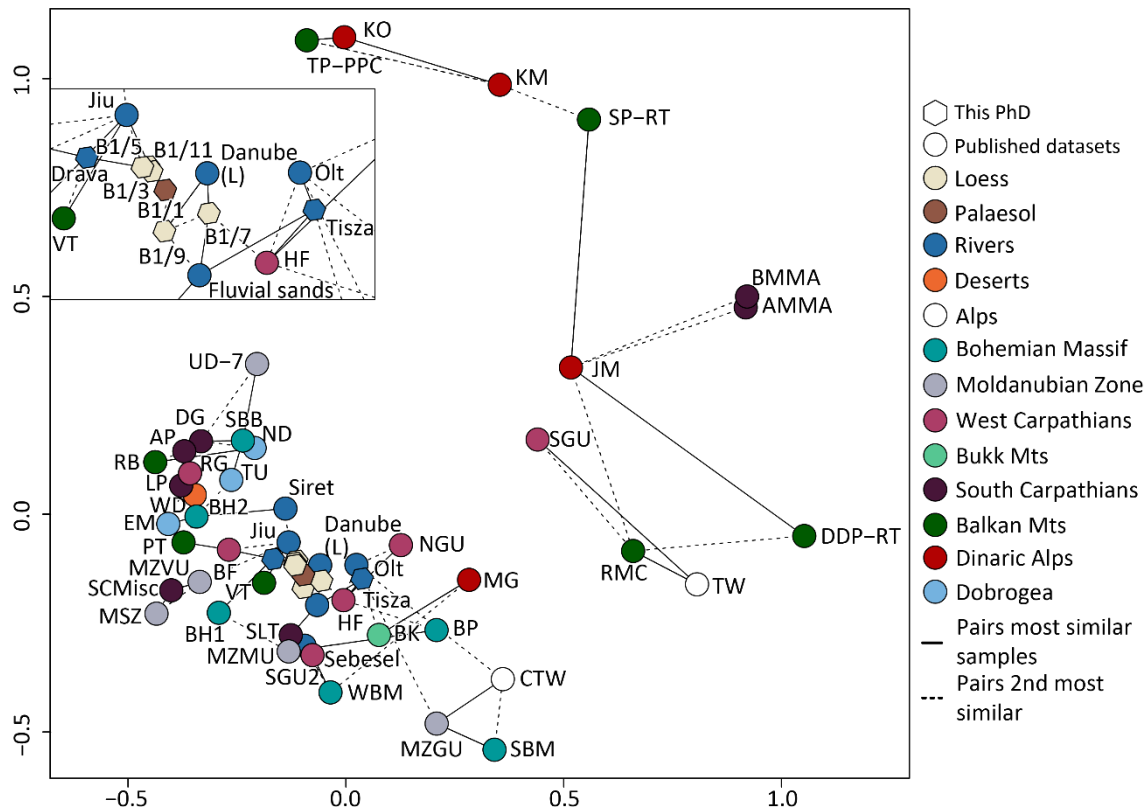


Figure 8.26 Multi-dimensional scaling (MDS) map for individual samples from Slivata I based on zircon U-Pb ages presented alongside of potential sediment sources. Full lines connect the two most similar samples, whereas dotted lines show the second closest data matches. Note that the Lower Danube is shortened to Danube (L).

8.5.3. Abrupt source shift

A potential for abrupt provenance shifts has never been confirmed, mainly due to (1) the low resolution of the investigations (although some authors have reported potential shifts through changes in luminescence properties (Stevens *et al.*, 2013a), or (2) the analysis of

small numbers of grains in some samples precluding detailed analysis of zircon single grain ages distributions (Fenn *et al.*, 2018).

Here several small provenance changes are described, e.g. at Surduk 2 (samples SER16/2/3), at Slivata 2 (post ~37 ka) and temporary shift at Slivata 1 (samples BUL17/1/5 and BUL17/1/3). In all cases the shifts do not completely change the zircon U-Pb or Hf distribution, rather they imply a shift in some components of the distribution. In many cases it is not possible to pinpoint the exact source lithological change, beyond switching on and switching off certain parts of the signal.

Nonetheless, these changes have important implications for the loess deposit research. Firstly, as the provenance changes do not appear to be linked to climatic events, they more likely represent responses to geomorphological changes in source regions or in proximity to loess sites, and/or lack of homogeneity of source rocks. This supports the suggestion of local and regional processes in loess development superseding the importance of major global and atmospheric influences (discussed in Chapter 4).

Superimposing potential abrupt shifts on mass accumulation at each site (Figure 8.27) reveals that changes correspond to the shifts and low stands in the MARs values at each site, rather than high stands as could be expected. At present it is not impossible to determine the strength of this correlation or in fact a causation of such patterns. One explanation, however could suggest that as one source becomes temporarily inactive or is reduced to a minor contributor, less sediment is available for deposition.

Lastly, sedimentary proxies (particle size and magnetic susceptibility) for the part of the profile between samples BUL17/1/3 and BUL17/1/5 (Figure 5.5), show a small shift. A proportion of coarse silt and very fine sand increases, a features which would usually be taken to infer atmospheric patterns such as wind direction change, increased windiness (Bokhorst *et al.*, 2011; Buggle *et al.*, 2008) or used to compare with other sites (Antoine *et*

al., 2009a; Rousseau *et al.*, 2011) or Greenland record (Rousseau *et al.*, 2002). The results of the provenance analysis show however that these changes are more likely related to the temporary provenance change, meaning that any correlations with Greenland ice-cores based just on grain size analysis are also likely inaccurate. Therefore, these results have implications for the interpretation of proxy records in loess and our lack of understanding of drivers behind loess proxies such as grain sizes.

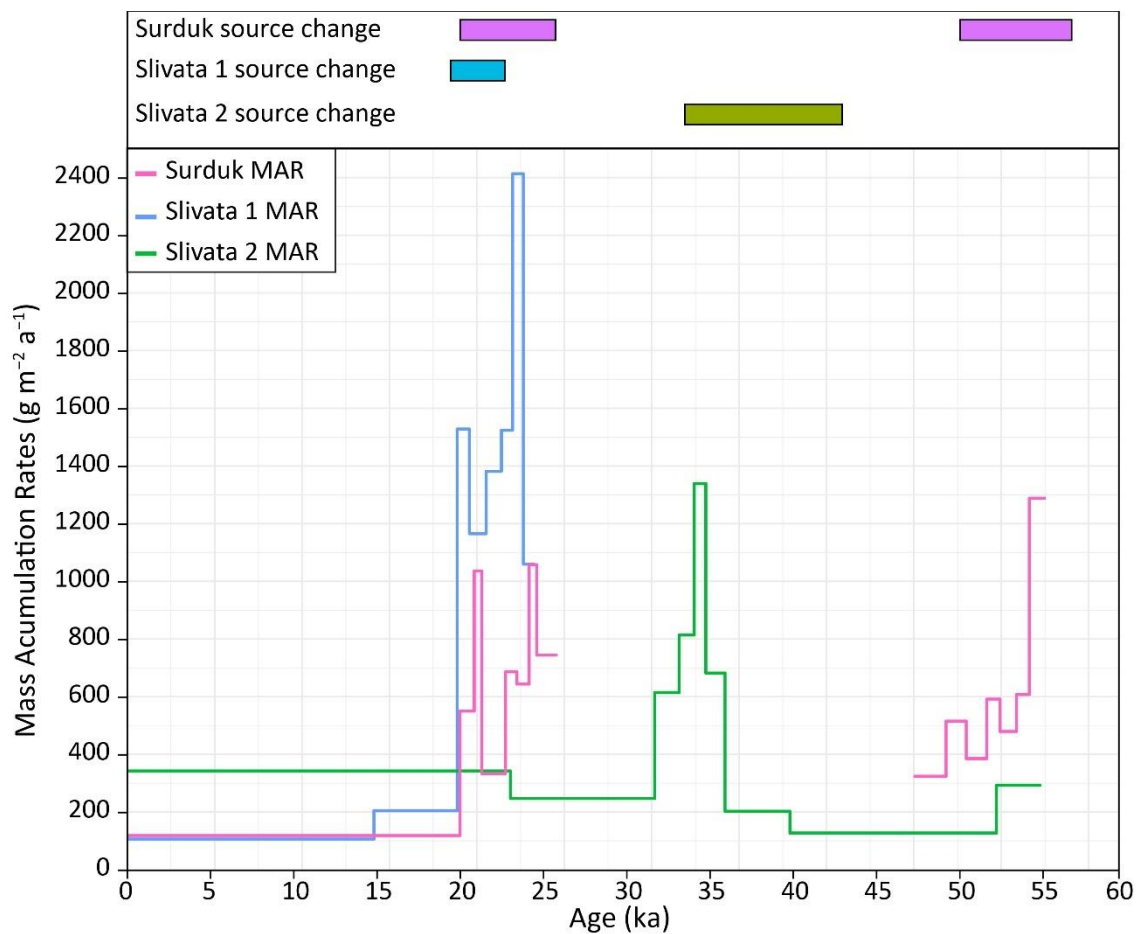


Figure 8.27 Mass accumulation rates for Surduk 2, Slivata 1, and Slivata 2 calculated based on the luminescence chronology presented in Chapters 5 and 6. Bold lines mark the location of the proposed provenance shift.

TEMPORAL VARIABILITY SUMMARY

Section 8.4 focused on examining hypothetical changes to sources of loess sediment over time, therefore addressing **Objective 2**. The analysis of temporal changes is also a foundation for exploring the drivers of sediment production, transport, and deposition on a basin scale (**Objective 5**).

A comparison of loess and palaeosol samples, which represent multiple glacial, interglacial and potentially interstadial events, shows that there are no changes in source on the orbital scale. Additionally, a comparison with Miocene and Pleistocene fluvial samples from within the Carpathian Basin also shows a homogenous source of sediment, suggesting that the sources of the sediment remained the same over the Cenozoic timescale. Consequently, it appears that climate shifts, and therefore climate, do not regulate and drive sediment production in the Carpathian Basin. Glaciers are therefore questioned as a sediment production mechanism.

On the sub-orbital scale, loess provenance also mostly remains the same. Any changes are manifested only as additional contributions or muted signals, therefore showing another proxy is needed to reconstruct these complex signals. The combination of U-Pb, Hf and luminescence chronologies identifies a shift in Erdut that is likely driven by fluvial reorganisation. At Slivata 2, in-wash of colluvial sediment is determined to be delivering “exotic” sediment to the loess profile. Finally, while a temporary source shift is identified at Slivata 1, it was not possible to determine the reason or the source for this change.

Lastly, a potential link between source changes and mass accumulation rates is presented, however at present it is not possible to identify a cause of that trend.

Chapter 9: Conclusions

This thesis has sought to understand the depositional history of the late Quaternary loess-palaeosol sequences along the Lower and Middle reaches of the Danube River. Chapters 4-6 focused primarily on luminescence dating and the environmental history of each site. The results of geochemical analysis were presented in Chapter 7. Finally, datasets produced in the previous chapters formed the basis for the discussion of loess sources in the Danube valley.

The main findings of this research are now presented in relation to the goals and research questions that formed the basis of this study and future work outlined.

9.1. *Research Question 1: What does loess in the Danube valley record in terms of accumulation timings and drivers?*

The first step taken to address this question was the production of relatively high-resolution chronology for each of the selected study sites (**Objective 1**). The environmental and climatic influences on the preserved loess-palaeosol sequences and each location could then be determined and evaluated.

Chapter 4 (submitted for publication to Journal of Quaternary Science) presented an updated chronology for the loess-palaeosol sequence at Erdut. It showed that previously published ages for this site (Galović *et al.*, 2009) are inaccurate due to the use of an uncorrected dating protocol, which did not account for the anomalous fading of feldspars. The work in the **Chapter 4** demonstrated that Erdut preserves loess accumulation over the last 180 ka, and is therefore a record of the last two glacial-interglacial cycles, rather than one. The results also confirm a fluvial event which disturbed the primary loess accumulation, and begun between 145.42 ± 6.10 ka and 146.71 ± 6.53 ka. Two other sites along the main Danube River channel, Stari Slankamen (Murray *et al.*, 2014) and Batajnica (Marković *et al.*, 2009), also show evidence of fluvial activity during the deposition of L2

loess, suggesting that the fluvial event could be more widespread. Finally, the relatively high resolution dating approach that was employed reveals that one of the loess profiles investigated as part of the Erdut sequence contains a hiatus and does not preserve fluvial sediments, implying that loess profiles are potentially heterogeneous on short spatial scales.

Chapter 5 (submitted for publication to *Quaternary Science Reviews*) presented the chronological, sedimentological (particle size and magnetic), and provenance results for a new site at Slivata. Data for this chapter was collected from two nearby profiles, which despite their geographical proximity, show distinctly different depositional histories. For the first time, sedimentological and chronological analysis was combined with provenance results to reconstruct a very complex stratigraphic and sedimentary sequence. Both profiles preserve thin soil like features, similar to the ones previously described outside the Carpathian Basin e.g. Stayky (Veres *et al.*, 2018) or Nussloch (Moine *et al.*, 2017), here interpreted as colluvial deposits rather than *in-situ* pedogenetic features. The results suggest a highly dynamic and spatially variable sedimentary system, that is strongly influenced by the local and regional drivers, rather than classically evoked distant archives of global change, e.g. Greenland and North Atlantic (e.g. Antoine *et al.*, 2009; Rousseau *et al.*, 2017).

Finally, **Chapter 6** (submitted for publication to *Boreas*) presented an updated chronology for the loess-palaeosol sequence at Surduk 2 (Serbia). It shows that a previously published luminescence chronology for Surduk 1 (Antoine *et al.*, 2009a; Fuchs *et al.*, 2008) is, as with Erdut, likely inaccurate due to the use of an uncorrected dating protocol. The profile spans ~30 ka, with primary loess deposition beginning after 56 ± 2 ka. The relatively high sampling resolution shows that Surduk 2 preserves a sedimentary hiatus that occurred after 48 ± 2 ka. Finally, the chronology formed the basis for the mass accumulation rates (MARs) calculation, which indicated that sediment accumulation periods were not

consistent in timing or rates across the Carpathian Basin, and are likely driven by local factors, such as sediment availability, geomorphological setting, topography and/or micro-climate, which are themes often not considered sufficiently in the literature.

In summary the palaeoenvironmental reconstruction of records at these three sites strongly suggests that loess accumulation and palaeosol development in the Danube river valley is strongly driven by local and/or regional factors. While the signal of glacial and interglacial climatic shift is preserved as loess and palaeosol units respectively, the individual units preserve information about the local and regional influences. Finally, this shows that loess-palaeosol deposits can provide much more paleoenvironmental information than just broad trans-continental site correlations and ties to global atmospheric or marine records.

9.2. *Research Question 2: What is the source of the loess-palaeosol deposits along the Danube River?*

Chapter 7 presents the results of bulk sample geochemical analysis, zircon U-Pb ages and Hf isotopic composition. These findings are discussed in **Chapter 8**; first the source areas for the loess-palaeosol deposits along the Danube are explored (**Objective 4**); the source shifts on the geographical scale is then investigated (**Objective 3**); and finally the temporal variability at each site is considered (**Objective 2**).

The discussion presented in section 8.2 strongly suggests that the Danubian loess deposits do not have a single lithological source, as previously advocated by research utilising a variety of approaches, including geomorphological (Jipa, 2014), geochemical (Schatz *et al.*, 2015), and heavy mineral counting (Thamó-Bozsó *et al.*, 2014). The results however indicate that all of the surrounding mountain belts (the Alps, the Bohemian Massif, the Carpathians, the Dinaric Alps, and the Balkan Mountains) are sources of the loess material

to a greater or lesser extent. While most of these sources have been proposed in some combination in the past, they have not been indicated together. The first of its kind application of zircon Hf isotopes as a provenance tool has been able to further discriminate the sources to regional mountain chains. The results provide a strong argument for significant contributions from the metamorphic rocks in the Alps (Tauern Window), Variscan granitoids (near Danube South Bohemian Massif), Apuseni and Banat Mountains (the South Carpathians), and Palaeogene igneous rocks in the Dinarics. This level of identification has not been achieved before. In terms of the most immediate source, sediment for loess deposits is sourced from the Danube's alluvium located along the river, confirming previous suggestions (e.g. Buggle *et al.*, 2008; Jipa, 2014; Újvári *et al.*, 2012).

The investigation of the source variation along the Danube valley shows that, for the most part, source is homogenous across all investigated sites, supporting the results of Buggle *et al.*, (2008), Schatz *et al.* (2015), and Újvári *et al.* (2008). Minor source shifts can nonetheless be identified. These changes do not represent a complete change of a source however, but rather a small addition (e.g. Palaeogene age Balkan and Dinaric grain in Bulgaria), or an increase/reduction in sources (e.g. smaller contributions of Gondwanian sources at Surduk). Moreover, no progressive shift is seen along the course of the Danube River that would represent a gradual input of new signatures by a tributary. In the absence of a gradual change in source, the provenance variability is likely driven by smaller, local geologies that may not be fully captured by the collected datasets, and by local sediment erosion, transport and delivery processes.

Finally, no provenance shifts through time are observed, with mostly homogenous source within individual units. The results suggest that sources remained constant and active, not only between glacial and interglacial times, but potentially over timescales beyond the Quaternary period. Any identified temporal shifts potentially represent abrupt

sedimentary change. However, in all cases the shifts do not completely change the zircon U-Pb or Hf distribution, rather they imply a change in a few components of the distribution. At Erdut the shift is likely related to the fluvial event, and therefore geomorphological and potentially watershed reorganisation. At Slivata 2 the change is likely linked to an appearance of colluvial sediments, in-washed from the nearby area, and therefore likely representing local source inputs. At Slivata 1 a temporary shift in sources is also seen, though at present it is not possible to identify the lithological source of that change beyond the beyond switching on and switching off of certain parts of the signal. In all cases the changes seem to correspond to a decrease and low stands in mass accumulation rates, though at present this link is only tentative and requires additional research.

9.3. *Research Question 3: What are the main sediment transport pathways in the context of the sedimentary basin dynamics during the late Quaternary?*

Finally, **Chapter 8** also investigates the sediment production, transport, and deposition across the Carpathian Basin by the analysis of the provenance and chronological results (**Objective 5**).

The identification of the alluvial plains as the geomorphological source of sediment for the loess-palaeosol sequences along the Danube river supports the loess formation model proposed by Smalley *et al.* (2009). This involves sediment generation, often in mountainous regions, transport via rivers and final re-distribution via aeolian processes. Despite a general acceptance of this model, loess deposits are still seen in the literature as a landform generated by far-travelled silt particles (e.g. Lehmkuhl *et al.*, 2016; Obreht *et al.*, 2015, 2019; Rousseau *et al.*, 2011). The alluvial source however indicates relatively

short-distance transport, and therefore has implications for the palaeoenvironmental interpretation of this archive and the attempts to correlate grain size data with distant Greenland ice-core records.

An absence of provenance shifts between glacial and interglacial periods suggests that climatic shifts, and therefore climate, bears no effect on the sediment production mechanism in the mountainous areas surrounding the Carpathian Basin. The identification of the Carpathians, the Dinaric, or the Balkan Mountains as sources of sediment for the loess deposits along the Danube River raises questions regarding the necessity of glacial action for sediment generation, as most of these regions are thought to have supported only small, mostly unconnected, glaciers during the LGM (Ehlers and Gibbard, 2007; Hughes and Woodward, 2017; Urdea, 2004; Urdea *et al.*, 2011). Obviously large glaciers may still be a valid production mechanism for the Alpine region, but small glaciers may also be sufficient to generate large quantities of sediment. Alternatively, other mechanisms such as periglacial processes, mass wasting, or fluvial action may have to be considered, especially as there is no obvious source change between glacial and interglacial periods.

Finally, these results highlight the important role loess deposits play in the large scale source-to-sink transport, and therefore the interplay between climate and tectonics. The calculations of sediment budgets and denudation rates assumes a direct transport from source to deposition in the marine basins (Clift *et al.*, 2008; Covault *et al.*, 2011; Tinker *et al.*, 2008). However, this shows that loess deposits act as “temporary” continental sedimentary sinks, prior to the final sediment transport to the marine basins.

9.4. Future research

This final section will focus on areas which could be extended and build upon based on the results presented in this thesis.

This work focused on building a number of high sampling resolution chronologies and large provenance datasets. It was beyond the scope of this thesis to investigate any links between the two. The large body of work committed to understanding and using luminescence properties as discussed and summarised by Gray *et al.* (2019) in most cases has not been compared with the results of traditional provenancing techniques such as geochemistry. Paper 3 (**Chapter 6**) highlighted that such a link between luminescence signals, for example the fast ratio or fading and bulk sample geochemistry, may exist. Fitzsimmons, (2011) and Pietsch *et al.* (2008) advocated the use of test dose sensitivity changes as a provenancing tool, while there are a number of geochemical ratios or bulk sample normalising techniques that could be explored in relation to the existing U-Pb and Hf isotopic provenance data. The wealth of data gathered as a part of this thesis would allow for a relatively fast comparison between those two provenancing tools by simple reanalysis and exploration of the existing datasets

One of the criteria that resulted in the selection of sites in Croatia and Serbia (Erdut and Surduk) for this project was the existing sedimentological and luminescence data. The collected samples for this project were meant to supplement the chronology and draw on the published proxy data to better interpret the provenance data and sedimentological history of each site. The chronological results presented in **Chapters 4 and 6** contest previously published chronological work for both sites (Fuchs *et al.*, 2008; Galović *et al.*, 2009). Additionally stratigraphic discrepancies noted in the field at Erdut between the work published by (Galović *et al.*, 2009) mean the previously published data cannot be used. These challenges, in combination with the obstacles encountered in the field in

relation to sampling (which meant that parts of the profiles were not sampled), demand resampling at both sites. Samples should be collected for detailed sedimentological analysis (e.g. ~2 cm) such as particle size and magnetic susceptibility. At Erdut luminescence samples should be collected to capture the last glacial-interglacial period but also to provide a better timing for the fluvial event.

Unlike Erdut and Surduk, Slivata (**Chapter 5**) is a new site and considerable effort went into characterising the sedimentological record of this site. However, the upper part of the Slivata 2 profile was not sampled due to logistical constraints. The upper part of Slivata 2 preserves an unusual ~4 meters thick palaeosol unit and does not fit stratigraphically with other nearby profiles. Therefore, more time should be invested to understand the environmental record at this site. This would include sampling at high resolution for particle size and magnetic susceptibility the upper 6 meters of the profile. The nature of the unusually thin palaeosol units, their origin and depositional history, could be investigated through micromorphology. Further during the field visit large dunes capped by loess were observed along the course of the Danube. These should be sampled for provenance and luminescence as these could provide additional information about sediment transport and deposition. Further investigation into this under sampled region is crucial to gain a more complete picture of the environmental history and change of this upper Lower Danube region.

While there are a number of tools available for assessing the provenance signal in zircons the minimum number of grains required per analysis is still contested and varies between 10's and 100's (Andersen, 2005; Licht *et al.*, 2016; Vermeesch, 2004). Lately phrases such as “high-end zircon datasets” have also crept into language at conferences without any concrete description of the numbers required to achieve such datasets. It is widely accepted that the number of grains measured depends on the research question and the

rock type, i.e. if the aim is to characterise the timing of a specific igneous event then 10-30 grains may be sufficient. However, in sedimentary rock such as loess, which likely comprises multiple sources but also experiences multiple recycling stages, it is agreed that more grains are needed. Vermeesch (2004) argues that 117 grains will avoid missing out populations >5%, however as with a geological setting each loess site/sample will need a separate statistical assessment on when the KDE distribution “becomes” stable, stops changing shape and therefore becomes representative. There does not seem to be a tool available that will test the stability of the distribution. Such tool could be used to verify if more analyses were needed for each individual sample.

Another area that requires more focus is the grain size and its influence of the zircon age KDE distributions and Hf isotopes diagrams. At present the U-Pb and Hf analyses include a variety of grain sizes as only grains below 20 μm were removed. There is a lot of debate over the distance travelled by loess particles prior to their deposition, from long distance >1000s km (e.g. Tarim Basin in the context of Chinese loess (Jahn *et al.*, 2001; Maher *et al.*, 2009), or Sahara for Carpathian loess (Longman *et al.*, 2017; Stuut *et al.*, 2009; Varga *et al.*, 2016)) to much shorter floodplain sources (Obreht *et al.*, 2014). It is therefore not known if there are any differences between dominant silt (which is thought to be the most distantly travelled), and sand (most likely travelled over a short distance through saltation) size fractions. If there are any large differences between these two fractions it could suggest different source regions and different modes of transport for the two fractions. The vast quantity of data collected during this research would allow to assess this question relatively quickly. CL images could be used to provide grain size information for all collected datasets and investigate any potential grain size variation.

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Appendices

Appendix A – Author contributions

Most of the research conducted for this thesis was my own (KF), however some contributions were made by the co-authors for the three submitted papers.

Sampling in Croatia and Serbia in the 2016 field season was conducted by KF, Dr Adriano Banak (AB), and Prof Slobodan Markovic (SB). Sampling in Bulgaria in 2017 was carried out by KF, Prof Dave Thomas (DT), Dr Julie Durcan (JD) and Dr Daniel Veres (DV). Luminescence sample preparation, laboratory analysis, and dating was conducted by KF after initial guidance from JD. Provenance sample preparation, and laboratory analysis was conducted by KF after initial guidance from Dr Ian Millar (IM). Individual author contributions for the papers are detailed below:

Paper 1 (Chapter 4)

AB assisted KF with sample collection in the field. All laboratory analysis, including sediment dating and particle size analysis, writing, and figure and table preparation for Paper 1 was conducted by KF. JD assisted with experiments planning, and discussion of results. JD, DT and AB provided comments prior to paper submission.

Paper 2 (Chapter 5)

KF, DT, JD, DV conducted fieldwork in Bulgaria. Laboratory analysis, including sediment dating, provenance, sedimentological, writing, and figure and table preparation was conducted by KF. JD and IM assisted with luminescence and provenance experiments planning, and discussion of results. Alma Piermattei (AP) and Christine Lane (CL) assisted with tephra analysis, and discussion of results. All authors contributed to discussion of interpretations and manuscript preparation following first drafting by KF. JD, DT, IM, DV, AP and CL provided comments prior to paper submission.

Paper 3 (Chapter 6)

SB assisted KF with sample collection in the field. All laboratory analysis, including sediment dating, writing, and figure and table preparation for Paper 3 was conducted by KF. JD assisted with luminescence experiments planning, and discussion of results. JD, DT and SM provided comments prior to paper submission.

Appendix B – Potential sites considered for this study

Table A.1. All sites screened using criteria in Section 2, as potential sites for this study (See Chapter 3, Figure 3.2 for location). The thickness, glacial-interglacial cycle, location, existing chronology, and existing proxies were taken into consideration before being assigned red (inappropriate), orange (not ideal, but has potential) and green (preferable) class.

*G-I – glacial-interglacial

	Site	Country	Potential source	Depth (m)	G-I cycle*	Along Danube	Confluence	Chronology	Proxies	Existing provenance	Access	Class
1	Krems	Austria	Alpine	5.5	No; last 40 ka	No; Krems River	N/A	TL + OSL	micromorphology, grain size, TOC, major elements, MS	U-Pb zircon, Hf zircon, rutile geochemistry	Ok	
2	Wels	Austria	Alpine	12.5	Yes; 277 ka	No; Traun	N/A	IRSL	MS	U-Pb zircon, Hf zircon, rutile geochemistry	Brickyard-may need permit	
3	Stillfried	Austria	Alpine	10	No; last 40 ka	No; Morava River	N/A	TL + IRSL	pedology, MS, grain size, CaCO ₃ , micromorphology	major and trace elements, Sr-Nd	Ok	
4	Stratzing	Austria	Alpine	19.2	No; last 30 ka	No; Krems River	N/A	IRSL	N/A	U-Pb rutile, rutile geochemistry	Ok	
5	Harletz	Bulgaria	Carpathian/Balkan Mts	20	Yes; in 4m	No; Ogosta River	Jiu	OSL	particle size MS, TOC	No	Good	

6	Koriten	Bulgaria	Carpathian/ Balkan Mts	34	Yes; in 8m	No	N/A	No	MS	No	No exact location	
7	Ljubenovo	Bulgaria	Balkan Mts	62	Yes; in 10m	No	N/A	No	MS	No	No exact location	
8	Orsoja	Bulgaria	Carpathian/ Balkan Mts	15	Yes; in 15m	Yes	Iron Gorge	No	MS	No	Good	
9	Viatovo	Bulgaria	Carpathian/ Balkan Mts	21	Yes; in 4m	No	N/A	No	MS, grain size, CaCO ₃ , organic content	No	No exact location	
10	Erdut	Croatia	Scandinavian/ Alpine	22	Yes; last 125 ka	Yes	Drava	IRSL	grain size, TOC, CaCO ₃ , pedology, mineralogical composition	mineralogical composition, major minor elements	Good; may need permit	
11	Šarengrad	Croatia	Scandinavian/ Alpine	16.2	Yes; last 125 ka	Yes	Drava	IRSL	grain size, TOC, CaCO ₃ , pedology, mineralogical composition	mineralogical composition, major minor elements	Good	
12	Vukovar	Croatia	Scandinavian/ Alpine	22.5	Yes; last 182 ka	Yes	Drava	IRSL	pedology	No	Good	
13	Zmajevac	Croatia	Scandinavian/Al pine	28	Yes; last 217 ka	Yes	N/A	IRSL	grain size, TOC, CaCO ₃ , bulk clay mineralogy, malacological	Sr-Nd, U-Pb zircons, mineralogical composition, major minor elements,	Good	
14	Červený Kopec	Czech Republic	Other	8	No info	No	N/A	TL	MS	No	Good	
15	Dolní Věstonice	Czech Republic	Other	17	Yes; 146 ka	No	N/A	OSL	pedology, grain size, 13C, organic carbon, CaCO ₃ , mollusc	No	Good	
16	Sedlec Suchdol	Czech Republic	Other	7.5	Yes; 90 ka	No	N/A	TL +IRSL	stratigraphy	No	No exact location	

17	Kutna Hora	Czech Republic	Other	5.5	Yes; 70 ka	No	N/A	TL+IRSL	stratigraphy	No	No exact location	
18	Lechovice	Czech Republic	Other	4	Yes; at least 55.8 ka	No	N/A	TL+IRSL	stratigraphy	No	No exact location	
19	Bulhary	Czech Republic	Other	3.5	Yes; at least 78.5ka	No	Moravian Gap	TL +IRSL	stratigraphy	No	No exact location	
20	Modrice	Czech Republic	Other	4	Yes; 620ka	No	N/A	TL +IRSL	stratigraphy	No	No exact location	
21	Albertirsa	Hungary	Scandinavian/ Alpine/ Carpathian	12	Yes; min 93ka	No	N/A	TL +IRSL	grain size, CaCO ₃ , organic content,	No	Good	
22	Basaharc	Hungary	Scandinavian/ Alpine/ Carpathian	21	Yes; min 140ka	Yes	Moravian Gap	TL +IRSL	pedology, pollen	Sr-Nd, U-Pb zircons, bulk clay mineralogy,	Good	
23	Dunaújváros	Hungary	Scandinavian/ Alpine	N/A	Unknown	Yes	Moravian Gap	No	CaCO ₃ , Organic content, pedology	heavy mineral assemblage	Ok	
24	Katymar	Hungary	Scandinavian/ Alpine/ Carpathian	9	No; last 30ka	No	N/A	14C	grain size; pollen	No	Ok; may need permit	
25	Madaras	Hungary	Scandinavian/ Alpine/ Carpathian	10	No	No	N/A	14C	pollen, mollusc	No	Ok; may need permit	
26	Majs	Hungary	Scandinavian/ Alpine	6	Unknown	Yes	N/A	No	LOI, Chemical Index Alteration	major and trace elements,	No exact location	
27	Mende	Hungary	Scandinavian/ Alpine/Carpathian	33	Yes; last 250ka	No	N/A	No	pedology, bulk clay mineralogy	Sr-Nd, U-Pb zircons,	Ok; may need permit	

28	Nagynyárád	Hungary	Scandinavian/ Alpine	5.5	Unknown	Yes	N/A	No	LOI, Chemical Index Alteration	major and trace elements,	No exact location	
29	Paks	Hungary	Scandinavian/ Alpine	46	Yes; last 287 ka	Yes	N/A	IRSL	pedology, bulk clay mineralogy,	Sr-Nd, U-Pb zircons, major and trace elements, heavy mineral assemblage	Good	
30	Süttő	Hungary	Scandinavian/ Alpine	17	Yes; last 138ka	Yes	Moravian Gap	IRSL + 14C	AAR, MS, CaCO ₃ , TOC	heavy mineral assemblage, major and trace elements,	Good	
31	Töttös	Hungary	Scandinavian/ Alpine	3.5	Unknown	Yes	N/A	No	LOI, Chemical Index Alteration	major and trace elements,	No exact location	
32	Dunaszekcső	Hungary	Scandinavian/ Alpine	17	Yes; last 150 ka	Yes	N/A	OSL + 14C+ IRSL	grain size	No	Good	
33	Tokaj	Hungary	Carpathian	15	No; last 60ka	No; Tisza River	N/A	OSL	Stratigraphy, TOC, 13C, 15N, MS	major and trace elements, Sr- Nd	Good	
34	Râmnicu Sărat	Romania	Carpathian	2.5	No; min 17.6 ka	No	N/A	OSL	MS	No	Good	
35	Căciulătești	Romania	Carpathian	4	No; last 40ka	No; Jiu River	N/A	OSL	tephra	No	Good	
36	Daneasa	Romania	Carpathian	6	No; last 40ka	No; Olt River	N/A	OSL	tephra	No	Good	
37	Draganesti- Olt	Romania	Carpathian	4.5	No; last 40ka	No; Olt River	N/A	OSL	tephra	No	Good	
38	Giurgiu	Romania	Carpathian/ Balkan Mts	N/A	No; last 20 ka	Yes	Jiu & Olt	IRSL	None	No	No exact location	

39	Lunca	Romania	Carpathian	4.5	No; last 40ka	No; Olt River	N/A	OSL	tephra	No	Good	
40	Mircea Voda	Romania	Carpathian/ Balkan Mts	30	Yes; last 279 ka	No	N/A	OSL	MS, MAP, grain size,	major and minor elements, REE	Good	
41	Mostiștea	Romania	Carpathian/ Balkan Mts	6	Yes; last 144 ka	Yes	N/A	OSL	MS	No	Good	
42	Tuzla	Romania	Other	20	Yes; last 250 ka	No; Black Sea	N/A	IRSL	None	No	Good	
43	Costinești	Romania	Other	5	Yes; last 150ka	No; Black Sea	N/A	OSL	MS	No	Good	
44	Durankulak	Romania	Other	14	Yes	No; Black Sea	N/A	No	MS	No	Good	
45	Vlasca	Romania	Carpathian/ Balkan Mts	10	No; last 40 ka	Yes	N/A	No	MS, grain size	major and minor elements,	Good	
46	Rasova	Romania	Carpathian/ Balkan Mts	7.5	No; last 50 ka	Yes	N/A	OSL	MS	No	Good	
47	Urluia	Romania	Carpathian/ Balkan Mts	14	Yes; dated last 60 ka	No	N/A	OSL	tephra, MS, grain size	major and minor elements,	Good	
48	Irig	Serbia	Scandinavian/ Alpine	8	Yes	No	N/A	No	MS, grain size, malacology, pedology, AAR, CaCO ₃	No	Good	
49	Miseluk	Serbia	Scandinavian/ Alpine	6.5	Yes	Yes	Drava	No	grain size, MS, AAR, malacology	No	Good	
50	Petrovardin	Serbia	Scandinavian/ Alpine	8	Yes	Yes	Drava	No	MS, grain size, malacology, CaCO ₃ ,	No	Good	
51	Ruma	Serbia	Scandinavian/ Alpine	20	Yes	No	N/A	No	grain size, MS, AAR, malacology,	bulk mineral composition	Good	

52	Crvenka	Serbia	Scandinavian/ Alpine	12	Yes; last 114 ka	No	N/A	OSL	MS, pedology, grain size, TOC, $\delta^{13}C$, $\delta^{15}N$, biomarkers	major and minor elements	Good	
53	Batajanica	Serbia	Carpathian	40	Yes	Yes	Tisza	No	MS, pedology, grain size,	major and minor elements, REE	Good	
54	Mošorin	Serbia	Carpathian	60	Yes	No; Tisza River	N/A	IRSL	grain size, MS, pedology	No	Good	
55	Orlovat	Serbia	Carpathian	10	Yes; last 159 ka	No	N/A	OSL	grain size, MS, pedology	No	Good	
56	Stari Slankamen	Serbia	Carpathian	40	Yes; last min 330 ka	Yes	Tisza	IRSL	MS, pedology, mineralogical composition, grain size,	major and minor elements, REE	Good	
57	Susek	Serbia	Scandinavian/ Alpine	10	Yes	Yes	Drava	No	MS, grain size, malacology	No	Good	
58	Surduk	Serbia	Carpathian	10	Yes; last 120 ka	Yes	Tisza	OSL + pIRIR	MS, pedology, grain size, TOC,	No	Good	
59	Titel	Serbia	Carpathian	19.8	Yes	No; Tisza River	N/A	IRSL	grain size, MS, major elements, pedology	No	Good	
60	Belotinac	Serbia	Balkan Mts	8	No	No; Great Morava River	N/A	IRSL	MS, colour, grain size, organic content, C & N isotopes	No	Good	
61	Mošorin Veliki Surduk	Serbia	Carpathian	11	Yes	No; Tisza River	N/A	OSL	MS	No	Good	

Appendices C, D, E, F and G

Appendices C-G are presented in an electronic form attached to the thesis. These contain as follows:

C) Sedimentological results Bulgaria

D) Raw compositional tephra results

E) Raw zircon U-Pb data

F) Raw zircon Hf data

G) Bulk sample geochemistry

Appendix I – U-Pb source metadata

Sample name	n	Nature	Reference
<u>Loess</u>			
<i>Erdut</i>			
CRO16/2/9	114	Palaeosol (S2)	This study
CRO16/2/10	130	Fluvial unit within L2	This study
CRO16/2/11	66	Fluvial unit within L2	This study
CRO16/2/12	118	Fluvial unit within L2	This study
CRO16/2/15	137	Palaeosol (S1)	This study
CRO16/2/27	112	Loess (L2)	This study
CRO16/2/21	104	Loess (L2)	This study
<i>Slivata</i>			
BUL17/1/1	121	Palaeosol (S0)	This study
BUL17/1/3	115	Loess (L1)	This study
BUL17/1/5	114	Loess (L1)	This study
BUL17/1/7	124	Loess (L1)	This study
BUL17/1/9	117	Loess (L1)	This study
BUL17/1/11	117	Loess (L1)	This study
BUL17/2/1	107	Palaeosol (S1)	This study
BUL17/2/3	90	Palaeosol - loess complex (L1)	This study
BUL17/2/5	86	Palaeosol - loess complex (L1)	This study
BUL17/2/7	86	Palaeosol - loess complex (L1)	This study
BUL17/2/9	115	Palaeosol - loess complex (L1)	This study
BUL17/2/11	117	Palaeosol - loess complex (L1)	This study
<i>Surduk</i>			
SER16/2/1	97	Loess (L1)	This study
SER16/2/3	109	Loess (L1)	This study

	SER16/2/4	101	Loess (L1)	This study
	SER16/2/6	118	Loess (L1)	This study
	SER16/2/7	113	Loess (L1)	This study
	SER16/2/9	115	Loess (L1)	This study
	SER16/2/20	116	Loess (L1)	This study
	SER16/2/21	115	Loess (L1)	This study
	SER16/2/22	109	Loess (L1)	This study
	SER16/2/23	116	Loess (L1)	This study
<i>Paks</i>				
	Pa-L1	70	Loess (L1)	Újvári <i>et al.</i> 2012
<i>Mende</i>				
	Me-L1	69	Loess (L1)	Újvári <i>et al.</i> 2012
<i>Basaharc</i>				
	Bh-L3	62	Loess (L3)	Újvári <i>et al.</i> 2012
<i>Zmajevac</i>				
	Zm-L1	72	Loess (L1)	Újvári <i>et al.</i> 2012
<i>Krems</i>				
	K23	31	Loess (L1)	Újvári <i>et al.</i> 2015
<i>Wels</i>				
	A16	14	Loess (L1)	Újvári <i>et al.</i> 2015
<i>Stratzing</i>				
	S1	49	Loess (L1)	Újvári <i>et al.</i> 2015
<u>Rivers</u>				
<i>Danube</i>				
	Turnu	116	Modern Danube	Duceat <i>et al.</i> 2018
	Tulcea	102	Modern Danube	Duceat <i>et al.</i> 2018
	Braila	101	Modern Danube	Duceat <i>et al.</i> 2018
<i>Drava</i>				
	CRO16/1/1	122	Modern Drava	This study
<i>Olt</i>				
	Olt	130	Modern Olt	Duceat <i>et al.</i> 2018

Jiu

Jiu 118 Modern Jiu Duceat *et al.* 2018

Tisza

SER16/1/1 132 Modern Tisza This study
Tisza 132 Modern Tisza Duceat *et al.* 2018

Sebeşel

6-PSR 90 Modern Sebeşel Soica et al 2016
5-PS 84 Alluvial terrace deposits Soica et al 2016

Siret

Siret 132 Modern Siret Duceat *et al.* 2018

Fluvial sands

Bh-Fs 66 Late Pleistocene fluvial sand Újvári *et al.* 2012
Dp-Ps 64 Late Miocene fluvial sand Újvári *et al.* 2012

Deserts

Egypt

WD03C 193 Western Desert - Great Sand Sea Fielding *et al.* 2018
WD07C 242 Western Desert - Great Sand Sea Fielding *et al.* 2018

Eastern Alps

Central Tuern Window

1168 17 Coarse-grained garnetiferous metagabbro Kebede et al 2005
1173 6 Banded amphibolite Kebede et al 2005
1170 17 Medium-grained amphibolite Kebede et al 2005
1169 8 Two-mica granite gneiss Kebede et al 2005
1171 5 Banded porphyroblastic biotite schist Kebede et al 2005
1174 3 Banded garnetiferous leucocratic gneiss Kebede et al 2005
1156 5 Meta-agglomerate Kebede et al 2005
RDT 6 Rounded detrital zircons Kebede et al 2005
AHO2 55 Ahorn gneiss Petra et al 2011
GKAR 50 Grierkar - meta-rhyodacite (Austria) Petra et al 2011
SNA1 21 Schönach valley - meta-andesite (Austria) Petra et al 2011

	VE1	21	Vennatal meta-rhyolite (Austria)	Petra et al 2011
<i>Tuern Window</i>				
	TUX	30	Schlegeis water reservoir - granodiorite-gneiss (Austria)	Petra et al 2011
	PJF	42	Pfitscher Joch - meta-rhyolite (Italy)	Petra et al 2011
<u>Bohemian Massif</u>				
<i>Bohemian Massif 1 (BH1)</i>				
	PJ1/3	52	Žitce-Hluboš-Fm. (L Cambrian) - Sandstone	Drost et al 2011
	CB3	52	Chumava-Baština-Fm. (L/M Cambrian) - Sandstone	Drost et al 2011
	Oh3	66	Ohrozenice-Fm. (M/U Cambrian) - Sandstone	Drost et al 2011
	TrTo3	47	Třenice Fm. (L Ordovician) - Sandstone	Drost et al 2011
	Tocnik	47	Třenice Fm. (L Ordovician) - Sandstone	Drost et al 2011
	M1-10	10	Medenec - orthogneisses	Kosler et al 2004
	K1-5	3	Klinoves -orthogneisses	Kosler et al 2004
	C1-11	10	St Catherines Dome - orthogneisses	Kosler et al 2004
	OKR	9	Křivoklát-Rokycany Volcanic Complex - Rhyolite	Drost et al 2004
	HT-99-1	2	Mariaske Lazne Complex	Timmermann et al 2004
<i>Bohemian Massif 2 (BH2)</i>				
	LiBS2	50	Libeň Fm. (U Ordovician) - Sandstone	Drost et al 2011
	Roblin	70	Srbsko Fm. (M Devonian) - Greywacke	Drost et al 2011
	BL	69	Kralupy-Zbraslav Group - Greywacke	Drost et al 2011
	Dob	41	Štěchovice Group - Greywacke	Drost et al 2011
	KoLeD1d	54	Kosov Fm. (U Ordovician) - diamicton	Drost et al 2011
	LeZb6	48	Letná Fm. (U Ordovician) - Sandstone	Drost et al 2011
	Dobris	10	Štěchovice Group - Greywacke	Drost et al 2004
	SPI-1	9	Drosendorf unit- Spitz gneiss	Friedl et al 2004
<i>Western Bohemia Massif (WBM)</i>				
	HT-99-4a	7	Mariaske Lazne Complex	Timmermann et al 2004
	HT-99-6	9	Mariaske Lazne Complex	Timmermann et al 2004

HT-99-9	10	Mariaske Lazne Complex	Timmermann et al 2004
HT-99-11	5	Mariaske Lazne Complex	Timmermann et al 2004
HT-99-13	6	Mariaske Lazne Complex	Timmermann et al 2004
HBW11-1	15	Leucosome	Teipel et al 2004
HBW1-1	18	Metagranitoid	Teipel et al 2004
HBW31-2	13	Metagranitoid	Teipel et al 2004
SOW33-6	11	Metabasite	Teipel et al 2004
GFO-1	11	Gföhl unit - Gföhl gneiss	Friedl et al 2004
GRA-1	11	Gföhl unit - Granulite	Friedl et al 2004

Bavarian Pfahl (BP)

PA8-2	11	Metarhyolite	Teipel et al 2004
PA9-3	13	Metabasite	Teipel et al 2004
PA11-1	17	Metarhyolite	Teipel et al 2004

South Bohemia Massif (SBM)

Li-3	22	Lisov Granulite Massif - Diaoritic granulite	Janousek et al 2006
Li-4	24	Lisov Granulite Massif - Tonalitic granulite	Janousek et al 2006
Sie12	43	Migmatite/Palite Complex	Siebel et al 2012

Bükk Mts.

BN	61	Balvany North	Zajzon et al 2011
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Moldanubian Zone

Varied Unit (MZVU)

BPN-1	38	Miličín - Gneiss	Kosler et al 2014
BPN-2	45	Těchobuz - Gneiss	Kosler et al 2014
BPN-5	75	Nihošovice - Gneiss	Kosler et al 2014
BPN-9	69	Šebkovice - Gneiss	Kosler et al 2014
D-92-ZR2	48	Uherčice - Gneiss	Kosler et al 2014
BPN-7	76	Černá - Gneiss	Kosler et al 2014
UD-6	65	Štěpánov - Schist	Kosler et al 2014

Monotonous Unit (MZMU)

BPN-4	86	Neznašov - Gneiss	Kosler et al 2014
BPN-6	62	Ktiš - Gneiss	Kosler et al 2014
BPN-8	74	Police - Gneiss	Kosler et al 2014

Gföhl Unit (MZGU)

D-540-ZR4	81	Raabs an der Thaya - Gneiss	Kosler et al 2014
D-540-ZR5	49	Raabs an der Thaya - Gneiss	Kosler et al 2014

Moravo-Silesian Zone (MSZ)

BPN-10	84	Květnice - Conglomerate	Kosler et al 2014
BPN-11	61	Brno - Conglomerate	Kosler et al 2014
THA-1	9	Thaya batholith - Eggenburg metagranite	Fiedl et al 2004
BIT-1	19	Gföhl unit - Bittesch gneiss	Fiedl et al 2004
An	5	Silesian Unit	Burda et al 2019
Bu1	9	Silesian Unit	Burda et al 2019

South Bohemian Batholith (SBB)

NAT-1	13	South Bohemian batholith - Natschlag migmatite	Fiedl et al 2004
SAR-1	8	South Bohemian batholith- Weinsberg granite	Fiedl et al 2004
SPI-1C	7	Drosendorf unit- Spitz gneiss	Fiedl et al 2004
BIT1C	8	Gföhl unit - Bittesch gneiss	Fiedl et al 2004

Miscellaneous

UD-7	70	Lhota - Gneiss	Kosler et al 2014
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Western Carpathians

South Gemeric Unit (SGU)

SM	17	Rozanova Frm. Rhyolite-Dacite	Vozarova et al 2009
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South Gemeric Unit (SGU 2)

	GZ-VF	45	Vlachovo Formation - metavolcaites	Vozarova et al 2010
	GZ-BP	37	Bystry Potok Form. - metavolcaites	Vozarova et al 2010
	LA88	33	Hamor Formation	Vozarova et al 2013
<i>Rakovec Group (RG)</i>				
	GZ-25	42	Smrecinka Formation - deep-water basin facies	Vozarova et al 2019
	GZ-24	35	Smrecinka Formation - deep-water basin facies	Vozarova et al 2013
<i>North Gemericum Unit (NGU)</i>				
	LA81	43	Hradok Formation - turbidite	Vozarova et al 2013
	LA66	11	Petrova Hora Formation - alluvial lacustrine facies	Vozarova et al 2013
	GZ20	11	Rudnany Formation - fan delta	Vozarova et al 2013
	LA69	19	Novoveska Huta Formation - alluvial	Vozarova et al 2013
<i>Hronicum Formation (HF)</i>				
	NTZ-1	34	Nižná Boca Fm	Vozarova et al 2018
	NTZ-2	23	Malužiná Fm. First megacycle	Vozarova et al 2018
	NTZ-3	23	Malužiná Fm. Second megacycle	Vozarova et al 2018
	NTZ-4	18	Malužiná Fm. Third megacycle	Vozarova et al 2018
	MK-31	25	Malužiná Fm. Second megacycle	Vozarova et al 2018
<u>South Carpathians</u>				
<i>Apuseni Mountains (AP)</i>				
	189	76	Metamorphic grade quartzite	Balintoni et al. 2009
	107	87	Metamorphic grade quartzite	Balintoni et al. 2009
<i>Apuseni Mountains Magmatic Arc (AMMA)</i>				
	DG077-115	777	Late Cretaceous igneous rocks	Gallhofer et al 2015
<i>Banat Mountains Magmatic Arc (BMMA)</i>				
	DG001-076	1063	Late Cretaceous igneous rocks	Gallhofer et al 2015
<i>Sebeş–Lotru terrane (SLT)</i>				

283	39	Metaigneous rocks - orthogneiss	Balintoni <i>et al.</i> 2010
271	20	Metaigneous rocks - augen gneiss	Balintoni <i>et al.</i> 2010
272	9	Metaigneous rocks - granite-gneiss	Balintoni <i>et al.</i> 2010
273	25	Metaigneous rocks - orthogneiss	Balintoni <i>et al.</i> 2010
275F	23	Metaigneous rocks - biotite granite	Balintoni <i>et al.</i> 2010
274	59	Metasedimentary rock - paragneiss	Balintoni <i>et al.</i> 2010
279	25	Metaigneous rocks - leucosome	Balintoni <i>et al.</i> 2010
275	35	Metaigneous rocks - granitoid	Balintoni <i>et al.</i> 2010
4-TR	80	Turnu Formation	Soica et al 2016

Lainici Păiuș (LP)

R3	83	Paragneiss	Balintoni and Balica 2013
R4	165	Paragneiss	Balintoni and Balica 2013
331	55	Dyke	Balintoni and Balica 2013
R7	75	Paragneiss	Balintoni and Balica 2013
10-401	18	Granite	Balintoni and Balica 2013
10-404	25	Dyke	Balintoni and Balica 2013
231	119	Fagaras terrane	Balintoni <i>et al.</i> 2009

Dragsan Terrane (DG)

R11	33	Valea de Brazi rhyolite	Balintoni and Balica 2013
330	77	Dobrota paragneiss	Balintoni and Balica 2013
261	79	Făgețel augen gneiss	Balintoni and Balica 2013

Bucegi Formation (BF)

1-DG	84	Bucegi Formation, Upper Member	Stoica et al 2016
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	2-BB	84	Bucegi Formation, Upper Member	Stoica et al 2016
	3-SP	94	Bucegi Formation, Middle Member	Stoica et al 2016
<i>Miscellaneous</i>				
	152b	102	Păiușeni unit - chlorite schist	Balintoni et al. 2009
	219	88	Caras unit	Balintoni et al. 2009
<u>Balkan Mountains</u>				
<i>Pirgadikia Terrane (PT)</i>				
	SM201	60	Serbo-Macedonia Massif - Metaquartzite	Meinhold et al 2010
	SM205	48	Serbo-Macedonia Massif - Metaquartzite	Meinhold et al 2010
<i>Vertiskos Terrane (VT)</i>				
	SM157	60	Serbo-Macedonia Massif - Garnetiferous mica schist	Meinhold et al 2010
	SM151	58	Serbo-Macedonia Massif - Garnet-bearing biotite gneiss	Meinhold et al 2010
<i>Rhodope Metamorphic Complex (RMC)</i>				
	KUL-22	42	Orthogneiss	Georviev et al 2016
	KUL-21	36	Schist	Georviev et al 2016
<i>Rhodope Basement (RB)</i>				
	KUL-6	25	Orthogneiss	Georviev et al 2016
<i>Teshovo Pluton (TP-PPC)</i>				
	BG147	27	Pangaion-Pirin Complex - Teshovo (South Pirin) Pluton	Jahn-Awe et al 2010
	BG157	26	Pangaion-Pirin Complex - Teshovo (South Pirin) Pluton	Jahn-Awe et al 2010
<i>Spanchevo Pluton (SP-RT)</i>				
	BG161	13	Rhodope Terrane - Spanchevo Pluton	Jahn-Awe et al 2010
<i>Dolno Dryanovo Pluton (DDP-RT)</i>				
	BG16	3	Rhodope Terrane - Dolno Dryanovo Pluton	Jahn-Awe et al 2010
	BG15	13	Rhodope Terrane - Dolno Dryanovo Pluton	Jahn-Awe et al 2010
<u>Dinares</u>				
<i>Moslavačka Gora (MG)</i>				
	BS2	20	Central Granite	Starijaš et al 2010
	BS3	18	Garic- metagranite	Starijaš et al 2010

	BS21a	14	Garic- metagranite	Starijaš et al 2010
	BS26	35	Central Granite	Starijaš et al 2010
	BS36G	22	Jelen - metagranite	Starijaš et al 2010
<i>Kopaonik Oligocene</i>				
	11	6	Kopaonik -Monzonite	Schefer et al 2011
	16	6	Drenje - Granodiorite	Schefer et al 2011
	21	6	Željin - Granodiorite	Schefer et al 2011
	30	6	Željin - Diorite	Schefer et al 2011
<i>Kopaonik Miocene</i>				
	509	7	Golija - Granodiorite	Schefer et al 2011
	513	6	Polumir - Granite	Schefer et al 2011
<i>Jastrebac Mountains (JM)</i>				
	JAS09	34	Sava Zone - granodiorites	Erak et al 2017

Basements and sedimentary covers

North Dobrogea

	12-500	66	Beştepe Formation	Balintoni and Balica 2016
	12-503	62	Beştepe Formation	Balintoni and Balica 2016
	12-512	63	Măcin unit	Balintoni and Balica 2016
	344	80	Megina Group	Balintoni and Balica 2016
	171-GPS	90	Megina Group	Balintoni and Balica 2016

	167-GPS	25	Orliga Group	Balintoni and Balica 2016
	168-GPS	34	Orliga Group	Balintoni and Balica 2016
	337	22	Boclugea Group	Balintoni and Balica 2016
	335	15	Orliga Group	Balintoni and Balica 2016
	12-495	54	Altîn Tepe Group	Balintoni and Balica 2016
	12-496	82	Altîn Tepe Group	Balintoni and Balica 2016
	172-GPS	63	Altîn Tepe Group	Balintoni and Balica 2016
<i>Tulcea Unit</i>				
	12-498	72	Horia Formation	Balintoni and Balica 2016
	12-499	91	Horia Formation	Balintoni and Balica 2016
<i>East Moesia</i>				
	5082	81	Drill core samples	Balintoni and Balica 2016
	GM-087	94	Drill core samples	Balintoni and Balica 2016

Appendix J – Hf source metadata

Sample name	n	Nature	Reference
<u>Loess</u>			
<i>Erdut</i>			
CRO16/2/9	68	Palaesol (S2)	This study
CRO16/2/10	125	Fluvial unit within L2	This study
CRO16/2/11	65	Fluvial unit within L2	This study
CRO16/2/12	120	Fluvial unit within L2	This study
CRO16/2/15	130	Palaesol (S1)	This study
CRO16/2/27	109	Loess (L2)	This study
CRO16/2/21	109	Loess (L2)	This study
<i>Slivata</i>			
BUL17/1/1	105	Palaesol (S0)	This study
BUL17/1/3	105	Loess (L1)	This study
BUL17/1/5	100	Loess (L1)	This study
BUL17/1/7	103	Loess (L1)	This study
BUL17/1/9	98	Loess (L1)	This study
BUL17/1/11	100	Loess (L1)	This study
BUL17/2/1	89	Palaesol (S1)	This study
BUL17/2/3	88	Palaesol - loess complex (L1)	This study
BUL17/2/5	71	Palaesol - loess complex (L1)	This study
BUL17/2/7	78	Palaesol - loess complex (L1)	This study
BUL17/2/9	100	Palaesol - loess complex (L1)	This study
BUL17/2/11	112	Palaesol - loess complex (L1)	This study
<i>Surduk</i>			
SER16/2/1	92	Loess (L1)	This study
SER16/2/3	104	Loess (L1)	This study

	SER16/2/4	100	Loess (L1)	This study
	SER16/2/6	115	Loess (L1)	This study
	SER16/2/7	70	Loess (L1)	This study
	SER16/2/9	113	Loess (L1)	This study
	SER16/2/20	114	Loess (L1)	This study
	SER16/2/21	112	Loess (L1)	This study
	SER16/2/22	105	Loess (L1)	This study
	SER16/2/23	90	Loess (L1)	This study
<i>Krems</i>				
	K23	4	Loess (L1)	Újvári <i>et al.</i> 2015
	S1	12	Loess (L1)	Újvári <i>et al.</i> 2015
<i>Wels</i>				
	A16	1	Loess (L1)	Újvári <i>et al.</i> 2015
<u>Rivers</u>				
<i>Drava</i>				
	CRO16/1/1	119	Modern Drava	This study
<i>Tisza</i>				
	SER16/1/1	80	Modern Tisza	This study
<u>Western Alps</u>				
<i>Eastern Alps igneous (EAI)</i>				
	Alp 6-2	77	Mica schist - Late Cretaceous	Chu et al 2016
<i>Eastern Alps sedimentary covers (EAS)</i>				
	Alp 4-2	70	Arenite matrix - Early Oligocene	Chu et al 2016
	Alp 5-1A	86	Arenite - Late Eocene to Earliest Oligocene	Chu et al 2016
	Alp 5-1B	77	Conglomerate - Late Eocene to Earliest Oligocene	Chu et al 2016
	Alp 5-2C	46	Siltstone - Middle Eocene	Chu et al 2016

LO1	92	Sandstone - Late Eocene-Earliest Oligocene	Chu et al 2016
LO2	94	Sandstone - Late Eocene-Earliest Oligocene	Chu et al 2016

Eastern Alps

Tauern window (TW)

HER1b	10	metamorphic - GMB	Siegmund et al 2018
THU4	11	metabasites - Thurntaler Phyllite Group	Siegmund et al 2018
VIN1	11	phyllites, South Alpine Basement	Siegmund et al 2018
AX 20	19	Deferegggen Group	Siegmund et al 2018
WEISS 14-1	17	Deferegggen Group	Siegmund et al 2018
HUB 1a	11	Metaquartzite, Northern Deferegggen–Petzeck Group	Siegmund et al 2018
ALKSEE 1	22	paragneisses, the Prijakt Subgroup	Siegmund et al 2018
ALKSEE 3a	10	paragneisses, the Prijakt Subgroup	Siegmund et al 2018

Bohemian Massif

South Bohemian Massif (SBM)

3	Porphyritic dyke	Siebel and Chen 2009
14	Granite	Siebel and Chen 2009
3	Redwitzite	Siebel and Chen 2009
3	Intermediate granitoid	Siebel and Chen 2009

Moldanubian Zone

Rohy	19	Blansky´ granulite massif	Slama et al 2007
Ples	61		Slama et al 2008

Balkan Mts

Central Srednogorie (CW)

AvQ111	9	quartz-monzodiorite	Peytcheva et al 2009
AvQ112	7	granodiorite porphyries with plagioclase	Peytcheva et al 2009
AvQ038	6	granodiorite porphyries with hornblende-plagioclase	Peytcheva et al 2009
AvQ040	7	aplitic veins	Peytcheva et al 2009
AvQ210	5	dyke	Peytcheva et al 2009

Dinaric Alps

Voras massif (VoM)

PLB28	35	Quartzofeldspatic equigranular rock	Zlatkin et al. 2017
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Vernon Massif (VeM)

PLB16	7	Monzogranite porphyry	Zlatkin et al. 2017
PLB15	8	Kastoria pluton	Zlatkin et al. 2017
PLB14	23	Quartzofeldspatic schist	Zlatkin et al. 2017
PLB17	17	Actinolite-rich phyllite	Zlatkin et al. 2017

Kopaonik Oligocene (KO)

11	4	Kopaonik -Monzonite	Schefer et al 2011
16	4	Drenje - Granodiorite	Schefer et al 2011
21	4	Željin - Granodiorite	Schefer et al 2011

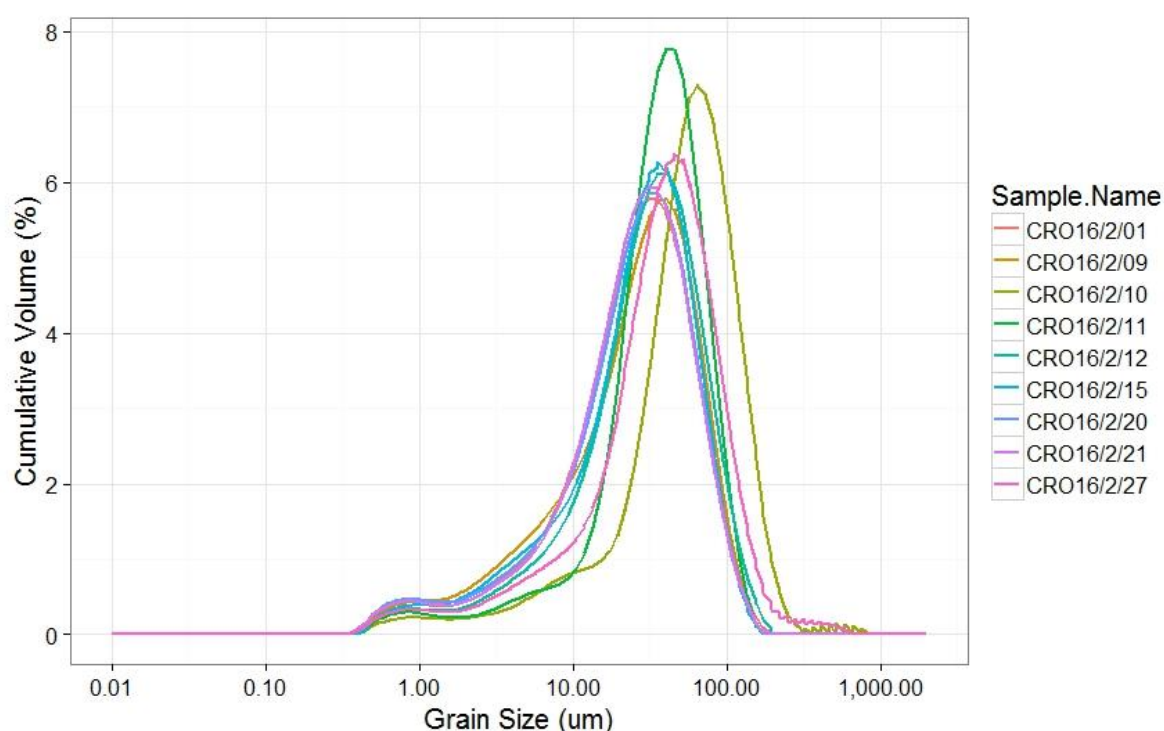
Kopaonik Miocene (KM)

509	3	Golija - Granodiorite	Schefer et al 2011
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Appendix K – Supplementary data Chapter 4

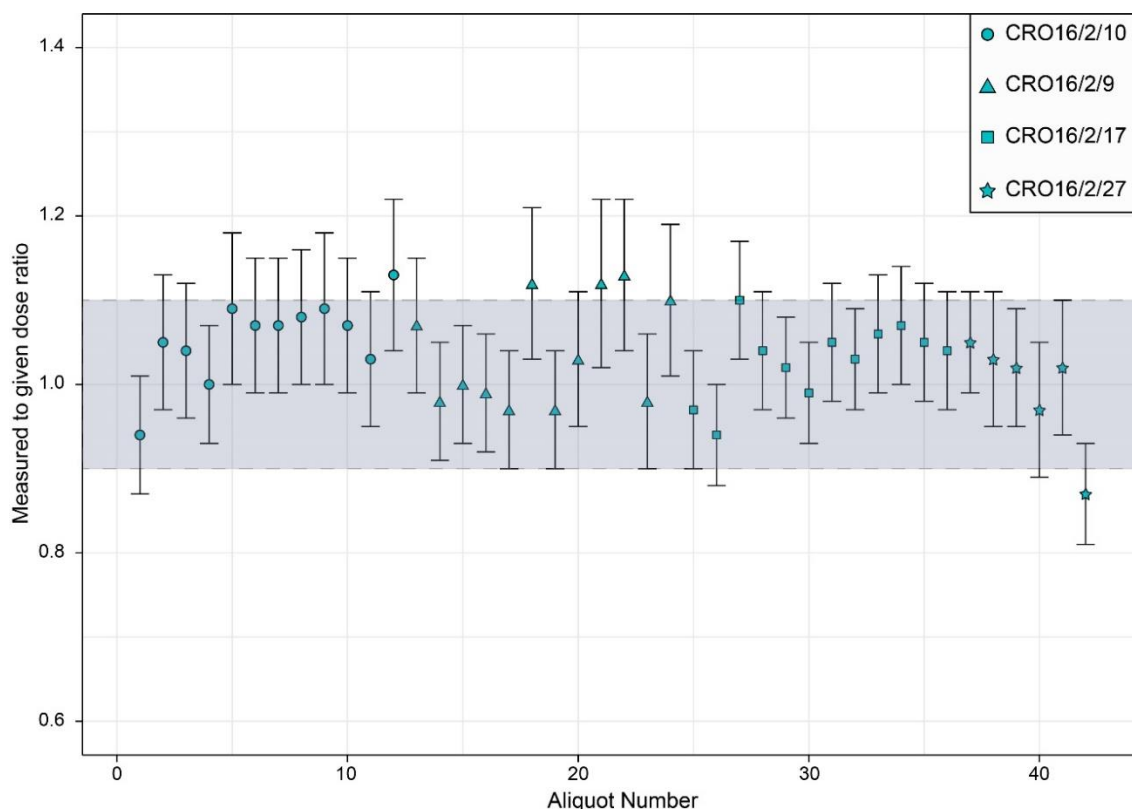
Particle size

Particle size was carried out on the collected luminescence samples, to support sedimentary field interpretations and compare with previously published datasets (Galović *et al.*, 2009). Subsamples for particle size analysis were disaggregated using sodium hexametaphosphate (calgon), to prevent clay flocculation, prior to measurement using a Malvern Mastersizer Hydro 2000MU laser diffraction particle size analyser.



Supplementary Figure S1. Grain size distributions for selected Croatian samples used for the luminescence analysis. Note a notable shift in size from coarse silt (~32 µm) to very fine sand (mean ~67 µm) in sample CRO16/2/10 (the top of the laminate horizon).

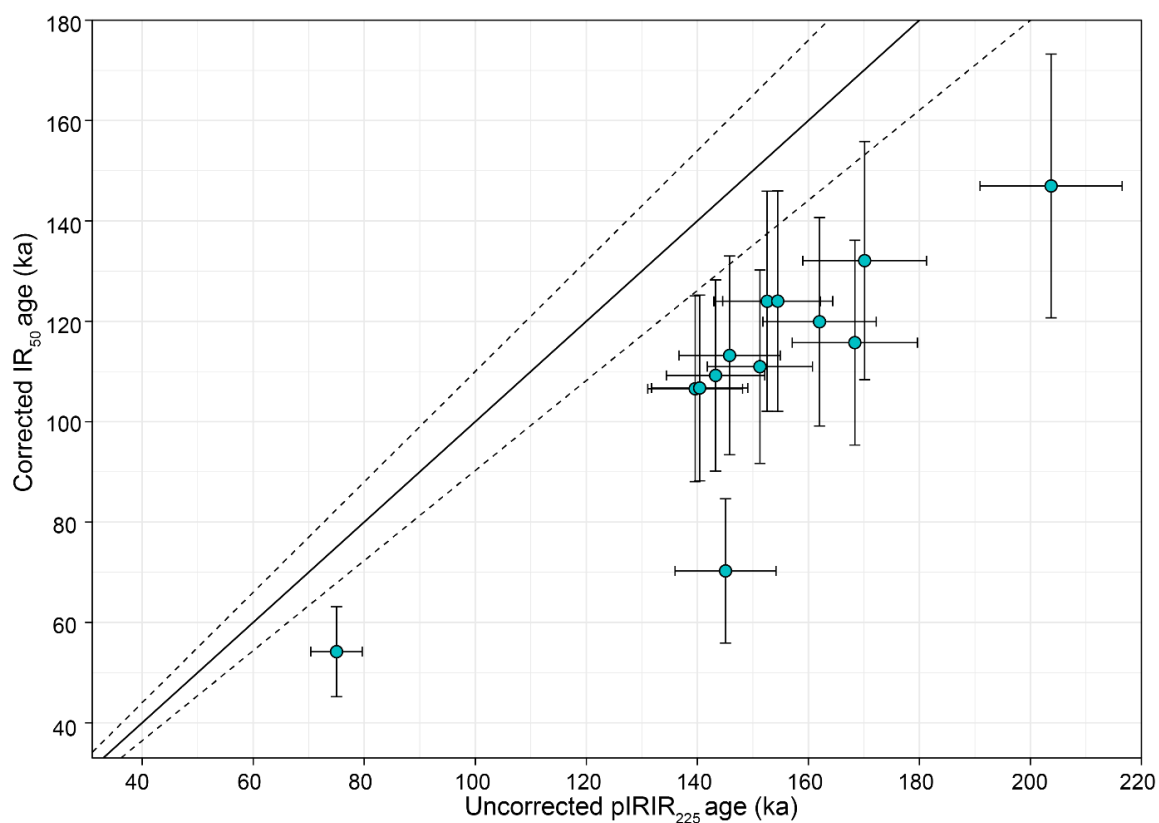
Luminescence



Supplementary Figure S2. Dose recovery results for individual disks in samples CRO16/2/9, CRO16/2/10, CRO16/2/17 and CRO16/2/27. The ratio between the recovered and administered dose is shown, and the grey shaded areas represents within 10% of unity.

Supplementary Table S1. Step by step dating protocol for dating potassium feldspars using pIRIR₂₂₅ protocol.

Feldspar		
Step	Treatment	Observed
1	Give dose, D_i	
2	Preheat, 250°C, 60s	
3	IR stimulation, 200s at 50°C	L_{xIR50}
4	IR stimulation, 200s at 225°C	$L_{xpIRIR225}$
5	Give test dose, D_T	
6	Preheat, 250°C, 60s	
7	IR stimulation, 200s at 50°C	T_{xIR50}
8	IR stimulation, 200s at 225°C	$T_{xpIRIR225}$
9	IR stimulation, 200s at 290°C	
10	Return to 1	



Supplementary Figure S3. Fading corrected IR₅₀ ages plotted against uncorrected pIRIR₂₂₅ ages. The errors shown are 1 σ . The dashed lines indicate $\pm 10\%$ around unity.

Supplementary Table S2. Comparison of the modelled and unmodelled pIRIR₂₂₅ luminescence ages.

Sample	Unit	Age and error (ka)	
		Unmodelled	Modelled
CRO16/2/15	V	75.01 $\pm$ 4.67	75.01 $\pm$ 5.44
CRO16/2/17	VI	139.61 $\pm$ 8.54	139.18 $\pm$ 8.75
CRO16/2/20	VI	140.42 $\pm$ 8.66	140.48 $\pm$ 7.75
CRO16/2/21	VI	143.29 $\pm$ 8.86	143.29 $\pm$ 7.76
CRO16/2/25	VI	145.08 $\pm$ 9.09	145.47 $\pm$ 9.33
CRO16/2/27	VI	170.14 $\pm$ 11.13	170.14 $\pm$ 13.49
CRO16/2/12	VII	151.27 $\pm$ 9.47	143.36 $\pm$ 7.43
CRO16/2/1	VIII	152.58 $\pm$ 9.58	148.69 $\pm$ 6.98

CRO16/2/14	VIII	145.81±9.11	152.43±6.11
CRO16/2/5	VIII	162.01±10.22	158.42±7.34
CRO16/2/7	IX	154.48±9.92	163.05±7.77
CRO16/2/9	IX	233.99±49.69	231.29±40.63

Supplementary Table S3. Samples, depths, De values obtained using IR₅₀ protocol applied to 63-90 µm potassium feldspars

Sample	Unit	D _e (Gy)	Uncorrected IR ₅₀ age (ka)
CRO16/2/15	V	139.9±2.9	41.19±2.61
CRO16/2/17	VI	219.7±5.9	80.12±5.20
CRO16/2/20	VI	236.0±4.8	80.24±5.06
CRO16/2/21	VI	239.7±6.3	82.08±5.35
CRO16/2/25	VI	153.0±17.0	53.19±6.72
CRO16/2/27	VI	299.8±10.7	98.96±6.94
CRO16/2/10	VII	319.4±8.4	109.92±7.14
CRO16/2/12	VII	276.6±6.5	83.38±5.37
CRO16/2/14	VIII	278.3±7.9	85.03±5.64
CRO16/2/1	VIII	295.32±9.3	92.99±6.28
CRO16/2/5	VIII	279.5±3.7	89.99±5.55
CRO16/2/7	IX	314.20±7.9	93.02±6.11
CRO16/2/9	IX	305.8±9.1	86.91±5.90

Appendix L – Supplementary data Chapter 5

Particle size analysis

All samples were dried overnight (<40°C) and homogenised prior to the analysis. Carbonates and organic material can cause grains to stick to each other and create aggregates. This in turn can have an effect on grain size distribution analysis. To determine the effect of organic matter and carbonates on the particle size distributions a comparison test was carried out. Seven samples were selected for the analysis for repeat analysis. Each sample was treated with 32% hydrochloric acid and 30% hydrogen peroxide, for 2 days and up to 2 weeks respectively. In each case sample was measured before treatment and then for comparison afterwards. Additionally, to compare any potential variability recorded during treatment a variability within a sample was also tested. For four untreated samples measurement was replicated up to five times. The selected samples are presented in Figure SI.

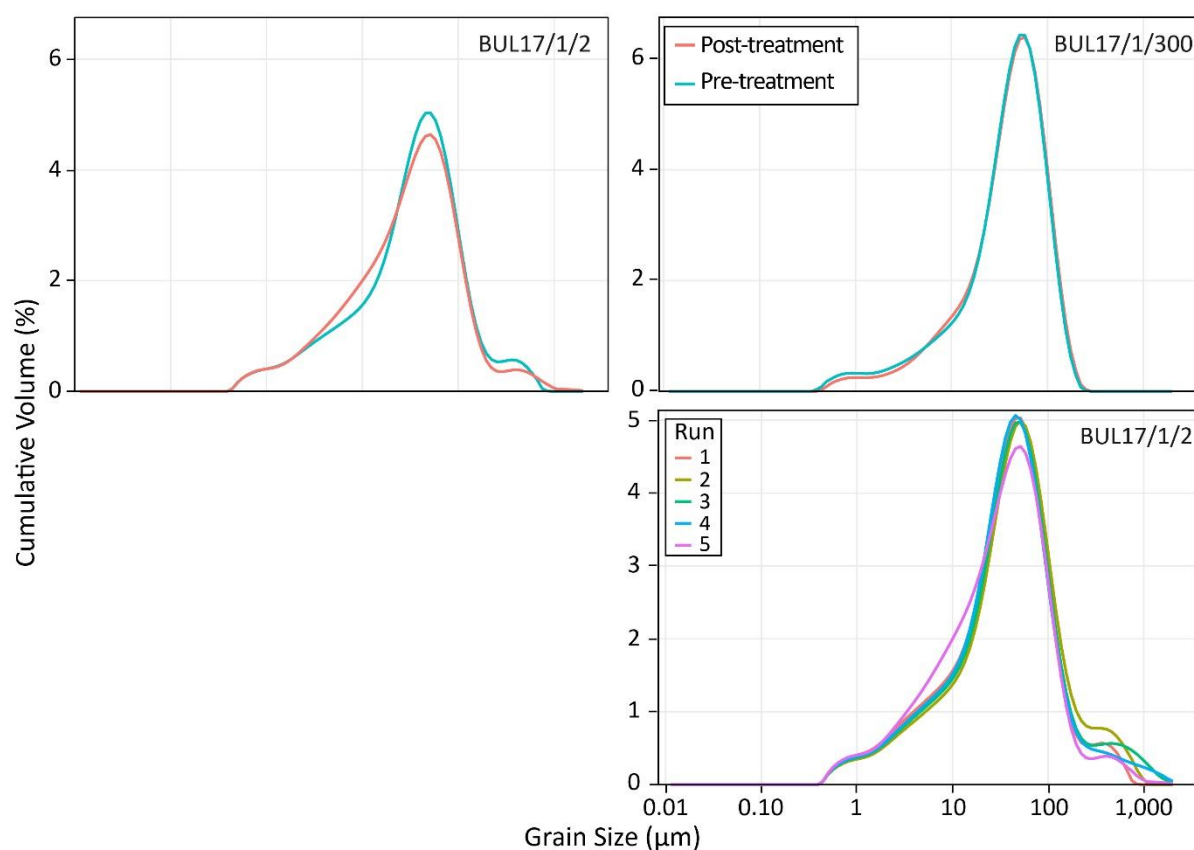


Figure SI. Comparison of the grain size distribution post and prior to removal of carbonates and organic matter. A) BUL17/1/2 B) BUL17/1/300 C) Comparison of grain distribution in the untreated sample BUL17/1/2.

Although some minor variability is shown between samples pre and post treatment, the comparison with variability within sample suggests that treatment only has a minor effect on the results. Therefore, the removal of carbonates and organic matter prior to measurement was concluded to be unnecessary.

Luminescence

Sample preparation

Samples for luminescence dating were opened and prepared under subdued orange light conditions at the Oxford Luminescence Dating Laboratory. Sediment from the light-exposed sample tube ends was removed and retained for dose rate measurements. To remove carbonates and organic matter, sediment was treated with 32% HCl and 30% H₂O₂ respectively. For equivalent dose (D_e) determination the 4-11 μm fraction was separated through a combination of sieving and settling. As the fine-grained (4-11 μm) polymineral fraction proved to be very dim, a coarser (63-90 μm) fraction was separated for feldspar analysis.

Quartz-enriched fine-grained fractions were obtained by immersing samples in 35% H₂SiF₆ for up to 3 weeks and subsequently washing with 32% HCl to remove fluorite precipitates. The coarse-grain potassium feldspar fraction was obtained through density separation using sodium polytungstate. Fine-grain aliquots were prepared by dispensing 0.5 mg of material onto 9.8 mm diameter aluminium discs, whereas coarse-grained K-feldspar was mounted with silicone oil using a small (2 mm) mask.

Risø TL/OSL luminescence readers fitted with a calibrated ⁹⁰Sr/⁹⁰Y beta source and a bialkali photomultiplier tube were used for all measurements. Quartz grains were stimulated with blue-light emitting diodes (470 nm) and the signal was measured in a UV detection window through 7.5mm U-340 glass filters (Botter-Jensen et al., 2000). K-feldspars aliquots were stimulated with infra-red emitting diodes (870 nm), and the signal was detected in the blue-violet region through a combination of Schott BG39/Corning 7-59 filters.

Quartz

To date and analyse all samples the single-aliquot regenerative-dose (SAR) measurement protocol (Table S.1; Murray and Wintle, 2000; Wintle and Murray, 2006) was used. The measurement conditions were determined through dose recovery tests and preheat plateau for each site.

For the preheat plateau analysis each aliquot was administered a dose approximating the natural dose, here 31.4 Gy. For each temperature three aliquots were measured. The same SAR protocol was administered to all aliquots, while varying the first pre-heat temperature (PH1) between 180 and 280°C, to test which temperature provides the closest match with the given dose. Figure S2 A shows results of the preheat test on the fine grained (4-11 μm) quartz. Five temperatures passed the dose recovery test, providing a range of temperatures to choose from. The lower two temperatures were slightly underestimating the given dose by 7-14% and temperatures >240°C overestimate by as much as 220%. While, 220°C and 240°C, appear appropriate, 240°C was chosen because of the lower spread of individual values.

For the dose tests natural luminescence signal was removed from the aliquots, by bleaching the signal in the reader. Here again the aliquots were irradiated with a known β -dose, that approximates a natural dose received by samples. Therefore, each sample

received a slightly different dose. They were analysed using the SAR protocol outlined in Table S2. The measured D_e values were normalised to the value of the administered dose and presented as a ratio Figure S2 C. All aliquots passed the dose recovery test within uncertainty.

Following pre-heat and dose recovery tests, a 240°C pre-heat and 160°C cut-heat, both for 10s, were selected. Luminescence was measured at 125°C for 40 seconds and D_e s were determined by subtracting the background (last 20s) signal from the first 0.5s of stimulation. All dose response curves were fitted with a single exponential and linear function. Due to quartz saturation for sample BUL17/2/1 an equivalent dose was obtained using the post-infrared infrared stimulated luminescence (pIRIR₂₂₅) signal (Buylaert *et al.*, 2012; Thomsen *et al.*, 2008).

Supplementary Table S2. Step by step dating protocol for dating fine grained quartz and potassium feldspars using pIRIR₂₂₅ protocol.

Quartz			Feldspar	
Step	Treatment	Observed	Treatment	Observed
1	Give dose, D_i		Give dose, D_i	
2	Preheat, 240°C, 10s		Preheat, 250°C, 60s	
3	Blue LED, 40s at 125°C	L_x	IR stimulation, 200s at 50°C	L_{xIR50}
4	Give test dose, D_T		IR stimulation, 200s at 225°C	$L_{xpIRIR225}$
5	Preheat, 160°C, 10s		Give test dose, D_T	
6	Blue LED, 40s at 125°C	T_x	Preheat, 250°C, 60s	
7	Return to 1		IR stimulation, 200s at 50°C	T_{xIR50}
8			IR stimulation, 200s at 225°C	$T_{xpIRIR225}$
9			IR stimulation, 200s at 290°C	
10			Hot bleach, 200s at 320°C	
11			Return to 1	

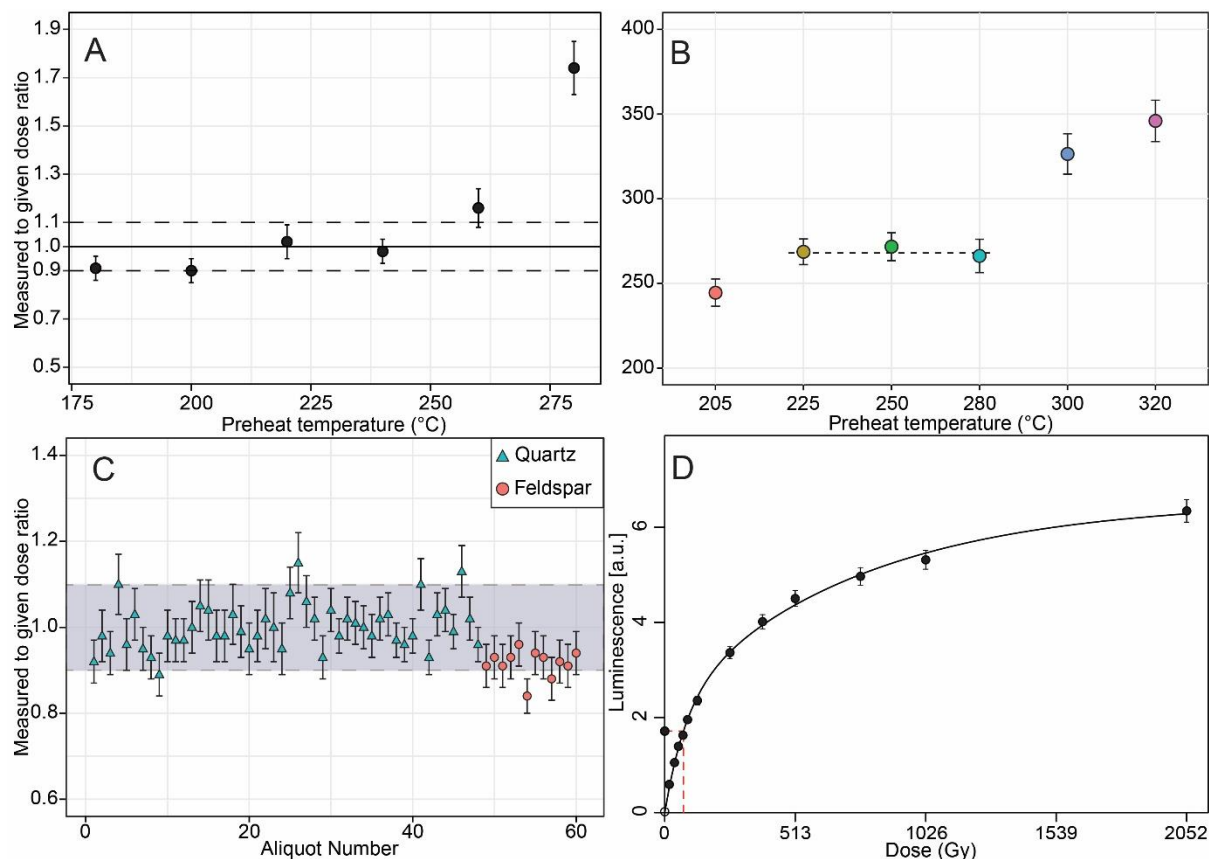


Figure S2. Preheat-plateaus for A) fine grained (4-11 μm) quartz; dashed line represents given dose B) coarse grained potassium feldspars (63-90 μm); dashed line marks the plateau. C) Dose recovery for quartz and potassium feldspars D) dose response curve for feldspar sample BUL17/2/1.

Feldspar

To determine the most appropriate protocol, a preheat plateau (Roberts, 2012), a dose recovery and residual and a check for anomalous fading (Auclair *et al.*, 2003) test were performed (Figure S2 and Table S3)

For the feldspar preheat plateau the analysis tests temperatures in pairs but is not combined with dose recovery. Six preheat temperatures (from 200°C to 320°C) and an elevated pIRIR temperature (25-30°C lower than the pre-heat) pairings were tested. Figure S2 B. shows a consistent D_e values measured using lower temperatures (between 205°C and 250°C), with the average D_e of 268 Gy. The pIRIR₂₂₅ protocol with a 250°C preheat was selected for further dose recovery and residual tests.

For dose recovery and residual tests sample was bleached in daylight for 7-10 days (in March, UK). Samples were then measured to determine the size of the unbleachable signal (Table S3), which is shown to be low and has negligible effect on final age

Table S3. The residual dose and dose recovery results for quartz and feldspar. All data are shown with 1 σ errors. Please note that all dose recovery tests were conducted on 12 aliquots and residual tests on 6 aliquots.

Sample	Fraction	Grain size	Residual dose (Gy)	Dose recovery*	Overdispersion (OD)
BULI7/2/1	K-feldspar	63-90 μm	4.06 $\pm$ 0.15	0.92 $\pm$ 0.05	1.4%
BULI7/1/1	Quartz	4-11 μm	N/A	0.97 $\pm$ 0.05	0.0%
BULI7/1/11	Quartz	4-11 μm	N/A	1.01 $\pm$ 0.05	0.0%
BULI7/2/1	Quartz	4-11 μm	N/A	0.92 $\pm$ 0.05	0.0%
BULI7/2/3	Quartz	4-11 μm	N/A	1.00 $\pm$ 0.07	0.0%
BULI7/2/9	Quartz	4-11 μm	N/A	1.02 $\pm$ 0.05	0.5%

*Residual subtracted dose recovery ratio

The suitability of the selected temperature pIRIR protocol was tested using the dose recovery test. Aliquots were irradiated β -dose approximating their natural dose, measured. The residual signal was subtracted from that measured, before calculation of the dose recovery ratio. Almost all aliquots recovered administered doses within 10% uncertainty (Figure S2 C), therefore pIRIR₂₂₅ protocol was used for De determination.

A standardised Auclair, Lamothe and Huot's (2003) protocol was used to investigate fading rates ($g_{2\text{days}}$). Six aliquots were irradiated with a fixed β -dose of 170 Gy and the luminescence signal measured after a pause. The pauses lasted 0h, 1h, 10h, 100h and 1000h. Fading rate (%/decade normalised) was then calculated in R Studio (Kreutzer and Burow, 2017) for both pIRIR₂₂₅ as well as the IR₅₀ signal. Mean g-value for the IR₅₀ and pIRIR₂₂₅ signal were 5.35 $\pm$ 1.37 and 2.06 $\pm$ 1.67 (norm. 2 days) (%/decade), respectively. The results suggest that fading recorded is a likely artefact of laboratory procedures, and that fading correction does not need to be applied.

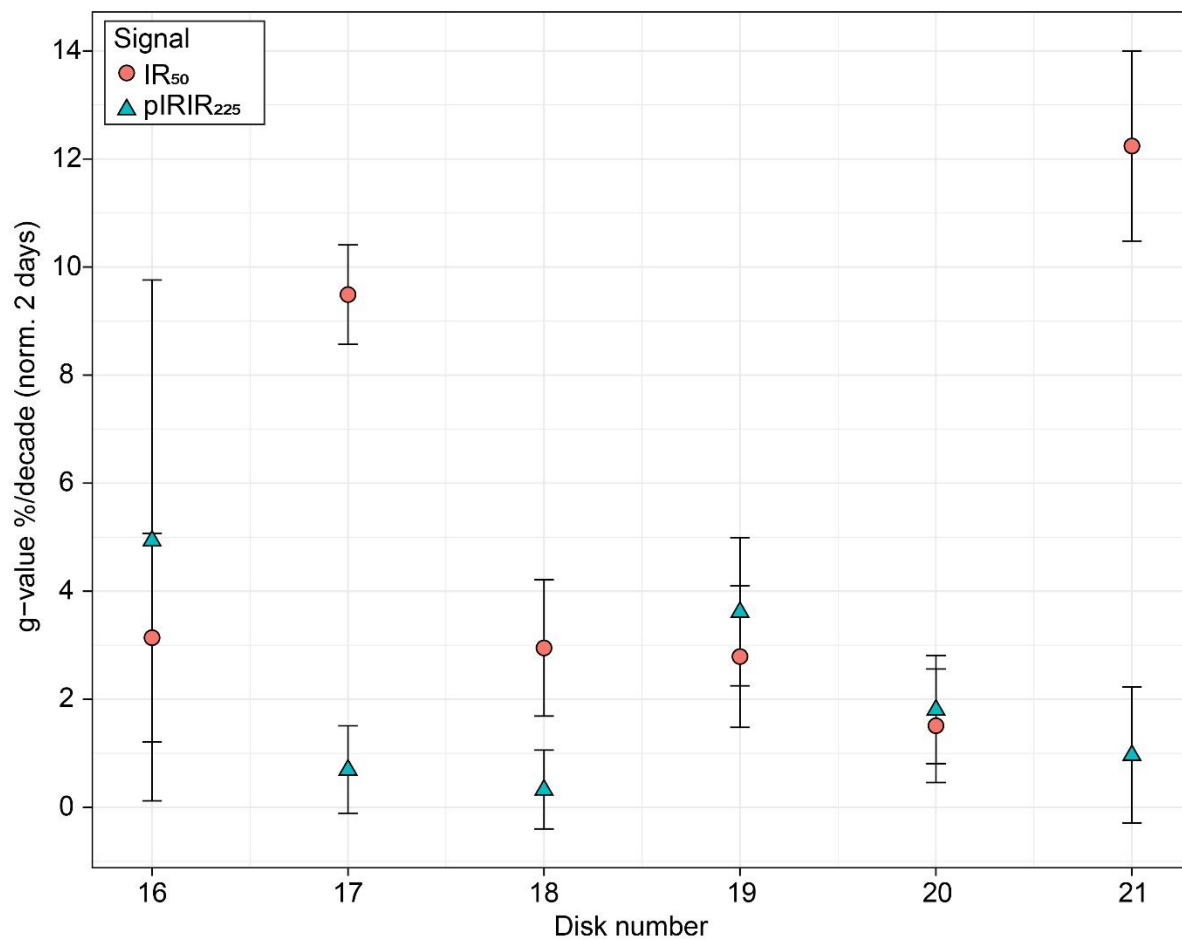
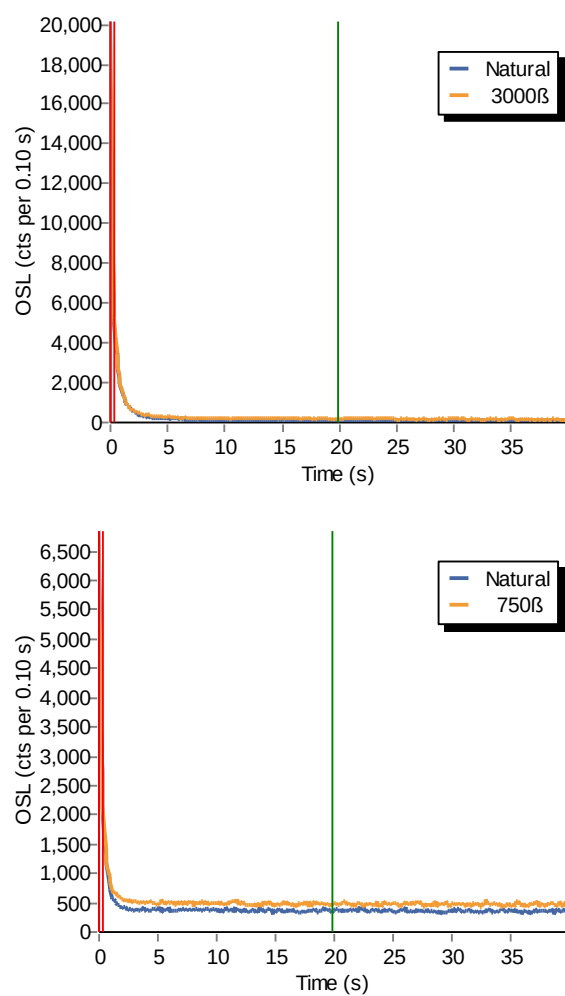
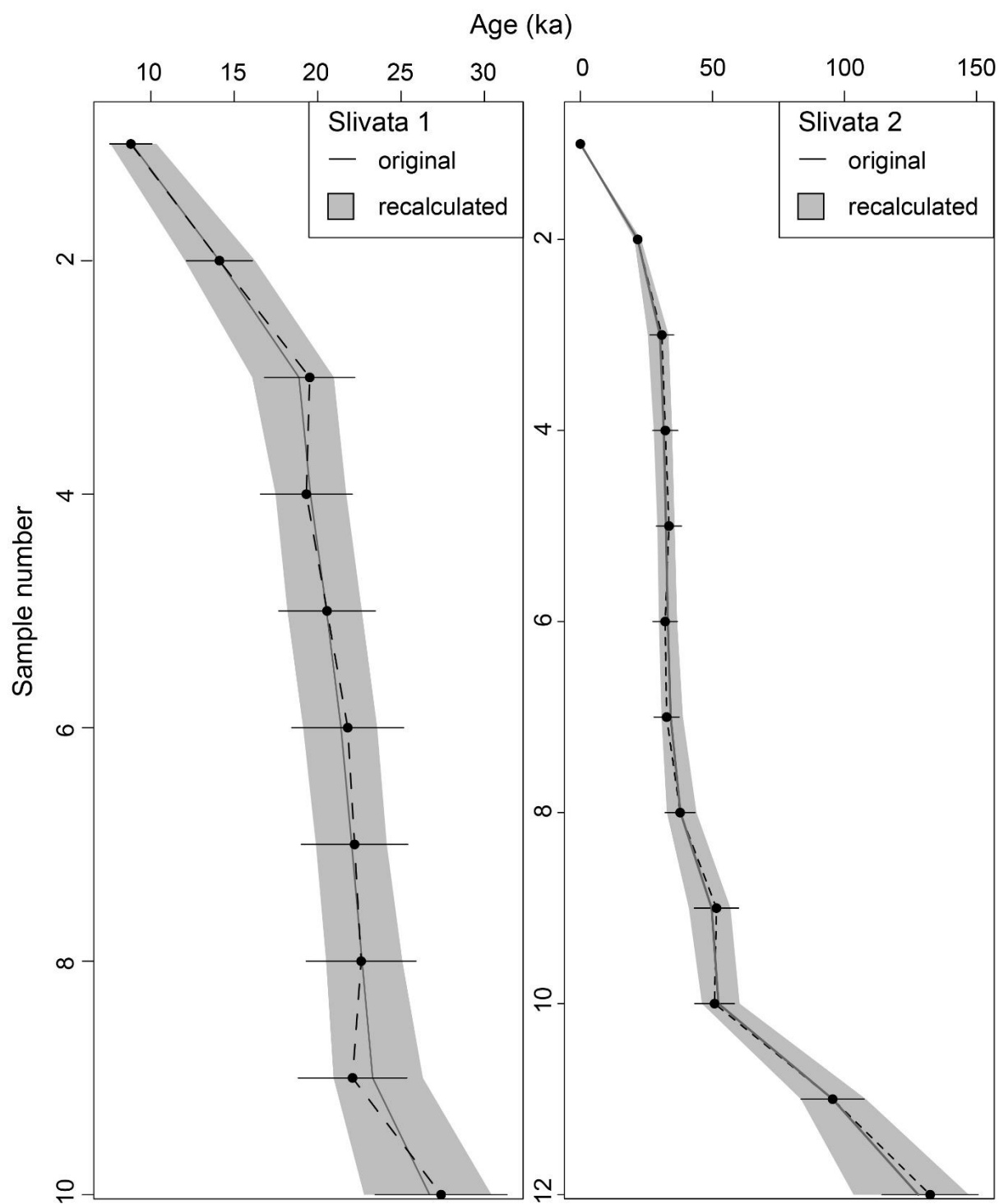


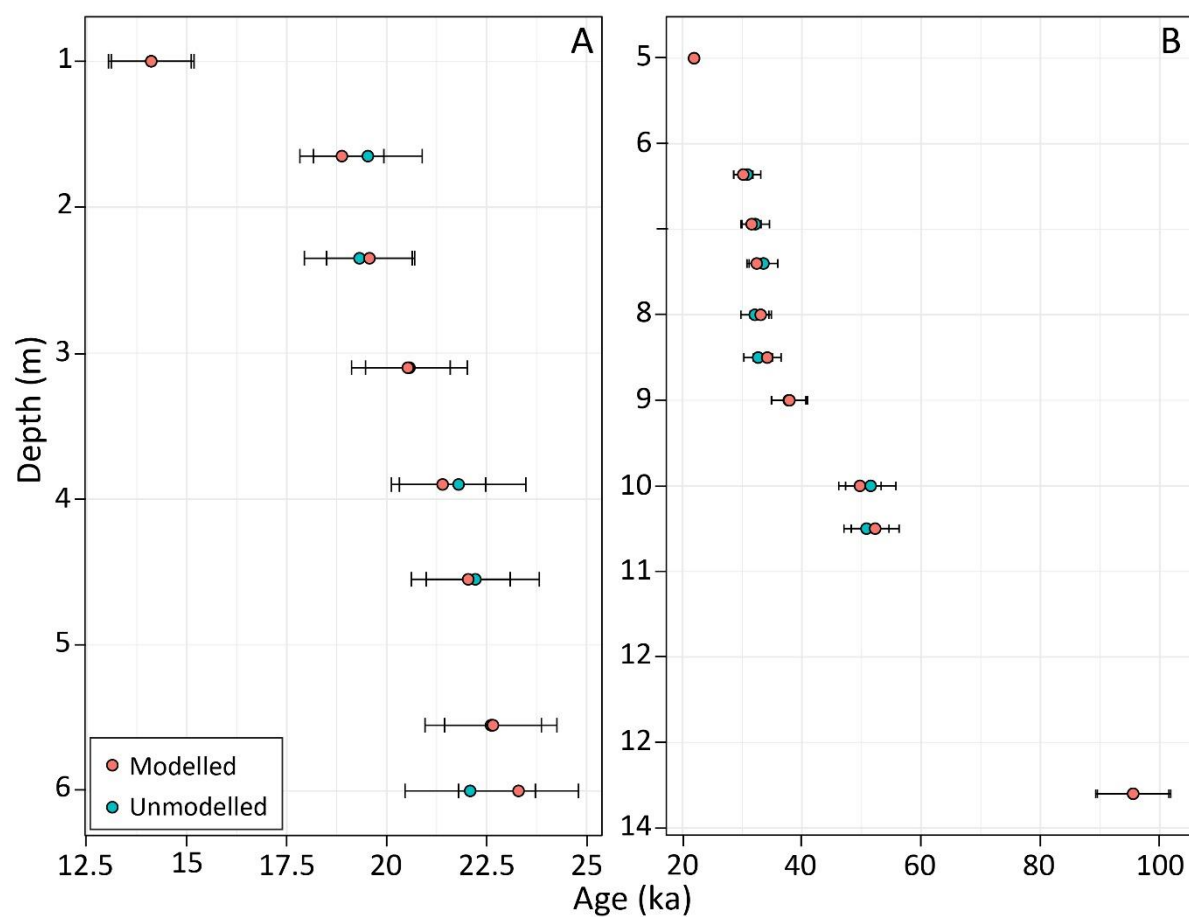
Figure S3. Calculated fading rates for the IR₅₀ and pIRIR₂₂₅ luminescence signals for all individual aliquots in sample BULI7/2/1. All data are shown with 1 σ errors.



Supplementary Figure S4. Typical decay curve for 4-11 μm quartz sample. Here samples BUL17/2/2 (left) and BUL17/1/3 (right).



Supplementary Figure S5. Age-depth model calculated using Zeeden et al. (2018) R package.



Supplementary Figure S6. Comparison of modelled and unmodelled ages for A) Slivata I B) Slivata B).

Appendix M – Supplementary data Chapter 6

Supplementary Table S2. The unmodelled and modelled ages for loess-palaeosol samples from Surduk 2 profile.

Sample	Depth (m)	Unit	Unmodelled		Modelled		Unmodelled		Modelled	
			OSL age (ka)	OSL error (ka)	OSL age (ka)	OSL error (ka)	pIRIR ₂₂₀ age (ka)	pIRIR ₂₂₀ error (ka)	pIRIR ₂₂₀ age (ka)	pIRIR ₂₂₀ error (ka)
SER16/2/1	1.5	II	20.23	1.49	19.03	1.03	-	-	-	-
SER16/2/2	1.8	II	20.13	1.4	19.85	0.81	-	-	-	-
SER16/2/3	2.1	II	18.85	1.33	20.28	0.92	-	-	-	-
SER16/2/4	2.4	II	22.35	1.61	21.64	1.03	-	-	-	-
SER16/2/5	2.7	II	22.52	1.66	22.29	0.99	-	-	-	-
SER16/2/6	3	II	23.37	1.7	22.99	1.01	-	-	-	-
SER16/2/7	3.3	II	-	-	-	-	22.57	1.46	23.42	1.07
SER16/2/9	3.9	II	24.35	1.79	24.62	1.31	-	-	-	-
SER16/2/10	4.4	IV	-	-	-	-	45.46	3.26	44.99	2.2
SER16/2/23	4.8	IV	-	-	-	-	47.29	3.09	46.84	2.21
SER16/2/12	5.2	IV	-	-	-	-	47.33	3.12	48	2.02
SER16/2/22	5.5	IV	-	-	-	-	49.94	3.24	49.17	2.37
SER16/2/21	5.8	IV	-	-	-	-	49.77	3.22	49.93	2.29
SER16/2/20	6.1	IV	-	-	-	-	51.99	3.37	50.87	2.37
SER16/2/15	6.4	IV	-	-	-	-	50.95	3.32	51.61	2.42
SER16/2/17	7.2	V	-	-	-	-	51.3	3.36	52.55	2.71

