

Exploring the use of mercury in reconstructing the environmental impacts of Large Igneous Provinces

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and Professor Steve Hesselbo

“...He fastened first those sandals of bright gold, which carry him aloft o'er land or sea, with airy wings that race the fleeting wind; then lifted he his wand, wherewith he summons from the grave pale-featured ghosts, or, if he will, consigns to doleful Tartarus; or by its power gives slumber or dispels; or quite unseals the eyelids of the dead: on this relying, he routs the winds or cleaves th'obscurity of stormful clouds. Soon from his flight he spied the summit and the sides precipitous of stubborn Atlas, whose star-pointing peak props heaven; of Atlas, whose pine-wreathed brow is girdled evermore with misty gloom and lashed of wind and rain; a cloak of snow melts on his shoulder; from his aged chin drop rivers, and ensheathed in stiffening ice glitters his great grim beard. Here first was stayed the speed of Mercury's well-poising wing; here making pause, from hence he headlong flung his body to the sea; in motion like some sea-bird's, which along the levelled shore or round tall crags where rove the swarming fish, flies low along the waves: o'er-hovering so between the earth and skies...”

The journeys of Mercury the messenger. Virgil's Aeneid, Book 4, starting line 238, translation by T.C. Williams (Boston, 1910).

Declaration

I declare that the work presented in this thesis is wholly my own, except where otherwise stated. The views and interpretations expressed herein are mine, and do not represent those of any other person or group except where this is cited to be the case.

Abstract

Large Igneous Provinces (LIPs) represent geologically rapid emplacements of vast quantities of igneous material into/onto Earth's crust. There is a marked correlation in the known ages of LIPs and Mesozoic extinctions and other environmental perturbations, suggesting a possible causal link between these events. However, uncertainties in matching LIP basalt ages to the stratigraphic record of Mesozoic events mean that a sedimentary tracer of volcanism would better indicate a precise coincidence between the two phenomena. Mercury (Hg) has shown potential as such a proxy. Volcanism is a major source of Hg to the natural environment, and its relatively long atmospheric residence time (0.5–2 years) allows global distribution of the element before it is deposited to sediments. However, questions remain about how the manner of LIP emplacement might influence its impact on the Hg cycle, as well as how sedimentary processes may locally overprint any global signal. Here, the Hg records of three Mesozoic events are investigated: the end-Triassic extinction (TJ: ~201.5 Ma), Cretaceous Oceanic Anoxic Event 2 (OAE 2: ~94 Ma), and the latest Cretaceous (K–Pg: ~67–66 Ma). These events coincided with markedly different LIPs: OAE 2 with multiple submarine LIPs; the K–Pg and TJ with subaerial LIPs; with the TJ also featuring release of additional thermogenic volatiles from intrusion of organic-rich lithologies by LIP sills. Additionally, mercury is used with osmium and carbon isotopes to study the temporal relationships between volcanism, weathering, and the carbon cycle during the Toarcian Oceanic Anoxic Event (~183 Ma). This work highlights the links between LIP volcanism and other surface processes, and shows that subaerial LIPs featuring thermogenic emissions are most likely to perturb the global Hg cycle, with the record of such perturbations dependent on the nature of the sedimentary archive.

Extended abstract

There is a strong correlation of the ages of Mesozoic extinctions and environmental perturbations with determined dates of Large Igneous Province (LIP) emplacement, which represent the geologically rapid intrusion and extrusion of immense amounts of igneous material (typically tholeiitic basalts) into/onto the Earth's crust. Due to the huge size of LIPs, the correlation between them and Mesozoic events, and the impact on Earth's climate following historical eruptions, a causal link between the two phenomena has been proposed. However, given the uncertainties associated with relating the stratigraphic records of environmental perturbations with LIP ages acquired by dating basalt units, a sedimentary proxy for volcanism would better indicate a precise coincidence between them.

Volcanism is a major source of mercury (Hg) to the natural environment in the modern, and volcanic Hg emitted to the atmosphere has a relatively long residence time (0.5–2 years), allowing the element to be globally distributed. On removal from the atmosphere, Hg is deposited to sediments geologically rapidly, typically bound to organic matter. Consequently, sedimentary Hg enrichment has been used as a proxy for local and/or distal volcanism, with Hg concentrations normalised against total organic carbon content (TOC) to account for the deposition of mercury with organics. Such peaks in Hg and Hg/TOC of lake sediments have been used to infer historical volcanic activity, and have also been used in uppermost Permian and lower Toarcian sedimentary rocks to support links between LIP volcanism and the end-Permian extinction (~252 Ma) and Toarcian OAE (T-OAE: ~183 Ma). However, it is unclear how the impact of a LIP on the Hg cycle varies with its situation/style of emplacement, as well as whether local processes can overprint of any global signal.

This work begins by investigating the global mercury record in uppermost-Triassic to lower-Jurassic sediments. The end-Triassic extinction (TJ: ~201.5 Ma) coincided with the emplacement of the largest known continental LIP, the Central Atlantic Magmatic Province (CAMP), which is also thought to have featured release of thermogenic volatiles. Thus, if the model that LIP volcanism perturbs the global Hg cycle is correct, significant peaks in sedimentary Hg/TOC should appear in uppermost Triassic strata. Such peaks are observed at the end-Triassic extinction horizon in all studied sections which record that level, indicating a global Hg-cycle perturbation at that time. The known correlation between the extinction horizon and lowest known CAMP basalt allows these Hg/TOC peaks to be linked to that basalt unit, thus strengthening the case for LIP volcanism perturbing the global Hg cycle. Additional Hg/TOC peaks are also seen stratigraphically higher in multiple records, supporting geological evidence for a pulsatory history of CAMP emplacement.

The second study in this thesis utilises mercury as a volcanic tracer alongside osmium (Os) isotopes and carbon isotopes ($\delta^{13}\text{C}$) in a multiproxy investigation of the Mochras Core record of the Pliensbachian–Toarcian (Pl–To) transition and the T-OAE. Two clear correlations are observed between excursions of these three proxies, indicating geologically synchronous LIP volcanism, flux of (isotopically light) carbon to the atmosphere, and enhanced continental weathering during both the T-OAE and the Pl–To transition. Importantly, analysis of sedimentary molybdenum and uranium enrichments indicate a hydrographically open marine environment during the Toarcian, indicating that the Mochras Os-isotope record is of global trends, and not a local signal. Numerical models based on the Os-isotope data indicate that weathering rates at least doubled during the Pl–To transition, and trebled during the T-OAE, with higher magnitude Hg/TOC and $\delta^{13}\text{C}$ excursions in

T-OAE strata compared to the PI–To boundary as well. In conjunction with previous models of the T-OAE, it is concluded that Karoo–Ferrar LIP volcanism led to a major flux of carbon to the atmosphere, warming the climate and elevating global continental weathering, which ultimately alleviated the environmental perturbation.

The final part of this work examines the mercury records of Cretaceous Oceanic Anoxic Event 2 (OAE 2: ~94 Ma) and the latest Cretaceous (K–Pg: ~66–67 Ma). OAE 2 has been linked to four oceanic LIPs, where submarine volcanism would have been prevalent. The KPg coincided with a subaerial LIP (the Deccan Traps), but this LIP is not thought to have featured release of additional thermogenic volatiles, unlike the CAMP or Karoo–Ferrar. The onset of LIP volcanism during both OAE 2 and the KPg has also been documented by shifts to unradiogenic Os-isotope ratios, allowing Hg/TOC and Os isotopes to be compared as sedimentary proxies of volcanism. The mercury records of both events are very inconsistent, and do not match the Os-isotope records of LIP volcanism. It is concluded that submarine LIP volcanism prevalent during OAE2 could only cause a local Hg-cycle perturbation, whilst the Deccan Traps did not perturb the global Hg cycle through much of their history. Thus, not all LIP eruptions manifestly produce major mercury emissions, with a global Hg-cycle perturbation most likely to result from a subaerial LIP featuring one or both of explosive eruptions or thermogenic emissions.

Combined, these studies highlight that mercury shows promise as a proxy for volcanism, particularly when combined with proxies of other surface processes. However, the impact of a particular sedimentary archive, and the manner of LIP emplacement, on the use of sedimentary Hg as a proxy for volcanism should not be underestimated. Further work utilising mercury alongside other proxies of volcanism, and LIP geochronology, will be crucial to the development of this proxy.

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List of regularly used abbreviations

Hg.....	mercury
TOC.....	total organic carbon
Hg/TOC.....	mercury/total organic carbon ratio
$\delta^{13}\text{C}$	carbon-13/carbon-12 ratio relative to PDB standard
Os	osmium
LIP.....	Large Igneous Province
OAE	Oceanic Anoxic Event
TJ.....	Triassic–Jurassic event
Pl–To.....	Pliensbachian–Toarcian transition
T-OAE.....	Toarcian Ocean Anoxic Event
OAE 1a.....	Cretaceous Oceanic Anoxic Event 1a (Early Aptian)
OAE 2	Cretaceous Oceanic Anoxic Event 2 (Cenomanian–Turonian)
K–Pg	latest Cretaceous–earliest Palaeogene transition
CAMP	Central Atlantic Magmatic Province
Ma	million years ago
Myr.....	million years
kyr	thousand years

Chapter 1

Mercury as a sedimentary proxy for volcanism

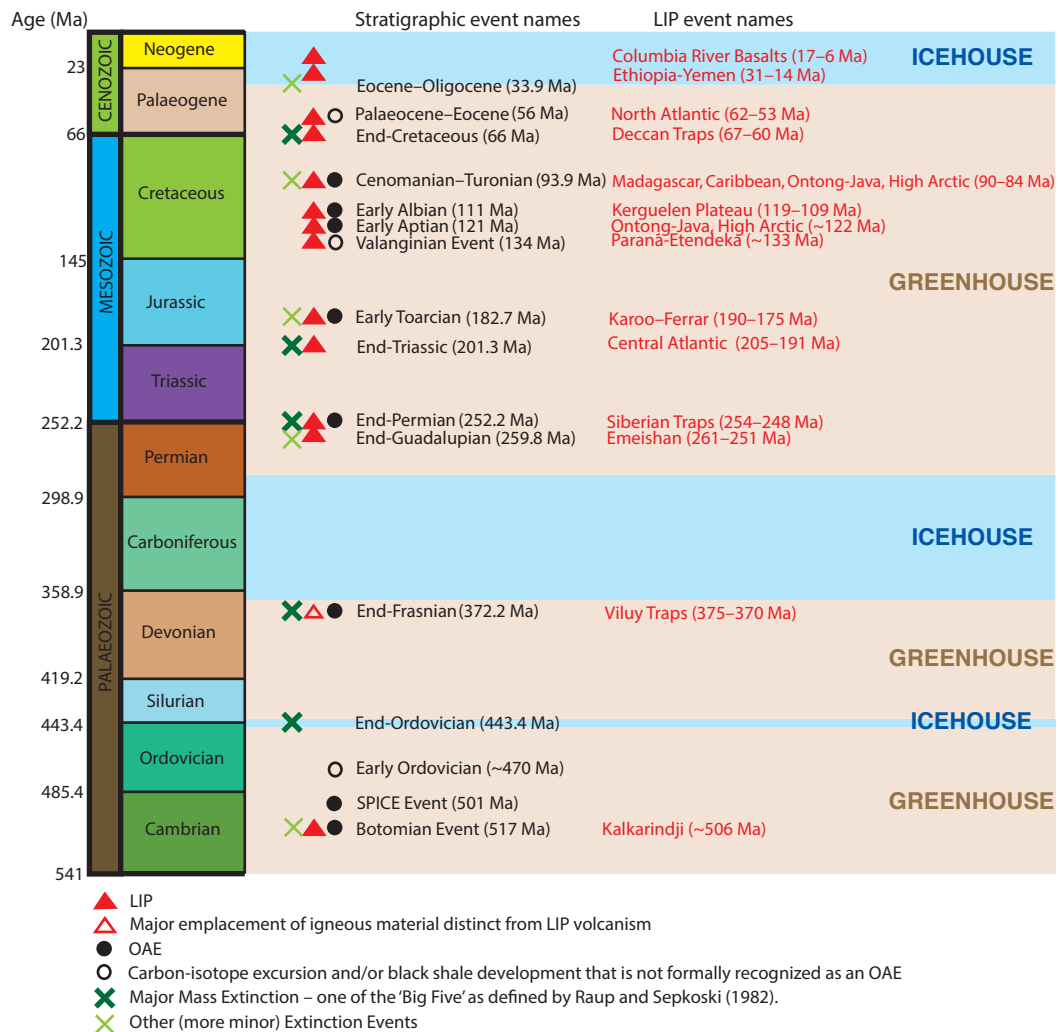


Figure 1.1: Illustration of the temporal correlation of Large Igneous Provinces with Ocean Anoxic Events and/or extinction events. Figure adapted from Percival *et al.* (2015).

1.1. Introduction

Large Igneous Provinces (LIPs) are seen in the geological record as immense emplacements of igneous material into/onto either oceanic or continental crust (Coffin and Eldholm, 1994; Bryan and Ernst, 2008; Bryan and Ferrari, 2013; Ernst and Youbi, 2017). Most provinces comprise on the order of 10^6 km³ of chiefly tholeiitic basalt, the bulk of which is thought to have been emplaced within a million years (Bryan *et al.*, 2010; Blackburn *et al.*, 2013). Given the impact on the climate system witnessed after the large-scale basaltic eruptions in Iceland at Laki in 1783 (Thordarson and Self, 2003), and the much greater volume and inferred eruption rate of LIPs, it has been proposed that these huge outpourings of magma resulted in catastrophic climatic effects. This hypothesis is reinforced by coincidences (within dating error) between the radiometric ages of LIPs and the dates of a number of mass extinctions and/or Oceanic Anoxic Events (OAEs) (Rampino and Strothers, 1988; Courtillot and Renne, 2003; Bond and Wignall, 2014; Figure 1.1).

In spite of this coincidence, there remains criticism of a simple cause-and-effect relationship between volcanism and disturbances to the global environment. The causal mechanism remains debated, usually featuring CO₂ emissions, but some quantitative estimates of LIP volatiles are not thought high enough to have significantly perturbed the carbon cycle (Caldeira and Rampino, 1990; Wignall, 2001; Self *et al.*, 2006; Self *et al.*, 2014). In addition, the coincidence between LIP emplacement and mass extinctions is not perfect. There are LIPs whose formation does not appear to have coincided with extinctions or major environmental change (e.g. the Ethiopian and Columbia River Provinces), whilst the end-Ordovician mass extinction did not coincide with the formation of a known LIP (Figure 1.1).

One of the issues with settling this debate is that whilst the extinction/climate record is preserved in sedimentary rocks, apart from rare LIP flows and/or volcanoclastic deposits interbedded with proximal sediments (e.g. Olsen *et al.*, 1996; Widdowson *et al.*, 1997), there has been no well-tested uniquely volcanic tracer in sedimentary deposits, particularly for deposits situated distally from the LIP. Biostratigraphic ages of sedimentary phenomena are difficult to compare with the dates of volcanism derived from astrochronology and radioisotopic techniques (such as U–Pb dating: e.g. Blackburn *et al.*, 2013), which all potentially carry attendant errors. Sampling of LIPs for dating is limited by their geographic and stratigraphic distribution; made worse by their typically poor preservation. Many oceanic LIPs may also have been partially destroyed by subduction, or broken up and obducted on to continents.

A global sedimentary proxy for volcanism would be a key piece of evidence to confirm the correlation between large-scale volcanism and major environmental change. Osmium isotopes have frequently been used to infer volcanic output, but cannot be unambiguously distinguished from a reduction in the effects of continental weathering (e.g. Ravizza *et al.*, 2001; Cohen *et al.*, 2004; Du Vivier *et al.*, 2014). Other isotope systems such as strontium, lead, neodymium, sulphur, chromium, and zinc, as well as sedimentary concentrations of mafic trace metals, have also been proposed as indicators of volcanism, but remain relatively unstudied, and may also be impacted by other surface processes such as weathering or marine redox chemistry (e.g. Jones and Jenkyns, 2001; Kuroda *et al.*, 2007; Zheng *et al.*, 2013; Holmden *et al.*, 2016; Jenkyns *et al.*, 2017; Liu *et al.*, 2017).

1.2. Mercury as a proxy of volcanism

It is known that volcanism represents a substantial source of mercury to the atmosphere (Pyle and Mather, 2003 and references therein). Most volcanic mercury is emitted as gaseous Hg^0 , which has an atmospheric residence time of 0.5–2 years, significantly longer than that of other volcanic metals emitted as aerosols and particles, which (depending on the size of the particle/aerosol droplet) have an atmospheric residence time on the order of weeks (Jaenicke, 1980; Slemr *et al.*, 1985; Schroede and Munthe, 1998; Hinkley *et al.*, 1999; Mather *et al.*, 2003; Bagnato *et al.*, 2007; Witt *et al.*, 2008). Thus, Hg has greater potential for global distribution than other volcanic trace metals, and can certainly achieve hemispheric exchange. Gaseous Hg^0 is removed from the atmosphere through oxidation by halogens, ozone, and other radicals to form reactive Hg^{2+} , which is soluble in water and typically deposited during rainfall (Figure 1.2). Particulate Hg represents a minor component of volcanic mercury, but has a much shorter residence time in the atmosphere than Hg^0 , restricting it to a more localised distribution (Schroeder and Munthe, 1998; Selin, 2009). In the aquatic realm, a number of biotic and abiotic processes may affect dissolved Hg^{2+} , which often result in the formation of organic–Hg complexes. Sulphur is thought to play an important role in this process. For example, ionic Hg^{2+} in HgS^0 compounds can be methylated to organophilic monomethyl-mercury by sulphate reducing bacteria, particularly in anoxic environments such as wetlands (Benoit *et al.*, 1999; Niessen *et al.*, 2003). Consequently, mercury is typically deposited in sediments adsorbed onto organic matter, resulting in a roughly constant Hg/TOC ratio (TOC: Total Organic Carbon) in modern sediments deposited at any single sedimentary location under otherwise

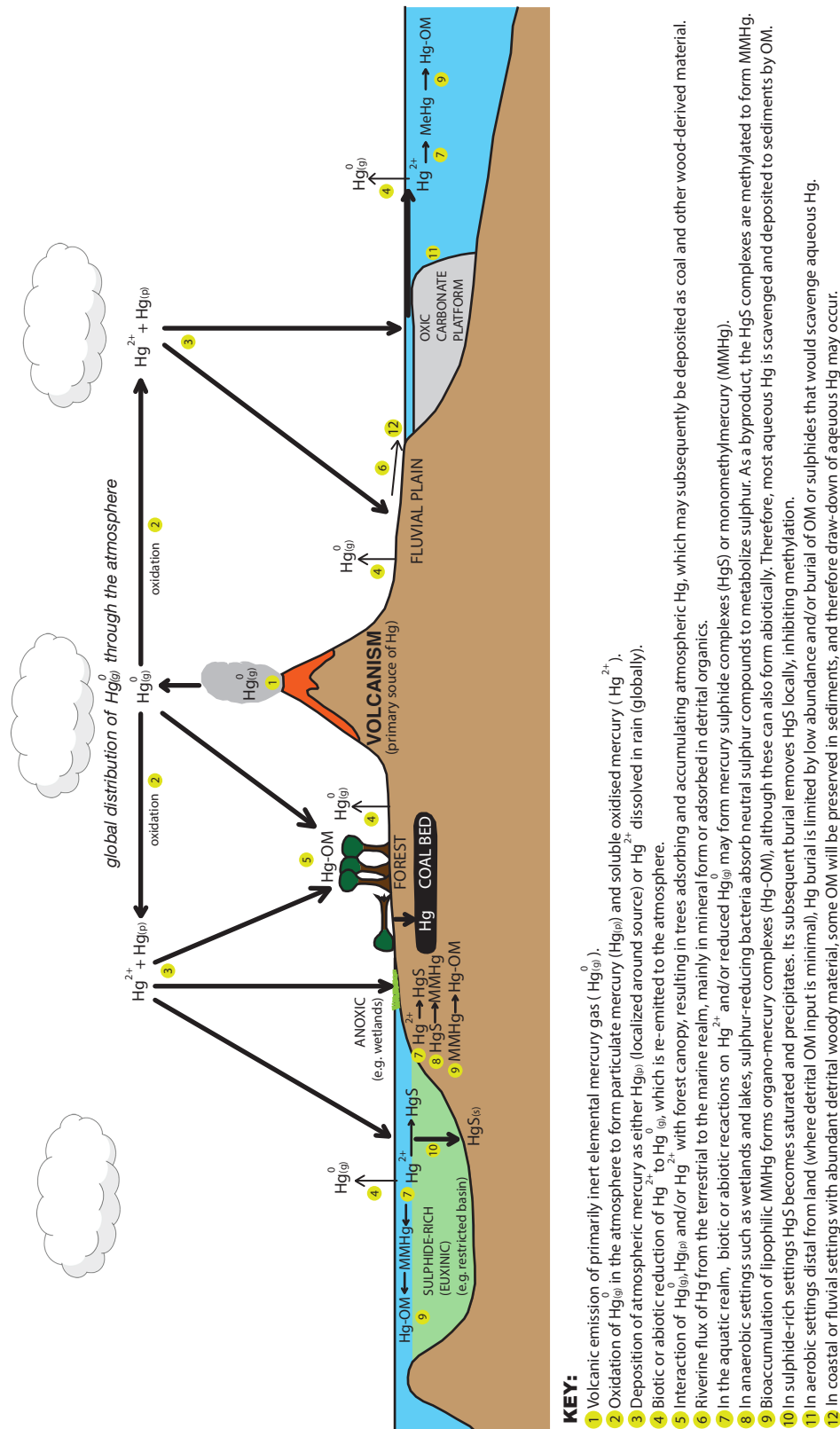


Figure 1.2: Simplified illustration of the natural mercury cycle, showing the major pathways of mercury from volcanic source to sedimentary sink. Figure adapted from Percival *et al.* (2015).

constant conditions (Benoit *et al.*, 2001; Outridge *et al.*, 2007; Gerkhe *et al.*, 2009; Liu *et al.*, 2012; Ruiz and Tomiyasu, 2015). Adsorption of mercury onto clays may also play a role in mercury drawdown in certain environments, particularly those where phyllosilicate runoff is high (Kongchum *et al.*, 2011; Jin and Liebezeit, 2013). In waters rich in sulphides, Hg-sulphide complexes may be remobilised from sediments, resulting in Hg concentrations trending with sulphur throughout much of the water column (Lamborg *et al.*, 2008).

In the terrestrial realm, mercury may be deposited in soil, or taken up directly by leaves in the tree canopy (Fleck *et al.*, 1999; Frescholtz *et al.*, 2003; Ericksen *et al.*, 2003), which may then result in enhanced Hg concentrations in plant tissue (Fleck *et al.*, 1999). Figure 1.2 illustrates the path from volcanism to sediment in a simplified mercury cycle.

Because volcanoes are known to expel Hg into the atmosphere, a number of studies have noted that the element could be a tracer for historical volcanism in both ice cores and sedimentary systems. Records of elevated atmospheric mercury following three historical eruptions (Tambora, Krakatau, and Mount St. Helens) are documented in a glacial ice core from Wyoming (USA), with additional atmospheric perturbations recorded at times of major industrial activity (Schuster *et al.*, 2002). Hg peaks in lake-sediment records of historical times have also been associated with volcanism (e.g. Ribeiro Guevara *et al.*, 2010; Daga *et al.*, 2016).

1.3. Sedimentary mercury records of Mesozoic events

At the commencement of this thesis, sedimentary mercury records of events in the geological record were still very sparse. The first attempt to use Hg as a proxy

for volcanism was by Sial *et al.* (2010), who reported Hg enrichment in uppermost Cryogenian sediments inferred to result from massive volcanism that triggered the end of the Neoproterozoic ‘Snowball’ glaciation. However, the Hg enrichments were not normalised against organic matter content, and therefore did not allow for potential lithological changes in organic-matter content governing Hg concentrations. Anomalous elevated Hg concentrations had also been documented in Cretaceous–Palaeogene (K–Pg) strata, and linked to Deccan Trap volcanism (Nascimento-Silva *et al.*, 2011; 2013; Sial *et al.*, 2014). However, again, without normalisation against TOC, their reliability as markers of volcanism as opposed to enhanced Hg drawdown by organic carbon remains ambiguous.

The first reported record of elevated Hg concentrations accompanied by a rise in Hg/TOC ratios was from the Permian–Triassic boundary in the Sverdrup Basin of the Canadian Arctic, which was attributed to Hg output from the emplacement of the Siberian Traps (Sanei *et al.*, 2012). Comparison with the stratigraphic record of Mo/Al (as a redox proxy) further highlighted that the Permian–Triassic Hg/TOC anomalies did not relate to decreases in oxygenation, indicating that marine anoxia was not the sole cause of the anomalous Hg/TOC ratios in end-Permian sediments (Grasby *et al.*, 2013). However, as a single record proximal to the LIP volcanism of the Siberian Traps, it does not represent proof of a global-scale perturbation to the Hg cycle at that time.

As part of my undergraduate master’s thesis work, a number of geographically widespread sedimentary records from Europe and South America were investigated for mercury content, and shown to document elevated Hg concentrations and Hg/TOC ratios during the Toarcian Oceanic Anoxic Event (T-OAE: ~183 Ma), linking the sedimentary Hg enrichment to emissions of the metal

by the Karoo–Ferrar LIP (Percival *et al.*, 2015). However, this study also highlighted the potential for local overprinting of any global changes to the Hg cycle, with two of the seven studied records showing elevated Hg concentrations overprinted by excess TOC increases (i.e. generating a Hg/TOC decrease) and a further record showing negligible Hg concentrations throughout the record due to the lack of organic matter or clays in those sediments.

Additionally, whilst the end-Permian and Toarcian events appear to have featured volcanically related mercury perturbations, both the Siberian Traps and Karoo–Ferrar LIP were continental LIPs where any volcanism would have been subaerial, and may also have featured release of additional thermogenic mercury generated by heating of organic rich country rocks by intruding LIP magmatics (McElwain *et al.*, 2005; Svensen *et al.*, 2007; 2009). It remains unclear whether different LIPs without the potential to generate thermogenic volatiles, or where the majority of volcanism was submarine, may have had a different impact on the mercury cycle of that time.

1.4. Testing mercury’s use as a link between LIP volcanism and major environmental change

This work looks to expand the existing records of sedimentary mercury in strata that document major environmental perturbations in the geological record. Because mercury remains in its infancy as a sedimentary proxy, it was decided to focus on the Mesozoic, for which Large Igneous Provinces and the events that they are associated with are relatively well understood, and when a range of styles of LIP volcanism occurred. Of key interest is whether perturbations to the global mercury

cycle are documented in records of most/all Mesozoic events from widespread locations, both proximal and distal to the stratigraphically associated LIP volcanism, and in a variety of different sedimentary facies. Additionally, a first attempt to use mercury in a multiproxy analysis to investigate the relationship between LIP volcanism (as reconstructed by mercury analyses) and other surface processes is presented.

Chapter 2 details the methods used as part of the various geochemical analyses undertaken in this work. The principle analyses performed were those of Hg concentration and TOC content of sedimentary rocks. However, analyses of osmium-isotope ratios, molybdenum, uranium, and aluminum concentrations, and carbon-isotope ($\delta^{13}\text{C}$) compositions of organic matter, were also undertaken. Additionally, a numerical model for estimating changes in continental weathering rates from sedimentary osmium-isotope records is presented.

Chapter 3 investigates the mercury record of the end-Triassic extinction (TJ: ~201.5 Ma), which has been linked to the Central Atlantic Magmatic Province (CAMP). The CAMP represents the largest known continental LIP, and so would be expected to cause a clear increase in sedimentary Hg/TOC if mercury is a reliable proxy for LIP volcanism. This event also presents a rare opportunity to tie stratigraphic Hg/TOC peaks to a specific LIP unit, using the established correlation between the oldest known CAMP basalt and the end-Triassic extinction horizon, which would greatly strengthen the link between LIP volcanism and sedimentary Hg enrichment. Six sedimentary records are examined for mercury, covering four continents and both hemispheres, and representing a range of terrestrial and marine palaeoenvironments, in order to reconstruct a global picture of the latest Triassic to earliest Jurassic Hg cycle. The presence or absence of additional pulses in Hg/TOC

stratigraphically above the end-Triassic extinction horizon is also investigated, as a new and independent test of geological and geochemical evidence for a pulsed emplacement of CAMP.

Chapter 4 explores the use of mercury in a multiproxy study, combined with studies of osmium- and carbon-isotopes from a single sedimentary record of the T-OAE: the Mochras Core. These analyses are combined with studies of molybdenum and uranium enrichment in order to demonstrate that the Mochras Core does record a hydrographically open environment connected to the global ocean, and thus that the observed osmium-isotope trends are representative of global changes in the seawater osmium-isotope composition. The combination of these particular proxies gives a good insight into the temporal relationships between changes in volcanism, weathering, and the carbon cycle, as recorded by these three proxies.

Chapter 5 explores the influence of different volcanic contexts and sedimentary processes on stratigraphic records of the mercury cycle. Eight new mercury datasets from sedimentary records of Cretaceous Ocean Anoxic Event 2 (OAE 2: ~94 Ma) are presented, together with four mercury datasets from sedimentary records of the latest Cretaceous (K–Pg: including the end-Cretaceous extinction: 66.0 Ma). Comparison of these multiple records helps to highlight the potential effects of local sedimentary processes in superimposing any global mercury signal. Moreover, OAE 2 and the K–Pg represent different styles of LIP volcanism compared to the TJ and T-OAE, with OAE 2 associated with submarine LIPs, the K–Pg coincident with a subaerial LIP, and the TJ and T-OAE both linked to subaerial LIPs which likely intruded into volatile-rich country rocks that may have provided an additional source of thermogenic mercury in addition to magmatic Hg emissions. Thus, investigating records of the mercury cycle during events

associated with different types of LIP will allow the potential impact of different LIPs on the mercury cycle to be assessed.

Finally, Chapter 6 will draw together the combined results of these studies to gain new insight into the following key questions regarding the interactions between the emplacement of LIPs and Earth's climate, and the use of sedimentary mercury as a proxy for LIP volcanism:

- 1) **How does the emplacement characteristics of the LIP volcanism affect the presence or otherwise of a global perturbation to the global Hg cycle?** The Central Atlantic Magmatic Province (TJ) was a subaerial LIP where any mercury emissions would have been atmospheric, and might also have featured thermogenic volatile release (Svensen *et al.*, 2009). The ocean plateaus associated with OAE 2 would have featured predominantly submarine volcanism, where emitted mercury might have not easily reached the atmosphere. The Deccan Traps (KPg) were subaerial, but are not thought to have featured intrusion into organic sediments (Ganino and Arndt, 2009), so that any emitted mercury would only be magmatic. This question will be addressed in Chapters 3 and 5.
- 2) **Do recorded Hg enrichments concur with other indications of the timing of LIP emplacement, strengthening the case for Hg/TOC peaks resulting from LIP volcanism?** Such correlations are attempted both through stratigraphic and geochronological correlation of the Hg/TOC peaks in the sedimentary record with preserved LIP basalts (Chapter 3), and by comparing stratigraphic Hg/TOC trends with those of other sedimentary

proxies for volcanism such as shifts to unradiogenic osmium-isotope compositions (Chapter 5).

- 3) Can mercury be used in multiproxy studies to investigate the temporal relationship between volcanism and other surface processes during major events?** This question is addressed chiefly through analyses of Hg concentrations and Hg/TOC ratios, radiogenic osmium-isotope compositions, and carbon-isotopes from a single sedimentary record of the T-OAE, in order to ascertain the temporal relationships and potential feedbacks of surface phenomena during this event (Chapter 4). Additionally, Triassic–Jurassic mercury records are correlated against stomatal indices data in order to establish whether atmospheric mercury and carbon were perturbed geologically simultaneously in the latest Triassic (Chapter 3).
- 4) How do sedimentary and local transport processes impact particular palaeoenvironments as potential archives of changes in the global Hg cycle?** Comparison of multiple mercury records from each individual event covering a range of locations and facies types, as well as comparing the overarching Hg signals of multiple events, will help underline whether a single mercury record can be taken as representative of the global Hg cycle, and to what extent local processes can overprint any global signal. This question will be investigated in Chapter 5.

Chapter 2

Analytical Methods

Samples from all sedimentary records of the events reported in this work were analysed for mercury (Hg) and total organic carbon (TOC) content. Additionally, samples from the uppermost Pliensbachian to lower Toarcian interval of the Mochras core were analysed for Rhenium–Osmium (Re–Os) isotopes, and molybdenum (Mo), uranium (U), and aluminium (Al) concentrations. Samples from the end-Cretaceous record of Montana, the Pliensbachian–Toarcian record of the Mochras core, and end-Triassic record of Arroyo Malo were analysed for organic carbon isotopes ($\delta^{13}\text{C}_{\text{org}}$). Finally, changes in weathering rates during Pliensbachian–Toarcian times were modelled on the basis of osmium-isotope data generated through Re–Os analysis. All the methods described here were undertaken myself, except where stated otherwise, and where referenced as being previously established.

2.1. Hg/TOC analysis

2.1.1. Mercury analysis

Samples were crushed using a clean agate pestle and mortar to avoid possible contamination from metals. Once a homogenous powder was produced, no further physical or chemical preparation was necessary for analysis of either mercury (Hg) or total organic carbon (TOC).

Mercury analysis was conducted using a RA-915 Portable Mercury Analyzer with PYRO-915 Pyrolyzer, Lumex, as established by Bin *et al.* (2001). Typically, 50 ± 2 mg of powdered sample was precisely weighed into a glass measuring boat and its precise mass determined. The glass boat was then placed into the Pyrolyzer, which was set to machine Mode 1 in order to heat the sample to 700 °C. The pyrolysis stage volatilised the mercury in the sample, with the resulting gas fed

through to the Analyzer, and detected through Zeeman atomic absorption spectroscopy (Sholupov and Ganeyev, 1995). The mercury concentration can then be calculated using the original sample mass. The detection limit of the RA-915 Analyzer is approximately 0.5 ng. Consequently, for samples with low mercury content, an increased amount (either 100 ± 2 or 150 ± 2 mg) of powdered sample was analysed.

To calibrate the machine, each sample run was preceded with measurement of six peat standards of varying masses between $20\text{--}80 \pm 2$ mg. An additional standard was analysed after every 10 sample measurements. The standard used was NIMT/UOE/FM/001 – Inorganic Elements in Peat, which has a known mercury concentration of 169 ± 7 ppb. Each sample was measured at least twice, with a typical repeatability within 10%. All mercury analyses were performed at the Department of Earth Sciences, University of Oxford.

2.1.2. TOC analysis

Where previous data were not available, TOC abundances were ascertained using either a Rock-Eval VI unit from Vinci Technologies (as described in Espitalié *et al.*, 1977) or Strohlein Coulomat 702 (following the methodology in Jenkyns, 1988) at the Department of Earth Sciences, University of Oxford.

2.1.2.1 Rock-Eval VI analysis

In addition to TOC content, the Rock-Eval also provides Hydrogen Index (HI) values and %wt Mineral Carbon. Rock Eval analysis was performed on ~20–30 mg of homogenised powdered sample aliquots. Each sample was heated with incremental temperature steps from room temperature to up to 850 °C in oxidation

and pyrolysis ovens. Mineral carbon content was calculated from the $S3_{\text{MINC}}$ and $S5$ peaks that were generated following analysis of the CO and CO₂ flux from the sample by infrared detector. The TOC content was simultaneously obtained in the same sample-run and was calculated from the combined CO and CO₂ fluxes from the pyrolysis (PC: $S1 + S2 + S3_{\text{CO}} + S3_{\text{CO}_2}$) and oxidation (RC: $S4_{\text{CO}} + S4_{\text{CO}_2}$) heating stages. Precision and accuracy of the Rock-Eval analyses was checked by regular measurement of the in-house standard SAB134 (a Lower Jurassic shale) and the international reference standard IFP160000. Repeated long-term analyses of the TOC content of the in-house SAB134 standard shows an average of 2.80 %wt and a reproducibility of ± 0.47 %wt (2 S.D., $n = 45$). Repeated long-term analyses of the TOC content of the IFP160000 standard showed an average concentration of 3.27 ± 0.02 %wt, which is within error to the certified TOC content of this standard ($3.28 \pm 0.14\%$ wt).

2.1.2.2 Coulomat analysis

Coulomat analysis provided TOC and carbonate content, by analysing two aliquots of homogenised sample. The first aliquot consisted of ~50 mg of bulk sample; the second of ~75 mg of sample heated at 420 °C overnight in order to remove all organic carbon. Both samples were placed, successively, in a furnace that heated them in pure oxygen to 1200 °C, oxidising all carbon to CO₂. The CO₂ was then bubbled through a barium perchlorate solution of known pH, and the change in pH measured via a change in the charge as the carbon passed through the solution. The amount of charge required to restore the solution to its original pH would then be back calculated to give the total quantity of carbon in each measured aliquot. The first (unheated) aliquot of a sample would yield the total carbon (TC) content of the

sample; the second (heated) aliquot would yield the total inorganic carbon (TIC) content of the sample. Subtracting the TIC from TC gives the TOC content of a sample, whilst multiplying TIC by 8.33 (the atomic mass percentage of carbon in pure calcium carbonate) estimates the carbonate content of a sample.

2.2. Rhenium–Osmium analysis

2.2.1. *The Re–Os proxy*

A key property of osmium (Os) as an ocean chemistry proxy is its seawater residence time of 10–50 kyr (Peucker-Ehrenbrink and Ravizza, 2000). This residence time is sufficiently long for the oceans to be well mixed, whilst short enough to record geologically abrupt changes. Rhenium (Re) and osmium have markedly different compatibility in silicate melts; consequently, the primitive lithospheric mantle is more enriched in Os/Re compared to the continental crust. The decay of crustal ^{187}Re enriches the continental crust in radiogenic ^{187}Os . As a result, primitive, mantle derived, basalts have unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratios of ~ 0.12 (Sharma *et al.*, 1999) whilst continental crust has a radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratio of ~ 1.4 (Peucker-Ehrenbrink and Jahn, 2001). Any change in the relative flux of those two sources to the ocean will affect the overall $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater. For example, higher continental weathering rates relative to the activity of mid-ocean ridge basalts will substantially increase seawater $^{187}\text{Os}/^{188}\text{Os}$ (refer to Cohen *et al.* 1999).

Recording of a global signature of seawater $^{187}\text{Os}/^{188}\text{Os}$ at a certain location is also dependent on the assumption that that location was hydrographically well mixed with the global ocean. A water body that has restricted mixing of water masses with the global ocean may not allow for water-mass interchange within the

seawater residence time of osmium, resulting in an osmium-isotope ratio influenced by local inputs to that water body, rather than a record of the global ocean signature. Proximity to land masses may also influence the seawater $^{187}\text{Os}/^{188}\text{Os}$ ratio, due to the relatively increased influx of detrital osmium to sediments accumulating near to continents compared to in the open ocean (Paquay and Ravizza, 2012; Du Vivier *et al.*, 2014; 2015). Consequently, knowledge of the palaeogeographic situation of the record being studied is of paramount importance when interpreting osmium-isotope trends in ancient sedimentary successions.

Osmium is concentrated from seawater in organic-rich sediments, allowing accumulating organic-rich mudrocks to record the contemporaneous seawater $^{187}\text{Os}/^{188}\text{Os}$. Rhenium is also concentrated in organic-rich sediments, in which ^{187}Re decays to produce radiogenic ^{187}Os . Knowledge of the present-day $^{187}\text{Os}/^{188}\text{Os}$ of a rock sample allows the Os-isotope composition of the sample at the time of sediment deposition (expressed as $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ or $\text{Os}_{(i)}$) to be calculated, if the age and Re and Os concentrations of the sample are also known, and if the system has been isotopically ‘closed’ since sediment deposition (e.g. Cohen *et al.* 1999). This calculation relies on the known decay equation of ^{187}Re to ^{187}Os (below), and the established decay constant of ^{187}Re decay ($1.666 \times 10^{-11} \text{ yr}^{-1}$: Smoliar *et al.*, 1996).

$$\left(\frac{^{187}\text{Os}}{^{188}\text{Os}} \right) = \left(\frac{^{187}\text{Re}}{^{188}\text{Os}} \right) (e^{\lambda t} - 1) + \left(\frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_i$$

Because most (often >98%) of the Os in organic-rich samples is hydrogenous (and if all the previous conditions are met), a value for the $^{187}\text{Os}/^{188}\text{Os}$

of contemporaneous seawater can be inferred (Ravizza and Turekian, 1992; Cohen *et al.*, 1999).

2.2.2. Preparation and analysis of rhenium and osmium

2.2.2.1 Separation of rhenium and osmium

The digestion of organic-rich mudrocks in sealed carius tubes, and the subsequent extraction, purification and measurement of osmium follows the procedure of Cohen and Waters (1996). The purification and analysis by mass spectrometry of rhenium are based on the procedures outlined by Birck *et al.* (1997), as detailed also in Fehr *et al.* (2011), and Dickson *et al.* (2015). The final stage of this procedure was amended to carry out the final dissolution of samples into 2 % HNO₃ spiked with 40 ppb Ir, as detailed below. All preparations and analyses of the powdered rock samples were carried out at the Open University (Milton Keynes, UK).

Samples were crushed using a clean agate pestle and mortar to avoid possible contamination from metals. One gram of the sample powder was weighed into acid-cleaned carius tubes. Half a gram of international standard Ohio Shale SDO-1 was also weighed out, and half a gram of a second, in-house, mudrock standard 00N118 (Monterey Formation mudrock) was also weighed. Two carius tubes were kept empty of solids, but were spiked with a diluted ¹⁸⁵Re–¹⁹⁰Os spike to estimate total procedural blanks. Powdered samples were decarbonated with 3 ml of twice distilled HCl, with a small amount of HCl added to carbonate rich samples (e.g. 0.5 ml extra for samples with 50% CaCO₃). Immediately prior to sealing, a pre-weighed aliquot of a mixed ¹⁸⁵Re–¹⁹⁰Os spike and 9 ml of sparged HNO₃ was added to each carius tube. The addition of HNO₃ to the HCl already present in each tube produced a

concentrated mixture of inverse aqua regia. The tubes were sealed with a blow torch and heated at 170 °C for four days to allow full digestion.

After four days the carius tubes were removed from the oven, frozen at -20 °C, scoured and broken open. The inverse aqua regia was quickly pipetted into clean PFA beakers containing 8 ml of CCl₄, and the beakers shaken vigorously. The osmium (as volatile OsO₄) was partitioned into the CCl₄, whilst the rhenium remained in the inverse aqua regia. CCl₄ and aqua regia are incompatible, and were left in a refrigerator overnight to separate, before the CCl₄ was pipetted into separate beakers containing HBr. The inverse aqua regia was then dried down at 100 °C over two to three days before the separation of rhenium.

2.2.2.1 Chemical preparation of osmium

The PFA beakers containing HBr and CCl₄ were shaken until well mixed. This mixture encourages the reduction of OsO₄ into the HBr. HBr and CCl₄ are incompatible, so the new mixture was left in a refrigerator overnight to separate. Once separated, the HBr was pipetted into a new PFA beakers and dried down at 100 °C over two to three days. Each dried down HBr residue was re-dissolved in 50 µl of an HBr-acetone mixture, transferred onto the upturned flat lid of a conical beaker, and left to dry on a hot plate at 100 °C. Meanwhile a tiny drop of HBr was placed in the bottom of each conical beaker, and the beaker upturned. Once the Os residue on the lid had dried, it was removed from the hotplate, and two drops of chromium VI dissolved in sulphuric acid were placed on the residue. The upturned beaker was then screwed on to the lid, and the whole beaker wrapped in Al foil, except for a cold spot at the top of the cone. Each wrapped conical beaker was then returned to the hot plate for three hours at 85 °C. The chromium–sulphuric acid

mixture would oxidise the Os residue, resulting in the production of OsO_4 vapour, which would be reduced from the vapour phase by the HBr drop at the top of the conical beaker. After 3 hours the conical beakers were removed, unwrapped, and the beakers unscrewed from the lids. The beakers with the HBr drops (now an Os solution) were turned back to upright, and sealed with a clean lid. The beakers were then individually heated to $120\text{ }^\circ\text{C}$ on a hot plate, to reduce the size of the HBr drops. The drops were then transferred to a de-gassed platinum filament with a 0.4A current running through it to increase the speed of evaporation. When only the residue of the HBr drop was left on the filament, three drops of emitter solution ($\text{Ba}(\text{OH})_2$ in NaOH solution) were added to the filament, and left to dry. This filament loading was repeated for all blanks, material standards, and samples, and also for 3 solution standards.

2.2.2.3 Chemical preparation of rhenium

The dried down aqua regia residue was dissolved in 2M HNO_3 overnight on a $120\text{ }^\circ\text{C}$ hot plate. The solutions were allowed to cool, before the dissolved residues were emptied from each beaker in to an individual centrifuge tube. 2 ml of iso-amylol alcohol was added to each centrifuge tube. The tubes were sealed, shaken thoroughly, and centrifuged at 4000 rpm for 5 minutes to separate the iso-amylol and nitric acid. Any remaining sediment was also separated at this stage. The rhenium preferentially partitioned into the iso-amylol. The iso-amylol was pipetted from each centrifuge tube into a new centrifuge tube, and the leftover nitric acid and sediment discarded. 2 ml of 2M HNO_3 was added to each new centrifuge tube of iso-amylol, before each tube was sealed, shaken, and centrifuged at 4000rpm for 5 minutes, and the lower layer of separated nitric acid pipetted out and discarded,

leaving the iso-amylol again. This addition and removal of nitric acid was repeated, before 2ml of milli-Q water was added to the iso-amylol. Once again, the mixture was shaken and centrifuged, but because the Re preferentially partitioned in to the milli-Q water, after separation the milli-Q water from each centrifuge tube was transferred to a separate beaker, and the iso-amylol discarded.

The beakers were placed on a hot plate at 120 °C, and the MQ water dried down over 2–3 hours to leave a small residue (containing the rhenium). The residue was re-dissolved in a mixture of 300 µl of sparged, twice distilled, HNO₃, and 60 µl hydrogen peroxide, to remove any residual organic compounds. This mixture was refluxed on a hot plate at 120°C for 2 hours, and dried down once again. This new residue was dissolved in 0.5ml of 2% nitric acid over 2–3 hours on a hot plate at 120°C. The nitric acid also contained 40 ppb iridium (Ir). Once the Re residue had been dissolved, the nitric acid solution from each beaker was emptied into a 1.5ml mini-centrifuge tube.

2.2.2.4 Analysis of rhenium and osmium

Analyses of Rhenium concentrations were carried out on a Thermo-Finnigan Neptune Plus Multicollector-ICP-MS at the Open University. Analysis of osmium-isotope ratios and osmium concentrations was carried out on a Thermo-Finnigan Triton N-TIMS at the Open University. Measured $^{187}\text{Os}/^{188}\text{Os}$ ratios were normalised to $^{192}\text{Os}/^{188}\text{Os} = 3.08271$. All data were blank corrected using averaged data for 4 procedural blanks run over the course of the analysis ($^{187}\text{Os}/^{188}\text{Os} = 0.1633$). Os concentrations for the blanks were < 1 pg, so blank contributions were consistently < 1 %. Precision of $^{187}\text{Os}/^{188}\text{Os}$ analyses was < ± 0.2 % (2 S.D.), determined from 6 measurements of a DTM Os standard solution; $^{187}\text{Os}/^{188}\text{Os} =$

0.173875 ± 0.005707 (2 S.D.). In addition, 3 measurements of the USGS standard reference material SDO-1 were included to give an indication of external reproducibility: $[\text{Os}] = 589 \text{ ppt}$ (2 S.D. = 1.3 ppt), $^{187}\text{Os}/^{188}\text{Os} = 7.94925 \pm 0.075575$ (2 S.D.). For rhenium analyses, instrumental mass fractionation was calculated and corrected by reference to added Ir ($^{193}\text{Ir}/^{191}\text{Ir}$ ratio of 1.68299). The total Re procedural blanks were $< 10 \text{ ppt}$, thus blank contributions were generally $< 0.02 \%$. Three analyses of SDO-1 gave an average Re concentration of 76.55 ppb (2 S.D. = 0.02 ppb).

2.3. Elemental concentration (Mo, U, Al) analysis

Samples were prepared for elemental concentration analysis using acid digestion at the Department of Earth Sciences, University of Oxford. Approximately 50 mg of rock sample powder was weighed into an acid-cleaned teflon beaker and its precise mass determined. 2 ml of 16M HNO_3 and 1 ml of 27M HF were added, and the samples digested in a hot block set to 120°C for 24 hours. The samples were then removed from the hot block to cool slightly, their lids rinsed with milli-Q water and the rinsing returned to the beaker, and the beakers returned to the hot block to dry down (with the lids upturned to dry off).

Once dried down, another 2 ml of 16M HNO_3 was added, and again left overnight to digest. Once again the beakers were dried down as described above, before another overnight digestion in 2 ml of 16M HNO_3 . Once this HNO_3 had been dried down, 1.3 ml of HNO_3 and 0.7 ml of milli-Q water was added, and left to reflux for at least 24 hours until the contents were dissolved. The solutions were left to cool, and then each digested sample emptied into a centrifuge tube and topped up with milli-Q water to give a total volume of 10 ml (and total dilution factor of 200).

For major-element analysis (Al), the samples were diluted twice more in 2% HNO₃, first by a factor of 200, and finally by a factor of 100, to give a total dilution of ~4,000,000-fold by volume. For trace-element analysis (Mo and U), samples were diluted in 2% HNO₃ by a further factor of 50, to give a total dilution of ~10,000-fold. Major- and trace-element analyses were performed using a Thermo-Finnigan Element 2 magnetic-sector ICP-MS by Phil Holdship at the University of Oxford. For major-element analysis, calibration standards were 1ppb, 5ppb, 10ppb, 20ppb, and 50ppb, with two 10ppb QC standard solutions that averaged 10.224ppb±0.204 (2 S.D.) for Al. For trace-element analysis, calibration standards were 1 ppt, 10 ppt, 50 ppt, 500 ppt, 10 ppb, and 100 ppb, with four 5ppb QC standard solutions that averaged 5.100±0.308ppb (2 S.D.) for Mo, and 4.804±0.339ppb (2 S.D.) for U.

2.4. Carbon-isotope analysis

Approximately one gram of homogenised sample material was decarbonated with 3M HCl in a warm water bath at 80 °C, for 5 hours. The sample was subsequently rinsed and centrifuged at least three times with milli-Q water to reach neutral *pH* levels. Between 0.1–25 mg of decarbonated sample (aiming for ~25 µg pure carbon, based on the established TOC content of the sample) was then weighed into 8×5 mm tin capsules for $\delta^{13}\text{C}_{\text{org}}$ analyses. Sample preparation was carried out in the Department of Earth Sciences, University of Oxford.

Preparation and analyses of Triassic–Jurassic samples from Arroyo Malo were carried out by Dr Micha Ruhl. Preparation and analyses of Pliensbachian–Toarcian samples from the Mochras core were carried out by Dr Weimu Xu, and Marisa Storm. All end-Triassic and Toarcian $\delta^{13}\text{C}_{\text{org}}$ analyses were performed at the Stable Isotope Laboratory at the Open University (Milton Keynes, UK), with a

Thermo Scientific Flash 2000 HT Elemental Analyser (EA) coupled to a Thermo Scientific MAT253 isotope ratio mass spectrometer via a ConFlo IV open split interface. The Thermo Scientific Flash 2000 HT EA has a MAS2000 carousel and, between the carousel and the EA, sits a Thermo No Blank Device (NBD), allowing for the single sample purging with helium. The EA is also equipped with a Thermal Conductivity Detector (TCD). Automated dilution of sample gas with the ConFlo IV open split interface allowed for a high dynamic range of carbon (and nitrogen) content, and controlled the introduction of the reference gases. Analytical precision was checked by routine analysis of three internal and referenced laboratory standards: IAEA CH6-sucrose, glutamic acid light and Alanine-A. These standards gave measured average $\delta^{13}\text{C}$ values of -14.2‰, -25.1‰ and -22.2‰, respectively, with standard deviations of 0.3‰, 0.2‰ and 0.1‰.

All end-Cretaceous sample analyses were performed on a SERCON 20-22 IRMS, coupled to a SERCON GLS, in the School of Archaeology, University of Oxford, by Dr Peter Ditchfield. Alanine-A was used as a standard, with a $\delta^{13}\text{C}$ value of -27.1‰. Five standards were analysed at the beginning of a sample-set run, with an additional two standards measured after each set of seven sample measurements. The twenty-six measured standards averaged -27.09‰, with a standard deviation of 0.15‰.

2.5. Estimating weathering fluxes from osmium-isotope records

Because osmium has an ocean residence time of 10–50 kyr, it may be assumed to be well mixed within the open ocean.

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2.5.1. *Sinks*

Being well mixed, it may be assumed that osmium drawn down to sediments will have the same isotopic ratio as the seawater at that time (a fundamental principle of osmium isotope stratigraphy). Therefore, $^{187}\text{Os}/^{188}\text{Os}_{\text{sw}} \equiv ^{187}\text{Os}/^{188}\text{Os}_{\text{sediment}} \equiv ^{187}\text{Os}/^{188}\text{Os}_{(i)}$.

2.5.2. *Sources*

Unradiogenic osmium is supplied chiefly by hydrothermal activity from submarine volcanism, mainly Mid Ocean Ridge Basalts (MORB), with subsidiary input from weathering of continental flood basalts and cosmogenic input (both assumed to be negligible through most of geological time). All unradiogenic sources have $^{187}\text{Os}/^{188}\text{Os}$ of ~ 0.12 . Radiogenic osmium is supplied chiefly by weathering of continental crustal material, which in the modern has $^{187}\text{Os}/^{188}\text{Os}$ of ~ 1.4 .

2.5.3. *Overall*

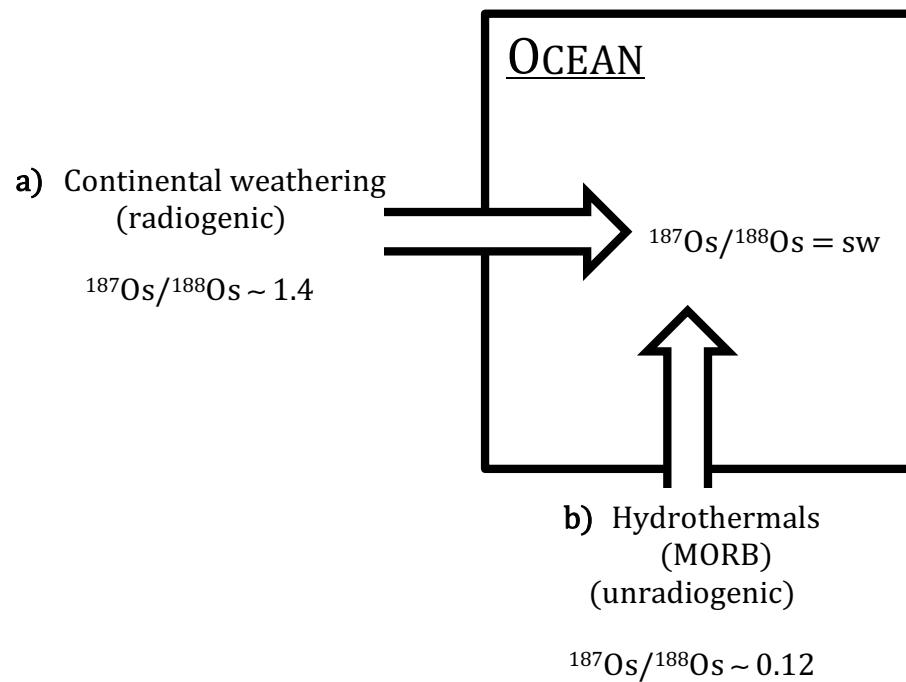
Therefore, since a water mass may be assumed to be well mixed with only two major inputs, osmium mixing in the global ocean may be calculated as a proportion of those two end-members (see box model, and equations 1 and 2).

Where **a** and **b** represent proportional fluxes of radiogenic and unradiogenic (respectively) osmium to the ocean:

1. $a + b = 1$
2. $1.4a + 0.12b = \text{sw}$

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sw is known from the $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ data generated from a sample, allowing a and b to be solved.



Using the equations 1 and 2 for the $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ data from Mochras (Chapter 4; section 4.3.), the following may be calculated:

2.5.4. *Upper Pliensbachian*

$$^{187}\text{Os}/^{188}\text{Os}_{(i)} = 0.40$$

$\therefore$

$$1.4\mathbf{a} + 0.12\mathbf{b} = 0.40$$

$$\mathbf{a} + \mathbf{b} = 1$$

$\therefore$

$$\mathbf{b} = 0.78, \mathbf{a} = 0.22$$

$$\mathbf{b} = 3.57\mathbf{a}$$

2.5.5. *Pliensbachian–Toarcian boundary*

$$^{187}\text{Os}/^{188}\text{Os}_{(i)} = 0.53$$

$$\therefore$$

$$1.4\mathbf{a} + 0.12\mathbf{b} = 0.53$$

$$\mathbf{a} + \mathbf{b} = 1$$

$$\therefore$$

$$\mathbf{b} = 0.68, \mathbf{a} = 0.32$$

$$\mathbf{b} = 2.12\mathbf{a}$$

2.5.6. *Upper tenuicostatum Zone*

$$^{187}\text{Os}/^{188}\text{Os}_{(i)} = 0.42$$

$$\therefore$$

$$1.4\mathbf{a} + 0.12\mathbf{b} = 0.42$$

$$\mathbf{a} + \mathbf{b} = 1$$

$$\therefore$$

$$\mathbf{b} = 0.77, \mathbf{a} = 0.23$$

$$\mathbf{b} = 3.26\mathbf{a}$$

2.5.7. *Toarcian OAE*

$$^{187}\text{Os}/^{188}\text{Os}_{(i)} = 0.68$$

$$\therefore$$

$$1.4\mathbf{a} + 0.12\mathbf{b} = 0.68$$

$$\mathbf{a} + \mathbf{b} = 1$$

$$\therefore$$

$$\mathbf{b} = 0.56, \mathbf{a} = 0.44$$

$$\mathbf{b} = 1.28\mathbf{a}$$

2.5.8. *Weathering rates*

Over geologically short timescales, submarine hydrothermal input from MORB may be assumed to be constant; therefore, any change in the ratio **b/a** must be due to changes in **a** (i.e. continental weathering rates).

Therefore, for the Pliensbachian–Toarcian boundary: $3.57\mathbf{a}/2.12\mathbf{a} = 1.68 \therefore$
~70% increase.

For the Toarcian OAE: $3.26\mathbf{a}/1.28\mathbf{a} = 2.58 \therefore$ **~160% increase.**

Chapter 3

Mercury evidence for pulsed volcanism during the end-Triassic mass extinction

A very similar version of this chapter is in the final stages of revision for the journal *Proceedings of the National Academy of Sciences of the United States of America*, with the following author list:

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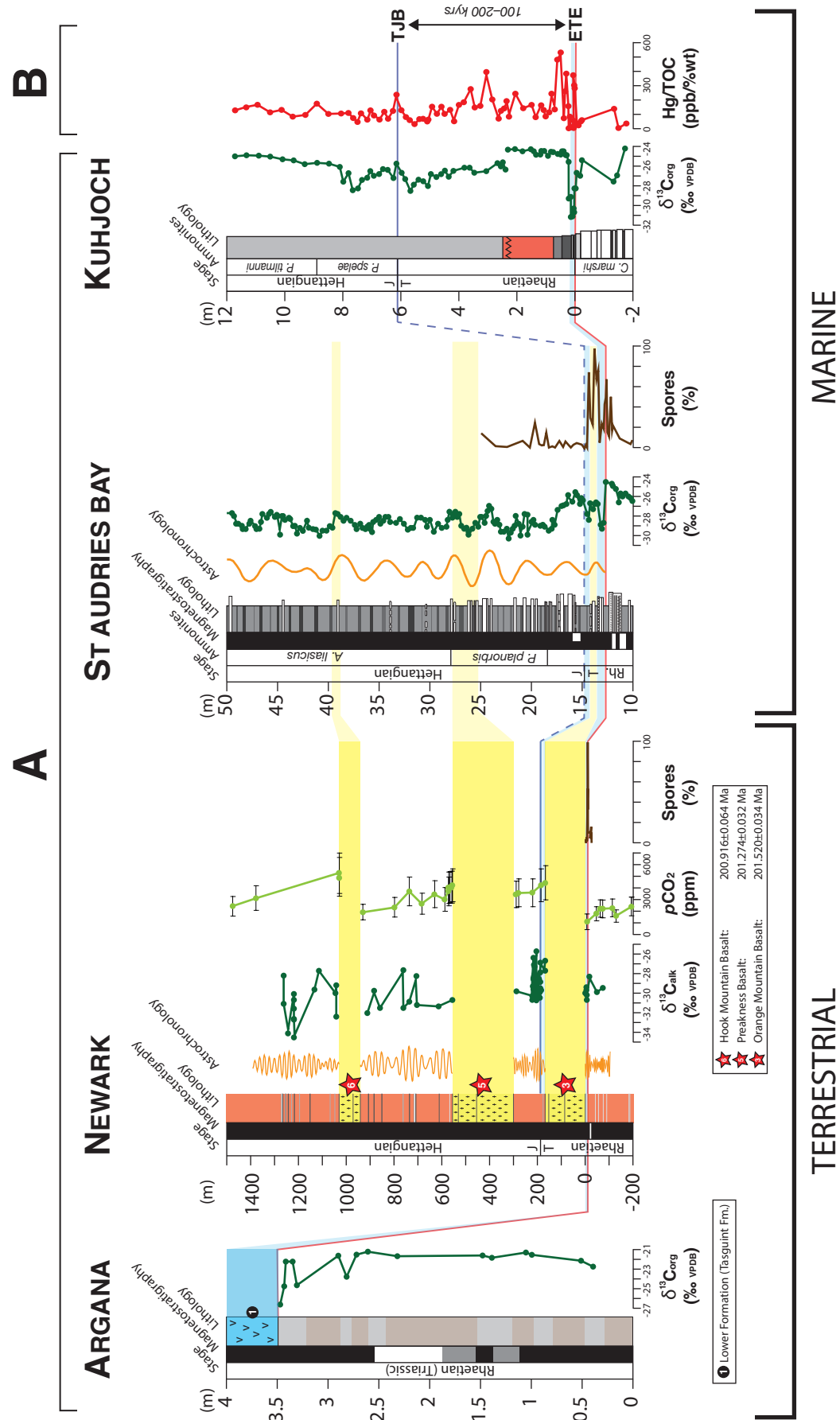
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Abstract

The Central Atlantic Magmatic Province (CAMP) has long been proposed as having a causal relationship with the end-Triassic extinction event (~201.5 Ma). In North America and northern Africa, CAMP is preserved as multiple basaltic units interbedded with uppermost Triassic to lowermost Jurassic sediments. However, it has been unclear whether this apparent pulsing was a local feature, or if pulses in the intensity of CAMP volcanism characterised the emplacement of the province as a whole. Here, six geographically widespread Triassic–Jurassic records, representing varied palaeoenvironments, are analysed for mercury concentrations and mercury/total organic carbon (Hg/TOC) ratios. Volcanism is a major source of mercury to the modern environment. Clear increases in Hg and Hg/TOC are observed at the end-Triassic extinction horizon, confirming that a volcanically-induced global mercury-cycle perturbation occurred at that time. The established correlation between the extinction horizon and lowest CAMP basalts allows this sedimentary mercury excursion to be stratigraphically tied to a specific flood basalt unit for the first time, strengthening the case for volcanic mercury as the driver of sedimentary Hg/TOC spikes. Additional Hg/TOC peaks are also documented between the extinction horizon and the Triassic–Jurassic boundary (separated by ~200 kyr), supporting pulsatory intensity of CAMP volcanism across the entire province and providing the first direct evidence for episodic volatile release during the initial stages of CAMP emplacement. Pulsatory volcanism, and associated perturbations in the ocean–atmosphere system, likely had profound implications for the rate and magnitude of the end-Triassic mass extinction and subsequent biotic recovery.



3.1. Introduction

The end of the Triassic Period was marked by a major mass extinction event (~201.5 Ma; e.g. Schoene *et al.*, 2010; Blackburn *et al.*, 2013), one of the five largest environmental perturbations of the Phanerozoic Aeon. Significantly increased extinction rates of marine fauna, and major turnovers in terrestrial vegetation and vertebrate groups, have been well documented (e.g. Raup and Sepkoski, 1982; Olsen *et al.*, 1987; 1990; McElwain *et al.*, 1999; 2009; Bonis *et al.*, 2009). The end-Triassic mass extinction predated the onset of the Jurassic by ~100–200 kyr, as defined by the first occurrence of the Jurassic ammonite species *Psiloceras spelae* (Hillebrandt *et al.*, 2013). The sedimentary record of the extinction correlates with a large (up to 6‰) negative excursion in organic-carbon isotopes ($\delta^{13}\text{C}_{\text{org}}$; Figure 3.1A), indicative of a severe carbon-cycle perturbation coincident with the biotic crisis (e.g. Hesselbo *et al.*, 2002; Ruhl *et al.*, 2009;

Figure 3.1: A: Stratigraphic correlation of the end-Triassic extinction with the Moroccan Lower Formation CAMP basalt. Argana lithology, carbon-isotope, and palaeomagnetic data are from Deenen *et al.* (2010). Newark lithology and $p\text{CO}_2$ data are from Schaller *et al.* (2011), palaeomagnetic and astrochronological data are from Kent and Olsen (1999); carbon-isotope data from Whiteside *et al.* (2010); trielite spore data from Olsen *et al.*, (2002). St Audries Bay lithology and astrochronology are from Ruhl *et al.* (2010a) and Xu *et al.* (2017), biostratigraphy and carbon-isotope data from Hesselbo *et al.* (2002) and Ruhl *et al.* (2010a), trielite spore data from Bonis *et al.* (2010), palaeomagnetic data from Hounslow *et al.* (2004) and Hüsing *et al.* (2014). Stratigraphic correlation of CAMP units between Argana, Newark, and St Audries Bay is based on Whiteside *et al.* (2010) and Xu *et al.* (2017). Kuhjoch biostratigraphy, lithology, and carbon-isotope data are from Ruhl *et al.* (2009). The end-Triassic extinction horizon (marked as ETE) and Triassic–Jurassic boundary (marked as TJB) are also shown. **B:** Example of new Hg/TOC data from this study (Kuhjoch, Figure 3.3) are shown to stratigraphically correlate with the lowest CAMP basalt unit that intersects the end-Triassic extinction at Argana. See Appendix 1A for a full stratigraphic correlation of end-Triassic records.

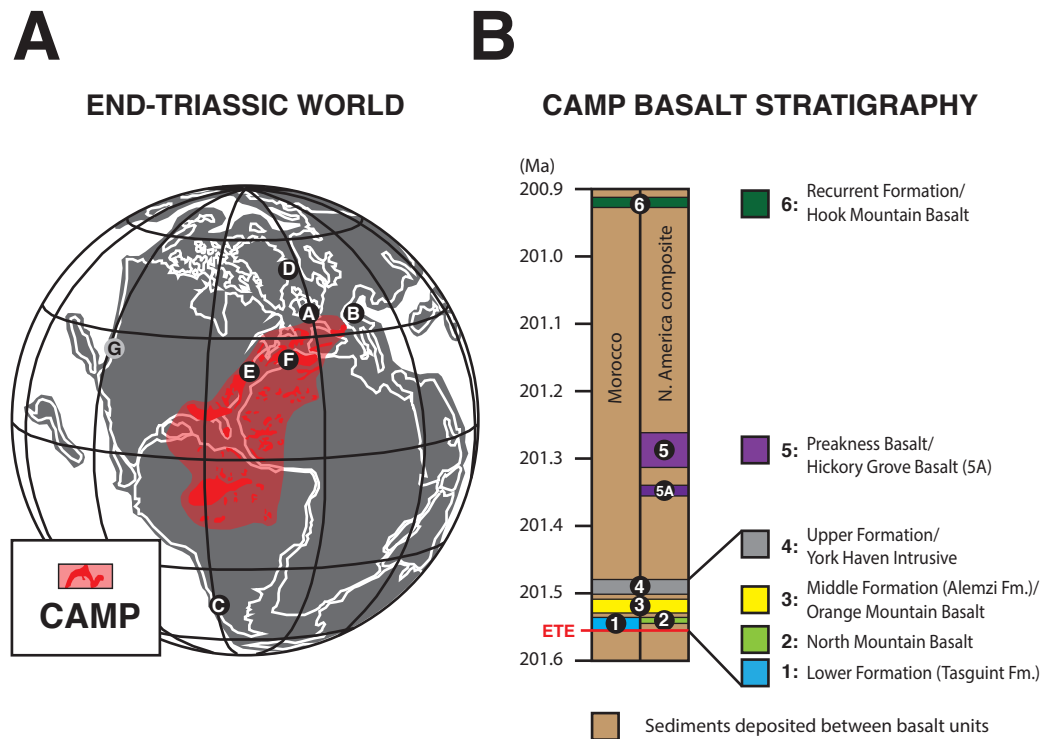


Figure 3.2: **A:** Palaeogeographic reconstruction of the end-Triassic world, with the modern continents overlain. The locations of the six studied sections are indicated (A: St Audries Bay, U.K.; B: Kuhjoch, Austria; C: Arroyo Malo, Argentina; D: Astartekløft, Greenland; E: Partridge Island, Canada; F: Igounane, Morocco). The New York Canyon section in Nevada, U.S.A. (G: note different colour) studied by Thibodeau *et al.* (2016), and the Central Atlantic Magmatic Province (CAMP) are also shown (based on Figure 1 from Blackburn *et al.*, 2013). **B:** Summarised composite stratigraphy of Moroccan and North American CAMP basalts, following the stratigraphic relationships and ages (in Myrs) from Deenen *et al.* (2010) and Blackburn *et al.* (2013). The Hickory Grove basalt is included with the Preakness due to their geochemical similarity. The age of the end-Triassic extinction (marked as ETE) is also indicated.

Whiteside *et al.*, 2010; Bartolini *et al.*, 2012 Moroccan strata that record this global carbon-cycle perturbation are transected by the lowest documented flows of the Central Atlantic Magmatic Province (CAMP). Consequently, the end-Triassic extinction has been postulated as precisely coincident with the onset of known CAMP volcanism (e.g. Blackburn *et al.*, 2013; Whiteside *et al.*, 2010; Deenen *et al.*, 2010; Dal Corso *et al.*, 2014).

CAMP represents the most aerially expansive continental Large Igneous Province (LIP) known on Earth, consisting of volumetrically large-scale flood-basalt sequences covering at least 7×10^6 km² across four continents and both hemispheres (Figure 3.2A: Marzoli *et al.*, 1999). In North America and Morocco, CAMP basalts are interbedded with continental sediments that have precise temporal constraints and are stratigraphically well correlated with marine sedimentary records (Figure 3.1A: refs Whiteside *et al.*, 2010; Deenen *et al.*, 2010). The apparent episodic intrusion of CAMP basalts over several 100 kyr, at least in Morocco and North America, is a key feature of this LIP.

The oldest known CAMP basalts are the lower Moroccan unit (termed the Lower Formation in the High Atlas and the Tasguint Formation in the Argana Basin: El Hachimi *et al.*, 2011; El Ghilani *et al.*, 2017). This unit is overlain by two further Moroccan basalt units, the Middle and Upper Formations in the High Atlas (the former named the Alemzi Formation in Argana: El Hachimi *et al.*, 2011; El Ghilani *et al.*, 2017). For clarity, the High Atlas names are used henceforth in this study. These three basalt groups are interbedded with sedimentary deposits. A fourth extrusive unit, the Recurrent Formation, is locally preserved higher in the Moroccan sequence, with much thicker sediments between it and the Upper Formation (Figure 3.2B; Marzoli *et al.*, 2004; Deenen *et al.*, 2010; El Ghilani *et al.*, 2017). These four

basalt units are defined and correlated on the basis of distinct igneous geochemistry. Based on geochemical correlation with North American CAMP units, which are temporally constrained by astrochronological and radioisotopic geochronology, the Moroccan Lower–Upper Formations are thought to have erupted in quick succession, with several 100 kyr then passing before the eruption of the Recurrent Formation (Deenen *et al.*, 2010; Blackburn *et al.*, 2013).

At least three major CAMP units are documented in North America: the Orange Mountain, Preakness, and Hook Mountain basalts in the Newark Basin (Olsen *et al.*, 1996), with time-equivalent basalts known from other North American Basins. The Orange Mountain Basalt overlies thin, usually lacustrine, sediments deposited above the extinction horizon, and is thought to have been extruded 14–20 kyr after that event (Deenen *et al.*, 2010; Blackburn *et al.*, 2013; Kent *et al.*, 2017). Radioisotopic dating has demonstrated that the Preakness Basalt and Hook Mountain Basalt were emplaced 270 kyr and 620 kyr later, respectively (Blackburn *et al.*, 2013). The Newark Basin Orange Mountain and Hook Mountain basalts have been geochemically established as equivalent to the Moroccan Middle and Recurrent Formations, respectively (Deenen *et al.*, 2010); the Preakness Basalts have no known Moroccan counterparts (Deenen *et al.*, 2010; Blackburn *et al.*, 2013). Consequently, North American and Moroccan records suggest that CAMP was emplaced in at least three major pulses of basalt extrusion over ~700 kyr, with the products of the first major pulse further divisible into at least three or four geochemically and stratigraphically distinct units. Thus, a total of at least six CAMP units are documented in Morocco/North America (Figure 3.2B), which were relatively close to one another at the end of the Triassic Period. However, more geographically dispersed CAMP basalts are also known from southern Europe,

Brazil, and elsewhere in western Africa, with potentially different temporal relationships with the end-Triassic extinction and the dated CAMP flows (Marzoli *et al.*, 1999). Therefore, it is not clear whether the intensity of CAMP volcanism was pulsatory across the entire province, or whether the apparent pulsing recorded in North America and Morocco was a local feature of the much larger scale LIP.

Proxy records of volcanic volatiles can aid in reconstructing the history of CAMP volcanism and its impacts. Analyses of pedogenic carbonates suggest increases in atmospheric $p\text{CO}_2$ following emplacement of each of the Newark CAMP basalts (CAMP pulses 3, 5, and 6 in Figure 3.2B), supporting a pattern of globally incremental emplacement (Schaller *et al.*, 2011). However, the effect of local processes, such as diagenesis, on this record cannot be ruled out. Reconstructions of $p\text{CO}_2$ based on stomatal indices (albeit at low temporal resolution) show no such pulsing during the Triassic–Jurassic transition (McElwain *et al.*, 1999; Steinthorsdottir *et al.*, 2011). Nor is there yet evidence of episodic CO_2 increases associated with the early Moroccan CAMP pulses (CAMP pulses 1, 3, and 4 in Figure 3.2B) that were extruded coincident with, and in the immediate aftermath of, the extinction event.

Here, the volatile emissions and ocean-atmosphere impact of CAMP volcanism is investigated by analysis of sedimentary mercury (Hg) concentrations across multiple Triassic–Jurassic sedimentary archives. Volcanism is known to be a major natural source of mercury, emitting it as an inert trace volcanic gas (Pyle and Mather, 2003). Inert atmospheric Hg has a typical atmospheric residence time of 0.5–2 years (Blum *et al.*, 2014), allowing the element to be globally distributed before being drawn down and eventually deposited in sediments. Several Phanerozoic events have previously been linked to approximately coeval LIPs

through documented increases in sedimentary mercury concentrations, including the end-Permian and end-Cretaceous extinctions, and Toarcian Oceanic Anoxic Event (e.g.: Sanei *et al.*, 2012; Percival *et al.*, 2015; Font *et al.*, 2016). Importantly, sedimentary drawdown of Hg is typically achieved via organic matter (Benoit *et al.*, 2001; Outridge *et al.*, 2007), although sulphides and clays may also play a role (Benoit *et al.*, 1999; Niessen *et al.*, 2003; Kongchum *et al.*, 2011). Consequently, sedimentary Hg concentrations are typically normalised against total organic carbon (TOC) to account for the effect on Hg drawdown by changes in organic matter deposition rates when looking for evidence of an elevated supply of Hg to the environment (Sanei *et al.*, 2012).

In addition to interrogating the pulsatory history of CAMP volatile emissions, mercury analysis of uppermost Triassic sediments also provides a unique opportunity to test the assumption that Hg-enriched sediments were deposited precisely coincident with the eruption of LIP basalts. There are excellent age constraints on numerous end-Triassic records (including those containing CAMP basalts), and the precise correlation between the end-Triassic extinction horizon and lowest Moroccan CAMP basalt (the Lower Formation) is well established. Such temporal constraints may allow some Hg/TOC peaks in uppermost Triassic sediments to be directly correlated with specific CAMP basalt units. This direct association between Hg/TOC excursions and specific basalt flows has not been possible for other events due to the poor preservation, or limited stratigraphic control relative to the sedimentary record, of many LIPs.

A recent study on the Triassic–Jurassic boundary section at New York Canyon (Nevada, USA) showed an abrupt increase in Hg concentrations and Hg/TOC ratios correlated with the negative excursion in $\delta^{13}\text{C}_{\text{org}}$ that marks the end-

Triassic extinction horizon (Thibodeau *et al.*, 2016). These Hg excursions were attributed to volcanic processes operating during the emplacement of CAMP. Here, the New York Canyon results are greatly expanded by analysing six further sedimentary records from around the world to test whether the end-Triassic mercury perturbation was a global phenomenon. The possibility of multiple episodic peaks in sedimentary mercury is also investigated, to examine whether the documented pulsatory nature of CAMP emplacement occurred province-wide, or was limited to specific areas of the LIP. The synchrony of any Hg excursions with respect to the earliest CAMP flows is also assessed using the established stratigraphic correlation between the end-Triassic extinction horizon and the stratigraphically lowest known CAMP basalts.

3.2. Study areas

Six sections were investigated for Hg concentrations and Hg/TOC ratios as part of this study, representing a range of different palaeoenvironments. Taken together with the previously published Hg/TOC dataset from New York Canyon (Nevada, USA: Thibodeau *et al.*, 2016), these sections provide a wide distribution of sedimentary mercury records from across Pangea, allowing a global insight in the mercury cycle of the latest Triassic–earliest Jurassic. The sections are: St Audries Bay, UK (a restricted shallow-marine environment in the Central European Seaway); Kuhjoch, Austria (a shallow-marine environment on the Tethyan continental margin); Arroyo Malo, Argentina (a shallow-marine environment in a back-arc basin along the palaeo-southeastern Panthalassic Ocean); Astartekløft, Greenland (a fluvio-deltaic continental environment); Partridge Island, Canada (a lacustrine environment in central Pangea); and Igounane, Morocco (an evaporitic-

lacustrine environment from central Pangea). Astartekløft has been correlated with St Audries Bay on the basis of carbon-isotope stratigraphy and micro- and macro-palynology (Hesselbo *et al.*, 2002). Similarly, Partridge Island is correlated with St Audries Bay on the basis of magnetostratigraphy and carbon-isotope stratigraphy. Igounane is stratigraphically matched to the nearby Argana section, which has been previously correlated with St Audries Bay on the basis of magnetostratigraphy, carbon-isotope stratigraphy, palynology, and astrochronology (e.g. Whiteside *et al.*, 2010; Deenen *et al.*, 2010). See Appendix 1A for a full correlation of all the above sections and other end-Triassic records.

3.2.1. *St Audries Bay, Bristol Channel Basin, UK*

The marine record of the latest Triassic to earliest Jurassic at St Audries Bay is one of the most extensively studied examples of this transition, and has been previously proposed as the GSSP for the base of the Hettangian Stage (Warrington *et al.*, 1994). Upper Triassic silts and marls make up the Westbury Formation, before a transition to laminated shales, accompanied by a 6‰ negative excursion in $\delta^{13}\text{C}_{\text{org}}$ that marks the end-Triassic extinction horizon, at the base of the Lillstock Formation (Hesselbo *et al.*, 2002). The Lillstock Formation is overlain by the Blue Lias Formation, consisting of alternating marls, (laminated) black shales and (diagenetic) limestones (Warrington *et al.*, 1994). The palaeoenvironment is interpreted as predominantly marine, likely in a shallow restricted basin formed during the early rifting of Pangea. The second, main, carbon isotope excursion is ~3m above the base of the Blue Lias (Hesselbo *et al.*, 2002), preceding the Triassic–Jurassic boundary at the base of the *Psiloceras planorbis* ammonite Zone. The

section has an excellent astrochronology record (Ruhl *et al.*, 2010a), allowing for a good age correlation with the sections from the Newark–Hartford Basin in North America, the CAMP basalts preserved there, and the radioisotopic ages of those basalts (Whiteside *et al.*, 2010; Blackburn *et al.*, 2013).

3.2.2. *Kuhjoch, Eiberg Basin, Austria*

The Kuhjoch site in Austria records a relatively shallow-marine environment, and represents the global stratotype section for the base of the Hettangian stage (and therefore for the Triassic–Jurassic boundary). The area formed part of the Eiberg Basin, which developed during the Late Triassic along the northwestern Tethys passive margin as an intra-platform basin between carbonate ramps (Golebiowski, 1990). The Upper Triassic is marked by massive limestones, followed by red and grey marls following the extinction horizon and across the Triassic–Jurassic boundary (Hillebrandt *et al.*, 2013). The extinction horizon itself is formed of a thin (~5cm) layer of laminated black shale (Hillebrandt *et al.*, 2007; Bonis *et al.*, 2009). The horizon is also marked by an abrupt negative excursion in $\delta^{13}\text{C}_{\text{org}}$ of up to 6‰ (Ruhl *et al.*, 2009; 2010b), before a brief rebound to pre-extinction values ahead of a second decrease in $\delta^{13}\text{C}_{\text{org}}$ 2.5m above the extinction horizon (Ruhl *et al.*, 2009). Aside from the black-shale horizon, organic matter content is very low throughout, and also shows very low Hydrogen Index (HI) values. Taken together with recorded terrestrial spores at Kuhjoch, such low HI values indicates the presence of terrestrial organic material (Ruhl *et al.*, 2010b).

3.2.3. *Arroyo Malo*, Neuquén Basin, Argentina

The Arroyo Malo Formation along the Rio Atuel river provides a southern hemisphere record of the Triassic–Jurassic transition and end-Triassic mass extinction. The lithology consists predominantly of shales, interbedded with sporadic thin (cm–m) siltstone beds, interpreted as a shallow marine slope environment, possibly proximal to a deltaic system (Riccardi *et al.*, 2004; Lanés *et al.*, 2008). The sedimentary record is also marked by major (1–10m) deltaic depositional units higher in the sequence. The stratigraphic position of the end-Triassic mass extinction horizon was originally approximated on the basis of bivalve and brachiopod recovery; the position of the Triassic–Jurassic boundary has been approximated on the basis of ammonite biostratigraphy comparable to that of the Northern Hemisphere, although poor fossil recovery means that there is considerable uncertainty in the precise position of the boundary (Riccardi *et al.*, 2004; Damborenea and Manceñido, 2012). Low resolution carbon-isotope stratigraphy from this section shows a 2–3‰ negative excursion in organic $\delta^{13}\text{C}$, similar to the trends observed at New York Canyon (Bartolini *et al.*, 2012), likely refining the accurate stratigraphic position of the end-Triassic mass extinction horizon (this study). TOC content is relatively low (1–2 %wt), likely due to thermal degradation of organic matter in the sediments during Andean uplift. The original abundance and type of organic matter is therefore not well constrained.

3.2.4. *Astartekløft*, Jameson Land Basin, Greenland

The Astartekløft section in Greenland records a terrestrial environment that persisted during the Late Triassic and Early Jurassic. The facies represented

comprise fluvio-lacustrine-deltaic cycles (Dam and Surlyk, 1993; Hesselbo *et al.*, 2002). The terrestrial nature of the sediments is supported by the presence of abundant wood fragments and fossil leaves, which record a botanical turnover at the Triassic-Jurassic boundary (Harris, 1937; Bonis and Kürschner, 2012); numerous terrestrial vertebrates have also been discovered in the region (Sulej *et al.*, 2014). The wood also records a negative excursion in $\delta^{13}\text{C}$ coincident with the floral turnover, indicating that the end-Triassic carbon-cycle perturbation affected the atmosphere (Hesselbo *et al.*, 2002). Stomatal density of the fossil leaves has been used to estimate palaeo-CO₂ concentrations, and the shape and size of the leaves to estimate palaeo-SO₂ concentrations. Atmospheric concentrations of both gases are shown to have been elevated during the Triassic–Jurassic transition, supporting a significant output of volcanic volatiles at that time (McElwain *et al.*, 1999; Steinthorsdottir *et al.*, 2011; Bacon *et al.*, 2013).

3.2.5. *Partridge Island, Fundy Basin, Canada*

The Fundy Basin is largest of the exposed, deeply eroded North American Pangean rifts. It formed by the Middle Triassic in a continental milieu, and from then until the Early Jurassic was filled with mostly red-bed sediments and tholeiitic basalt flows. During this depositional interval, the basin drifted from 15°N to 26°N palaeolatitude (Kent and Tauxe, 2005.) The Blomidon Formation of the Fundy basin is comprised of ≥ 300 meters of cyclically interbedded sandstone and mudstone, that is interpreted to represent deposition in saline playa, sandflat, lacustrine, aeolian and fluvial environments in a semi-arid to arid climate. Rhythmic sedimentation is attributed to variations in the rate of inflow and evaporation caused by the ~20 ky

cycle of climate precession with average sedimentation accumulation rates of 0.76-1.63 cm/ka (Kent and Olsen, 1999). Magnetostratigraphy of the Blomidon Formation (Kent and Olsen, 2000; Deenen *et al.*, 2011a) allows much of the Fundy basin section to be correlated with marine strata and other correlative continental basins. Outcrops exposed at Partridge Island consist of a distinctive sequence of red and grey to black mudstones and siltstones, unique within the Fundy Basin, comprising the Partridge Island Member (Sues and Olsen, 2015). The placement of the end-Triassic extinction within the Blomidon Formation is based on an abrupt turnover of palynomorphs, from a Late Triassic assemblage dominated by *Patinosporites densus* and *Corollina torosus* to a low-diversity assemblage dominated by *Corollina meyeriana* (Whiteside *et al.*, 2007). This transition occurs ~15–25 cm below the North Mountain Basalt of the CAMP (Fowell and Traverse, 1995; Whiteside *et al.*, 2007; Cirilli *et al.*, 2009), is coincident with a modest iridium anomaly (Tanner and Kyte, 2005; Tanner and Walker, 2008) and an excursion in $\delta^{13}\text{C}$ found independently by Deenen *et al.* (2011a). The Blomidon Formation is overlain by the North Mountain Basalt a high-titanium, quartz-normative series of basalt flows (Puffer, 1994) with a $^{206}\text{Pb}/^{238}\text{U}$ age of 201.566 ± 0.031 Ma (Blackburn *et al.*, 2013).

3.2.6. Igounane, Argana Basin, Morocco

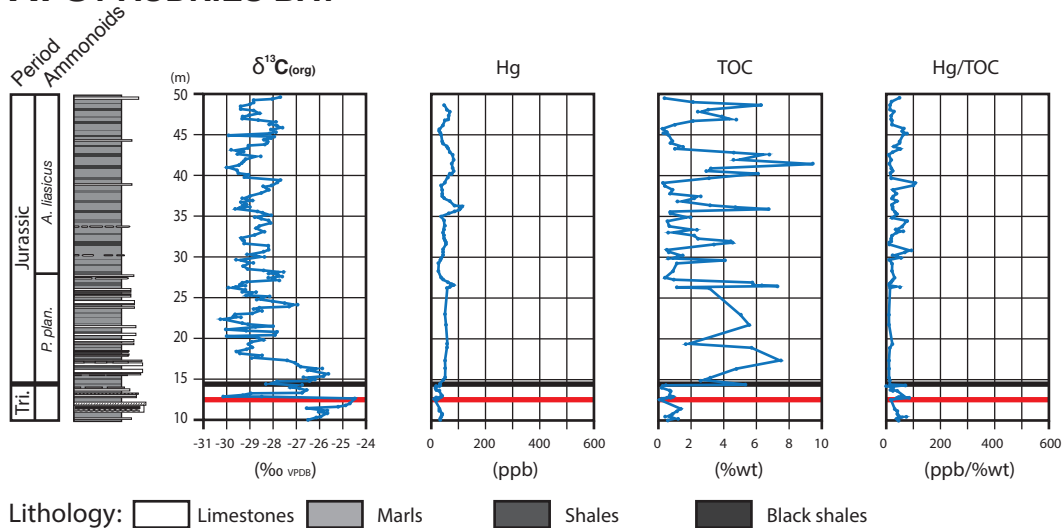
The Igounane section is located in the Argana Basin along the western flank of the High Atlas Mountains. The uppermost Triassic strata consist of a ~2300 m thick succession of alluvial, fluvial, lacustrine, aeolian and playa deposits (Olsen *et al.*, 2000; Medina *et al.*, 2011) that accumulated in a large westwards-tilting-half-

graben during the initial rifting phases of the Central Atlantic Ocean. Sedimentary strata at the Igounane section comprise the uppermost Bigoudine Formation, which is closely comparable to the Partridge Island Member of the Blomidon Formation, and likewise consist of red and grey to black mudstones and siltstones with local salt dissolution features. The level of the end-Triassic extinction apparently lies above the Bigoudine Formation plausibly at the contact with the overlying basalt flows because Triassic aspect palynomorphs, notably *Patinosporites densus*, are present just below the contact (Marzoli *et al.*, 2004; Blackburn *et al.*, 2013). About 175 m of basalt flows cap the red beds and are divided into the Tasquint and overlying Alemzi formations (El Hachimi *et al.*, 2011) corresponding to the Lower and Intermediate Formations of El Ghilani *et al.*, (2017). These flows are in turn overlain by a succession of largely red siliciclastic beds. These CAMP flows are all characterised by normal polarity with an astronomically calibrated duration of less than 20 kyr for the emplacement of the Tasquint Basalt near Argana, (Blackburn *et al.*, 2013). The $^{206}\text{Pb}/^{238}\text{U}$ age of the Alemzi Formation is 201.564 ± 0.054 Ma based on its feeder relationship with the Amelal Sill (Blackburn *et al.*, 2013). The Upper and Recurrent Formations, which complete the volcanic sequence in the Central High Atlas basin, have no equivalents in the Argana Basin.

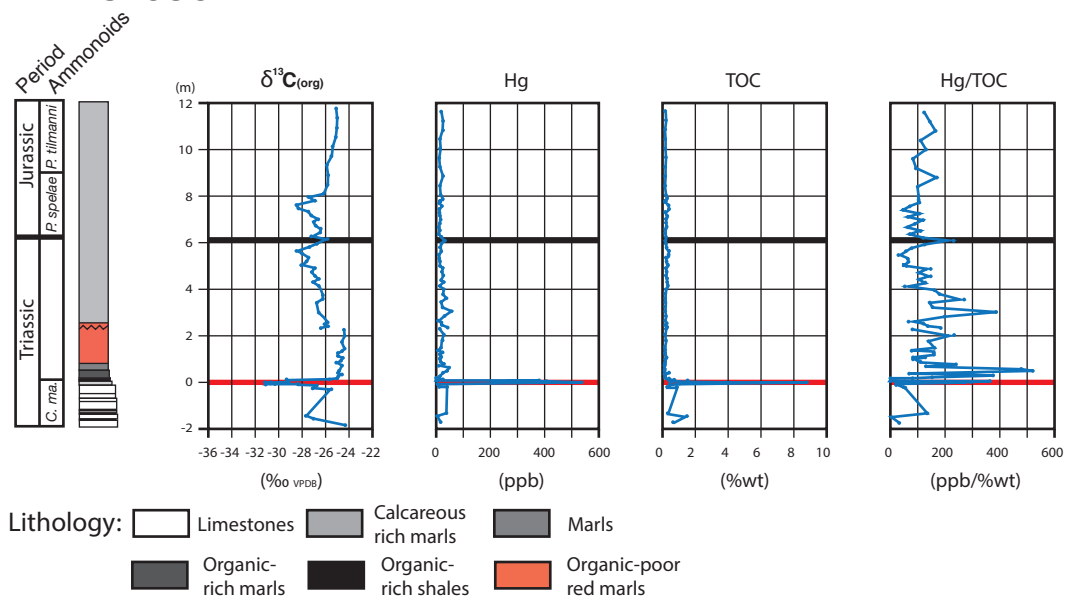
3.3. Methods

Mercury analysis was undertaken on the RA-915 Portable Mercury Analyzer with PYRO-915 Pyrolyzer, Lumex, at the University of Oxford (based on the methods in Percival *et al.*, 2015). Where previous TOC determinations were not available, new data were acquired using either a Strohlein Coulomat 702 (following

A: ST AUDRIES BAY



B: KUHJOCH



C: ARROYO MALO

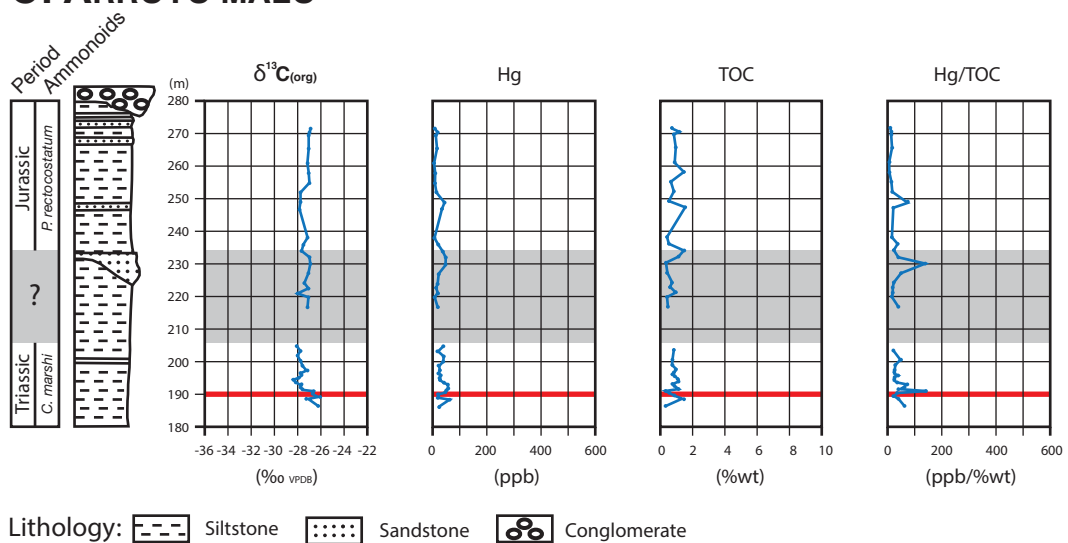


Figure 3.3 (overleaf)

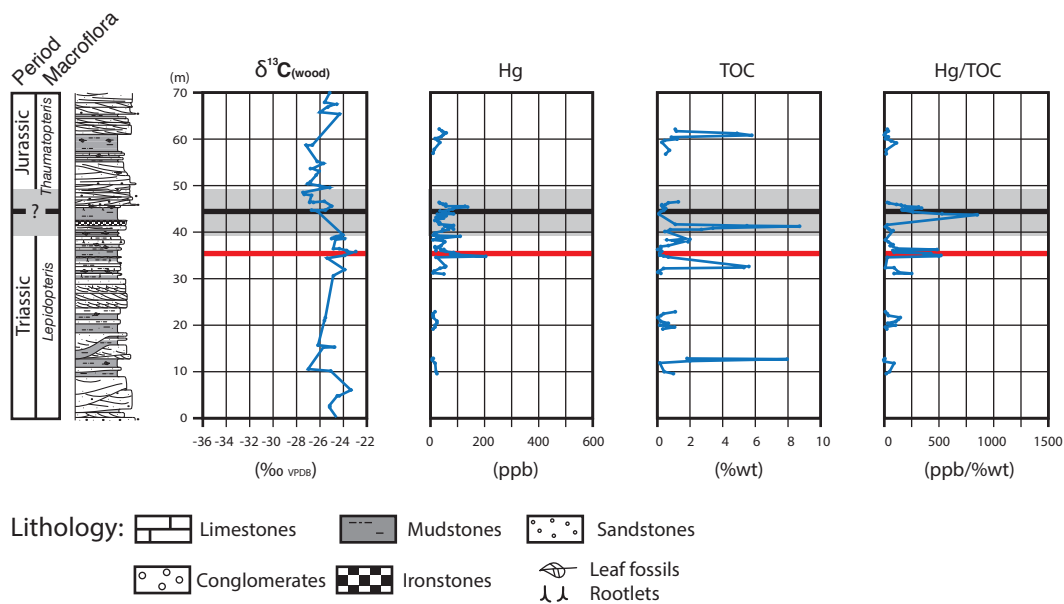
the methods in Jenkyns, 1988) or Rock-Eval VI (after Espitalié *et al.*, 1977) at the University of Oxford. $\delta^{13}\text{C}_{\text{org}}$ analyses were performed on decarbonated Arroyo Malo samples (prepared at the University of Oxford) with a Thermo Scientific Flash 2000 HT Elemental Analyzer (EA) coupled to a Thermo Scientific MAT253 isotope-ratio mass spectrometer via a ConFlo IV open-split interface at the Stable Isotope Laboratory at the Open University (Milton Keynes, UK). For full method details, see Chapter 2 (sections 2.1 and 2.4).

3.4. Results and Discussion

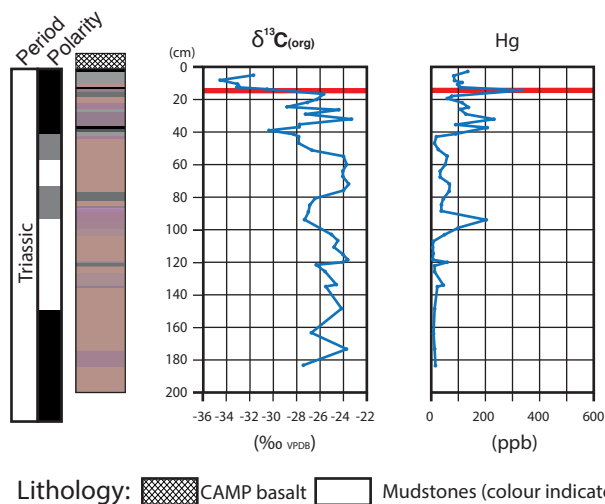
3.4.1. Mercury as a recorder of CAMP volcanism

Clear excursions in Hg/TOC ratios and/or Hg concentrations are observed at five of the six studied locations (St Audries Bay, Kuhjoch, Arroyo Malo, Astartekløft, and Partridge Island). The onsets of these excursions are stratigraphically coincident with the globally observed $\delta^{13}\text{C}$ negative excursion that marks the extinction horizon (Figures 3.3 and 3.4). Four sections also record additional peaks in Hg/TOC above that level. Crucially, at all sites where Hg has been normalised to TOC, the Hg/TOC peaks result from elevated Hg concentrations rather than decreased TOC content (Figure 3.3). For Partridge Island and Igounane sediments, Hg/TOC ratios were deemed unreliable due to the very low TOC content (typically below analytical uncertainty) in sedimentary samples. Consequently, Hg signals at these two locations are presented without normalisation to TOC. The mercury trends generated in this study are also compared to the existing New York Canyon record (Thibodeau *et al.*, 2016) in Figure 3.4, which appears to have a subtly different trend in sedimentary Hg/TOC increase, potentially resulting from atmospheric or local sedimentological processes.

D: ASTARTEKLØFT



E: PARTRIDGE ISLAND



F: IGOUNANE

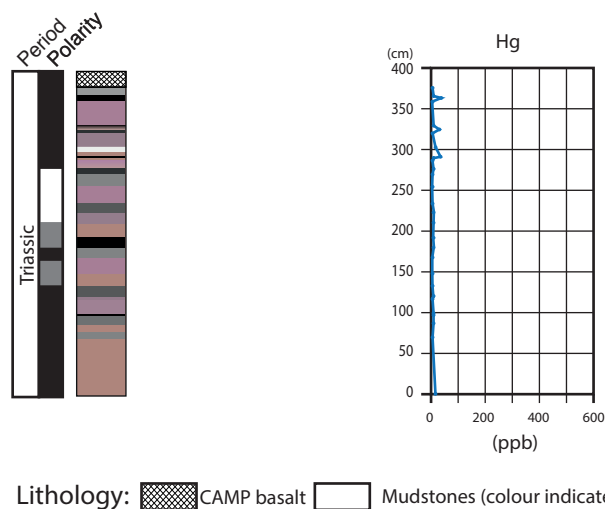


Figure 3.3 (opposite)

The observed peaks in sedimentary Hg and Hg/TOC strongly suggest that a perturbation to the global mercury cycle took place during the Triassic–Jurassic transition, beginning coincidentally with the end-Triassic extinction. The absence of a recorded mercury perturbation in sediments at Igounane is interpreted to result from their deposition being below the oldest known CAMP flows (thus at a time preceding the onset of CAMP basalt extrusion). A lack of change in terrestrial spores from Argana sediments below the CAMP basalts further suggest that these sediments were deposited prior to the end-Triassic extinction (Deenen *et al.*, 2010), and thus before the onset of CAMP volcanism.

The correlation between Hg excursions and the extinction horizon in the other five studied records is strongly suggestive of a perturbation to the global mercury cycle at that time. Variations in marine redox during the extinction may have influenced the marine Hg cycle, but the records at both Kuhjoch and Arroyo

Figure 3.3: Carbon-isotope, Hg, TOC, and Hg/TOC data plots. Stratigraphic logs and biostratigraphic information for St Audries Bay, Kuhjoch, and Astartekløft are taken from previously published figures in Hesselbo *et al.* (2002) and Ruhl *et al.* (2009; 2010a), respectively. The Arroyo Malo stratigraphic log is based on the logs of Riccardi *et al.* (2004) and Damborenea and Manceñido (2012), and biostratigraphic information sourced from Damborenea and Manceñido (2012). The stratigraphic logs for Partridge Island and Igounane are new for this study. Tri., *C. ma.*, and *P. plan.* indicate the Triassic Period, *C. marshi*, and *P. planorbis* Zones, respectively. Carbon isotope data are sourced as follows: St Audries Bay from Hesselbo *et al.* (2002) and Ruhl *et al.* (2010a); Kuhjoch from Ruhl *et al.* (2009); Arroyo Malo from this study; Astartekløft from Hesselbo *et al.* (2002); Partridge Island from this study. TOC data are all from this study, except for St Audries Bay (Hesselbo *et al.*, 2002; Ruhl *et al.*, 2010a; and this study) and Kuhjoch (Ruhl *et al.*, 2010b). Polarity data for Partridge Island is from Deenen *et al.* (2011a); for Igounane interpolated from the Argana results of Deenen *et al.* (2011b). Bold red lines indicate the end-Triassic extinction horizon; bold black lines indicate the Triassic–Jurassic boundary, except in the case of Arroyo Malo and Astartekløft, where the precise location of the boundary is unknown. Note also the expanded Hg/TOC scale for Astartekløft.

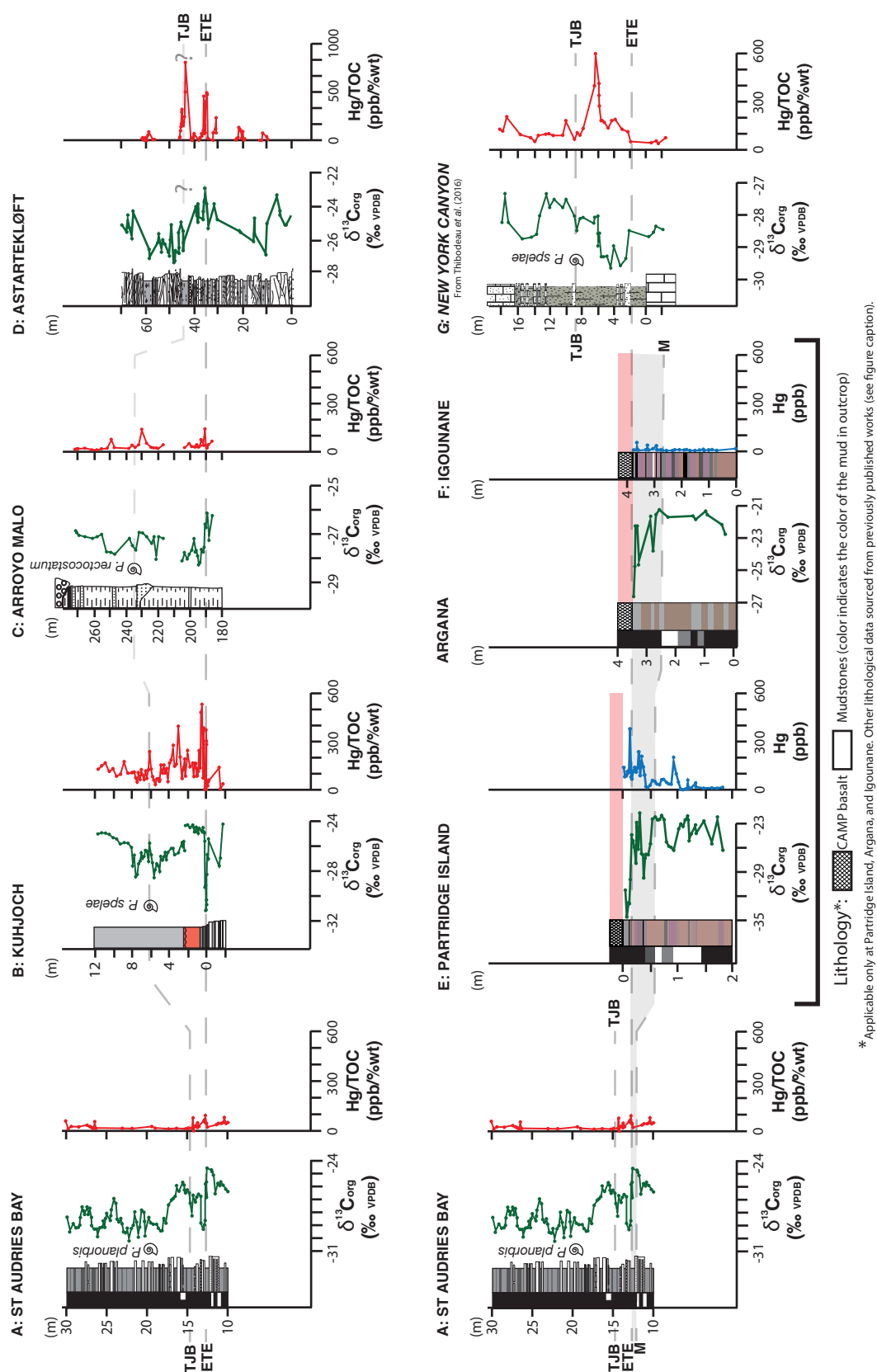


Figure 3.4 (opposite)

Malo do not show a consistent stratigraphic correlation between the observed Hg/TOC peaks and lithological or geochemical evidence for redox changes (Ruhl *et al.*, 2010b; this study). Additionally, the mercury excursions preserved in the terrestrial records from Astartekløft and Partridge Island could not have been caused by changes in the oceanic mercury inventory. Consequently, an atmospheric Hg perturbation is the most plausible cause.

The Hg perturbation also coincided with the established onset of an increase in atmospheric $p\text{CO}_2$, based on Hg/TOC and stomatal density records from Astartekløft (Steinthorsdottir *et al.*, 2011: Appendices 1A and 1B.). This correlation suggests a geologically simultaneous increase in atmospheric Hg and CO_2 , plausibly

Figure 3.4: Comparison of Hg/TOC data from St Audries Bay, Kuhjoch, Arroyo Malo, Astartekløft, and New York Canyon (Thibodeau *et al.*, 2016), and Hg data from Partridge Island and Iguonane (where TOC contents were below error). Carbon-isotope data, biostratigraphy (ammonite First Appearance), lithology, and magnetostratigraphy are also shown to allow stratigraphic correlation of the end-Triassic extinction horizon (marked as ETE) and Triassic–Jurassic boundary (marked as TJB). Lithological data are sourced as follows: St Audries Bay from Hesselbo *et al.* (2002); Kuhjoch from Ruhl *et al.* (2009); Arroyo Malo from Riccardi *et al.* (2004); Astartekløft from Hesselbo *et al.* (2002); Partridge Island from this study (shown in figure); Argana from Deenen *et al.* (2010); Igouane from this study (shown in figure); New York Canyon from Thibodeau *et al.* (2016). Carbon-isotope and biostratigraphic data are sourced as follows: St Audries Bay from Hesselbo *et al.* (2002) and Ruhl *et al.* (2010a); Kuhjoch from Ruhl *et al.* (2009); Arroyo Malo from Riccardi *et al.* (2004) and this study; Astartekløft from Hesselbo *et al.* (2002); Partridge Island from this study; Argana from Deenen *et al.* (2010); New York Canyon from Thibodeau *et al.* (2016). Line M indicates the magnetostratigraphic correlation at St Audries Bay, Partridge Island, Argana, and Igounane below the extinction horizon. The grey shading illustrates the stratigraphic gap between line M and line ETE. Magnetostratigraphic data are sourced as follows: St Audries Bay from Hounslow *et al.* (2004) and Hüsing *et al.* (2014); Partridge Island from Deenen *et al.* (2011a); Argana from Deenen *et al.* (2010). Note the expanded horizontal scale for Astartekløft data. Full $\delta^{13}\text{C}$, Hg, TOC and Hg/TOC data for each individual section are reported in Appendix 3A.

originating from magmatic degassing during CAMP emplacement. Emissions of both gases could also result from thermogenic gas release from kerogen in subsurface organic-rich sediments intruded by (CAMP-associated) sills. Thermogenic emissions have been previously suggested as a key contributor to LIP atmospheric perturbations (e.g. Ganino and Arndt, 2009; Svensen *et al.*, 2009). Thermogenic volatiles also explain the observed negative excursion in $\delta^{13}\text{C}$ at the extinction horizon more satisfactorily than magmatic carbon emissions (Beerling and Berner, 2002). However, peaks in Hg/TOC stratigraphically above the extinction horizon are not marked by distinct negative excursions in $\delta^{13}\text{C}$. Consequently, there is less evidence for these later mercury perturbations resulting from thermogenic emissions, and thus magmatic Hg emissions are a more probable cause.

Additional evidence for a volcanic origin of the perturbation to the global Hg cycle during the end-Triassic extinction comes from the established correlation between the lowest known CAMP flow (the Lower Formation in the High Atlas) and the extinction horizon. This correlation allows the Hg/TOC increase at the extinction horizon to be precisely stratigraphically matched with that particular unit of CAMP (Figure 3.1B: see also Appendix 1A and Deenen *et al.*, 2010; Dal Corso *et al.*, 2014). Consequently, it is highly likely that volcanic Hg associated with that lowest CAMP flow contributed to the global mercury perturbation during the end-Triassic extinction. The ability to correlate stratigraphically a Hg excursion directly with an individual CAMP basalt flow greatly strengthens the use of this element as a proxy for volcanism.

3.4.2. *The pulsatory release of magmatic volatiles*

In addition to the mercury excursion at the extinction horizon, four sections record distinct peaks in sedimentary Hg/TOC higher in the stratigraphy. These higher peaks are most clearly distinct at Kuhjoch and Arroyo Malo, but may also be recorded at New York Canyon and St Audries Bay (Figure 3.4). Pulsatory CAMP volcanism has been inferred from the stratigraphic record of CAMP basalts in North America and Morocco (Olsen *et al.*, 1996; Marzoli *et al.*, 2004; El Hachimi *et al.*, 2011; El Ghilani *et al.*, 2017). However, these lithological records only prove an apparent pulsing of CAMP basalts in specific locations of what is a much larger scale province. Episodic volcanism across the entire extent of CAMP has been inferred from pedogenic carbonate $p\text{CO}_2$ reconstructions (Schaller *et al.*, 2011), but these concretionary carbonates can be impacted by local (diagenetic) processes. The observed pulsatory signal of Hg perturbations in multiple, globally distributed, sedimentary records across the Triassic–Jurassic transition provides independent evidence that the intensity of CAMP volcanism, and likely CAMP emplacement, occurred in a non-continuous manner.

Although the mercury records shown in Figure 3.4 do show excursions in Hg/TOC in Jurassic strata and support the continuation of CAMP volcanism into the Jurassic, most of the Hg/TOC peaks are documented between the end-Triassic extinction horizon and the Triassic–Jurassic boundary. The data (Figure 3.4) suggest that at least two, and possibly three, major volcanic episodes occurred between the extinction and the beginning of the Jurassic (as defined by ammonite biostratigraphy). This interval is estimated as lasting only 100–200 kyr based on U–Pb geochronology and astrochronology (e.g. Whiteside *et al.*, 2007; Schoene *et al.*, 2010; Blackburn *et al.*, 2013; Xu *et al.*, 2017). Ar–Ar and U–Pb geochronology

suggests that the oldest three Moroccan basalt units (the Lower, Middle and Upper Formations: units 1, 3, and 4 in Figure 3.2B) and the first of the major North American CAMP pulses (units 2–4 in Figure 3.2B) were likely all emplaced during this interval (Deenen *et al.*, 2010; Blackburn *et al.*, 2013; El Ghilani *et al.*, 2017). It is possible that the observed three pulses in Hg/TOC observed in strata between the extinction horizon and the Triassic–Jurassic boundary may directly relate to atmospheric volatile release from the first three CAMP basalt units in the Moroccan Argana Basin, and their North American equivalents. However, further correlative work is needed to confirm such a hypothesis. The later North American CAMP basalts, and the Moroccan Recurrent Formation (units 5 and 6, Figure 3.2B), were emplaced 300–600 kyr after the extinction (Deenen *et al.*, 2010; Blackburn *et al.*, 2013; Kent *et al.*, 2017 and references therein). Thus, the Hg/TOC peaks between the extinction horizon and the Triassic–Jurassic boundary cannot be related to these later flows.

The observed record of multiple pulses in Hg/TOC is direct evidence that volatile release associated with CAMP volcanism was also pulsatory, likely including episodic emissions of carbon, sulfur, and mercury. Moreover, pulsatory emissions are shown to have occurred throughout the 100–200 kyr immediately following the end-Triassic extinction, in addition to the documented later pulses of volcanic emissions (Schaller *et al.*, 2011). Consequently, the large increase in atmospheric $p\text{CO}_2$ during the extinction event may have arisen as a series of episodic carbon-cycle perturbations to the atmosphere (and subsequently the ocean). Pulsatory perturbations of the ocean–atmosphere system caused by episodic volcanic events (and release of volatiles) associated with CAMP may explain the documented prolonged period of ecosystem deterioration and delayed recovery of

benthic fauna during the emplacement of CAMP (Self *et al.*, 2014; Schmidt *et al.*, 2015; Ritterbush *et al.*, 2015; Thibodeau *et al.*, 2016).

3.5. Conclusions

Investigation of the global history of CAMP volatile emissions is important for understanding the development of this igneous province and its potential environmental impact. This study demonstrates that the mercury cycle was perturbed on a global scale during the Triassic–Jurassic transition. Mercury excursions are recorded in five of the six sections studied; the one section with no record of Hg enrichment was likely deposited prior to the onset of CAMP volcanism. The onset of Hg enrichment occurred synchronously across the globe, coincident with the end-Triassic extinction and associated global carbon-cycle perturbation. The presence of Hg/TOC excursions in sedimentary records of terrestrial and marine palaeoenvironments, across both hemispheres, indicates that atmospheric mercury concentrations likely increased substantially. This atmospheric perturbation probably resulted from the emplacement of CAMP and the associated large-scale emission of magmatic volatiles, and potentially thermogenic volatiles from intruded country rock (including mercury). The appearance of a global Hg excursion at the end-Triassic extinction horizon and multiple Hg/TOC peaks between it and the Triassic–Jurassic boundary is further evidence that pulses in the intensity of CAMP volcanism (and associated volatile release) were not limited to North America and Morocco, but representative of the entire province. The direct correlation between the oldest preserved flows of CAMP and the end-Triassic extinction horizon allows the earliest pulse of elevated mercury in the sedimentary record of this time to be linked directly with these basalts. This correlation supports

a volcanic origin for the increased mercury abundances, and represents the first time that a globally observed mercury excursion has been tied to a specific basalt unit from a Large Igneous Province. The recording of multiple Hg/TOC excursions between the extinction horizon and the Triassic–Jurassic boundary highlights that the initial stages of CAMP emplacement were marked by multiple episodes of volcanic volatile release. Repeated volcanically driven perturbations of the ocean-atmosphere system in the 100–200 kyr during and immediately following the end-Triassic extinction may have had important implications for the biospheric impact of CAMP.

Chapter 4

Osmium-isotope evidence for two pulses of increased continental weathering linked to Early Jurassic volcanism and climate change

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Abstract

Large Igneous Provinces (LIPs) are proposed to have caused a number of episodes of abrupt environmental change by increasing atmospheric CO₂ levels, which were subsequently alleviated by drawdown of CO₂ via enhanced continental weathering and burial of organic matter. Here, the sedimentary records of two such episodes of environmental change, the Toarcian Oceanic Anoxic Event (T-OAE) and preceding Pliensbachian–Toarcian (Pl–To) event (both potentially linked to the Karoo–Ferrar LIP), are investigated using a new suite of geochemical proxies that have not been previously compared. Stratigraphic variations in osmium-isotope (¹⁸⁷Os/¹⁸⁸Os) records are compared with those of mercury (Hg) and carbon isotopes (δ¹³C) in samples from the Mochras Core, Llanbedr Farm, Cardigan Bay Basin, Wales. These sedimentary rocks are confirmed as recording an open-marine setting by analysis of molybdenum/uranium enrichment trends, indicating that the Os-isotope record in these samples reflects the isotopic composition of the global ocean. The Os-isotope data include the first results across the Pl–To boundary, when seawater ¹⁸⁷Os/¹⁸⁸Os increased from ~ 0.40 to ~ 0.53, in addition to new data that show elevated ¹⁸⁷Os/¹⁸⁸Os (from ~ 0.42 to ~ 0.68) during the T-OAE. Both increases in ¹⁸⁷Os/¹⁸⁸Os correlate with negative carbon-isotope excursions and increased mercury concentrations, supporting an interplay between terrestrial volcanism, weathering, and climate that was instrumental in driving these distinct episodes of global environmental change. These observations also indicate that the environmental impact of the Karoo–Ferrar LIP was not limited solely to the T-OAE.

4.1 Introduction

Oceanic Anoxic Events (OAEs) were times of abrupt carbon-cycle perturbations, driven by increases in atmospheric CO₂ proposed to result, at least partially, from the emplacement of Large Igneous Provinces (LIPs). Enhanced continental weathering and widespread organic-matter burial are proposed to have subsequently drawn down the excess CO₂, alleviating the carbon-cycle perturbation (Jenkyns, 2010). The Early Jurassic Toarcian OAE (T-OAE: 183 Ma) was one such event: geochemical evidence for LIP volcanism, oceanic anoxia, release of carbon to the atmosphere, and increased continental weathering rates, are found in a number of sedimentary sections (reviewed in Jenkyns, 2010; see also Brazier *et al.*, 2015; Percival *et al.*, 2015). However, there remains no single sedimentary record where evidence for volcanic activity, carbon-cycle perturbation, and enhanced weathering rates are compared using proxy data from the same succession. This situation is also the case for a preceding event during the Pliensbachian–Toarcian (Pl–To) transition, which took place less than a million years prior to the T-OAE and has also been associated with a carbon-cycle perturbation and an episode of LIP volcanism (Littler *et al.*, 2010; Percival *et al.*, 2015). Thus, the relationship between such processes during the T-OAE is based upon comparisons of geochemical proxies across multiple sedimentary sections which may not be precisely synchronous.

This study integrates new osmium-isotope data with both new and previously published results recording mercury (Hg) concentrations and carbon isotopes ($\delta^{13}\text{C}$) from a single record to investigate the relationships between volcanism, weathering, and the carbon cycle during Pliensbachian–Toarcian times. Large-scale volcanism during the Toarcian has previously been inferred from elevated concentrations of sedimentary Hg of assumed volcanogenic origin (Percival *et al.*, 2015), and attributed

to the Karoo–Ferrar LIP, which is radiometrically dated at ~183 Ma and therefore Toarcian in age (e.g. Rampino and Strothers, 1988; Duncan *et al.*, 1997; Svensen *et al.*, 2012; Burgess *et al.*, 2015). Volcanism is known to release gaseous Hg, which has an atmospheric residence time of 0.5–2 years, allowing global distribution before it is deposited in sediments. Thus, volcanic activity may be recorded as enrichments in sedimentary Hg, typically normalised against total organic carbon (TOC) to account for its strong association with organic matter (Sanei *et al.*, 2012, and references therein).

Changes in continental weathering rates can be estimated from the records of seawater osmium-isotope composition (Cohen *et al.*, 1999), which is controlled by proportional mixing of radiogenic fluxes from both fluvial input ($^{187}\text{Os}/^{188}\text{Os}$ of ~1.4) and the alteration and weathering of juvenile basalts ($^{187}\text{Os}/^{188}\text{Os}$ of ~0.12). Past seawater $^{187}\text{Os}/^{188}\text{Os}$ ratios calculated from a sedimentary sample are expressed as $^{187}\text{Os}/^{188}\text{Os}_{(i)}$, after accounting for additional radiogenic Os produced via decay of ^{187}Re to ^{187}Os after deposition (see Chapter 2, section 2.2.1 for further details of the Re–Os proxy). Strata recording the T-OAE in Yorkshire, England, show an increase in $^{187}\text{Os}/^{188}\text{Os}$ from ~0.3 to ~0.9, from which a major (400–800%) increase in continental weathering rates was inferred (Cohen *et al.*, 2004). However, this section is thought to have been deposited in a relatively restricted marine setting that had limited interchange with the global ocean. Thus, the seawater $^{187}\text{Os}/^{188}\text{Os}$ may have evolved away from the global composition towards that of local input fluxes (McArthur *et al.*, 2008).

The Mochras Borehole (Llanbedr Farm, Cardigan Bay, Wales, U.K.; Figure 4.1) cored a stratigraphically expanded section of Lower Jurassic calcareous mudrock, containing terrigenous and marine organic matter (0.5–2 %wt TOC in the interval of

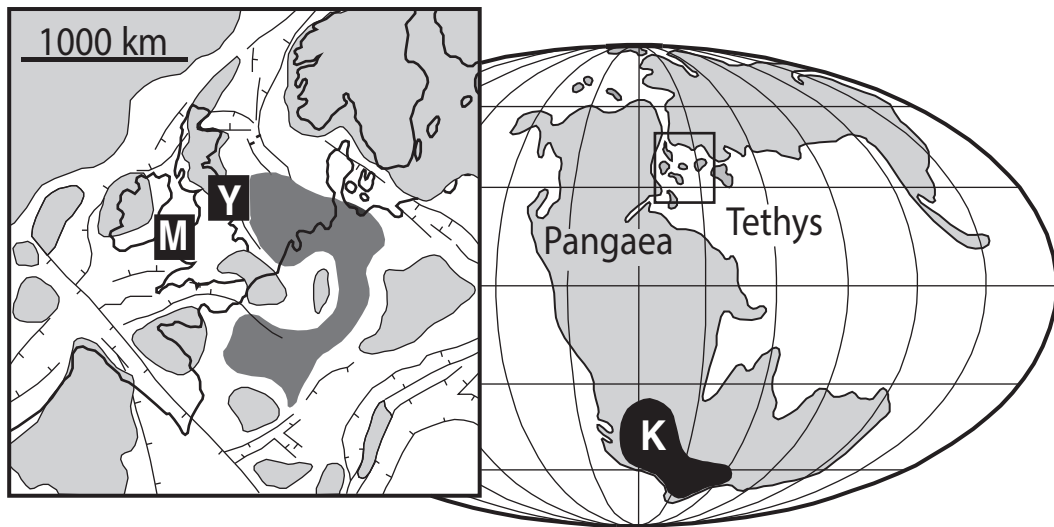


Figure 4.1: Global palaeogeography during the Toarcian, modified from Hesselbo *et al.* (2007). The dark grey area represents marine areas of Europe thought to have been hydrographically restricted during the Toarcian. The three marked locations are Mochras (M), Yorkshire (Y), and the Karoo–Ferrar LIP (K).

interest), and detrital clastics likely derived from the Welsh Massif (O'Sullivan *et al.*, 1972). Both organic carbon and carbonate document negative excursions in $\delta^{13}\text{C}$ at the Pl–To boundary and T-OAE level (Jenkyns and Clayton, 1997; this study). Palaeogeographic reconstructions indicate a hydrographically open setting (Sellwood and Jenkyns, 1975), allowing Os isotopes to be well mixed within the global ocean. This model is tested here by analysis of molybdenum (Mo) and uranium (U) sedimentary enrichments, which have been shown to vary depending on redox conditions and levels of hydrographic restriction in recent marine sediments (Algeo and Tribovillard, 2009).

4.2 Methods

Samples were prepared for Re-Os analysis at The Open University using procedures adapted from Cohen and Waters (1996) and Birck *et al.* (1997): see Chapter 2 (section 2.2.2.). Os-isotope compositions and concentrations were determined by isotope dilution and negative thermal ionisation mass spectrometry on a Thermo Finnigan Triton, and Re concentrations were determined by isotope dilution and multiple-collector inductively coupled plasma mass spectrometry (ICP-MS) on a Thermo Finnigan Neptune.

Mo, U and Al abundances were determined using a Thermo-Finnegan Element 2 magnetic-sector ICP-MS at the University of Oxford (see Chapter 2, section 2.3). New Hg and TOC data were generated using a RA-915 Portable Mercury Analyzer with PYRO-915 Pyrolyzer (Lumex), and Rock Eval 6, respectively, at the University of Oxford, using the methods given in Percival *et al.* (2015). New $\delta^{13}\text{C}_{\text{org}}$ data were generated by combustion in a Costech Elemental Analyzer on-line to a VG TripleTrap and Optima dual-inlet mass spectrometer at the British Geological Survey

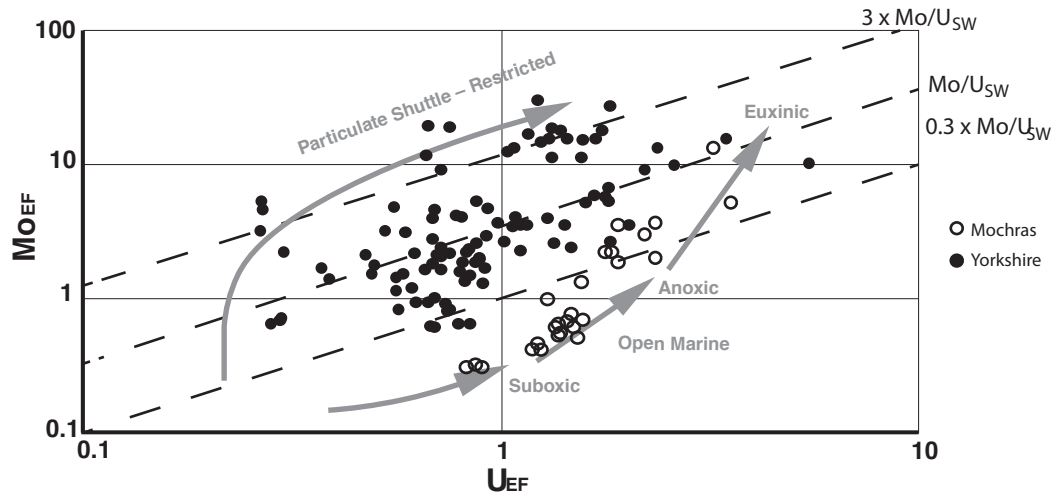


Figure 4.2: Comparison of the palaeoenvironmental settings at Yorkshire and Mochras using Mo/U enrichment ratios, following the model of Algeo and Tribovillard (2009). Yorkshire data are from the supplementary data in McArthur *et al.* (2008). Mo/U_{sw} indicates the modern-day Mo/U ratio of seawater. MoEF and UEF indicate the calculated enrichment factor of molybdenum and uranium, respectively, relative to average upper continental crust (UCC) abundances (Rudnick and Gao, 2003), using $([\text{element}/\text{Al}]_{\text{sample}} / [\text{element}/\text{Al}]_{\text{UCC}})$.

(Keyworth), as for Riding *et al.* (2013): see Chapter 2 (section 2.4).

4.3 Results and Discussion

Variations in Mo and U enrichment trends for samples from Mochras and Yorkshire are shown in Figure 4.2. The Mochras data show a trend of initial U enrichment, followed by increasing Mo enrichment, indicative of an unrestricted open-marine setting (Algeo and Tribovillard, 2009). Therefore, $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ trends recorded in Mochras samples are likely representative of worldwide trends in the seawater Os-isotope composition. The $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ data for the Mochras samples are presented stratigraphically in Figure 4.3, alongside $\delta^{13}\text{C}_{\text{org}}$ and Hg/TOC data from the same sediments, and published $\delta^{13}\text{C}_{\text{org}}$ and $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ data from Yorkshire. Although there is notable variation in $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ values of the Pliensbachian samples, only one value exceeds 0.44. The average $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of ~ 0.4 for Pliensbachian samples is therefore taken as a reasonable baseline against which to compare the Toarcian values. An increase in $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ to ~ 0.53 occurs at the Pliensbachian–Toarcian boundary and persists through the lower half of the *tenuicostatum* ammonite Zone, suggesting an increased flux of radiogenic Os to the ocean resulting from enhanced weathering of continental material. An increase in seawater $^{187}\text{Os}/^{188}\text{Os}$ at the Pl–To boundary has not been previously documented, and such an abrupt and significant rise in seawater $^{187}\text{Os}/^{188}\text{Os}$ is difficult to explain without invoking rapid changes in continental weathering rates. The return of seawater $^{187}\text{Os}/^{188}\text{Os}$ to background values (~ 0.42) throughout the upper half of the *tenuicostatum* Zone further indicates that the transient increase in continental weathering during the Pl–To transition was part of a distinct climate-weathering feedback, rather than the beginning of a long-term increase in weathering rates leading up to the T-OAE.

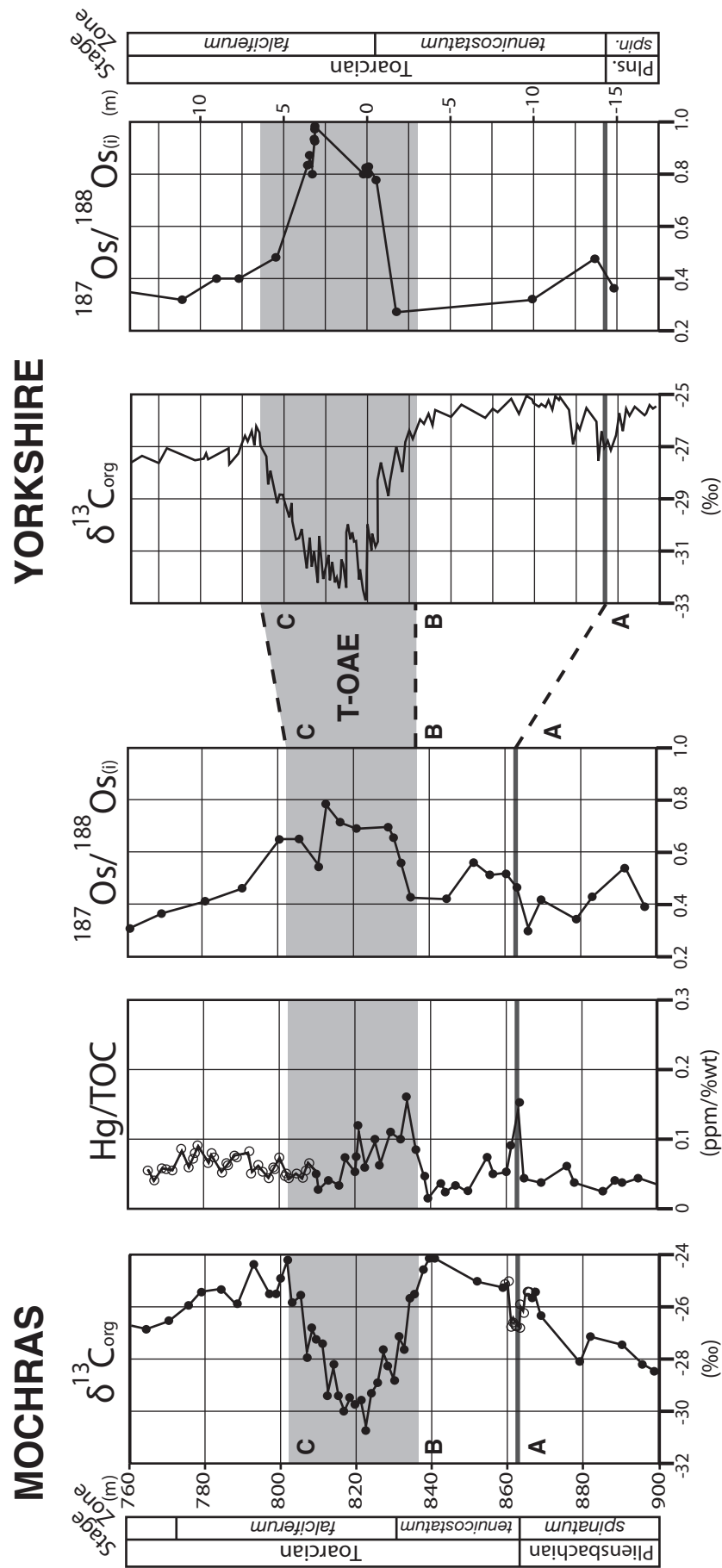


Figure 4.3 (opposite)

The lower part of the *falciferum* Zone records a second increase in $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ values to an average of ~ 0.68 at the base of the T-OAE level, indicating that, during the T-OAE, a second increase in continental weathering took place, appreciably greater than the one that occurred during the Pl–To transition. The onset of this increase correlates well with the similar pattern of increased $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ in Yorkshire, supporting the previous inferences of globally elevated continental weathering rates during the T-OAE (Cohen *et al.*, 2004). Additionally, both the Pl–To and T-OAE increases in $^{187}\text{Os}/^{188}\text{Os}$ correlate with perturbations observed in Toarcian Sr- and Ca-isotope records from Yorkshire and Portugal that have previously been used to infer increases in continental weathering rates (Pálffy and Smith, 2000; Cohen *et al.*, 2004; Brazier *et al.*, 2015). However, the new $^{187}\text{Os}/^{188}\text{Os}$ trends are a better indication of geologically abrupt increases in continental weathering rates due to the much shorter residence time of osmium in the ocean (~ 10 – 50 kyrs: Peucker-Ehrenbrink and Ravizza, 2000) compared with that of Ca or Sr.

Figure 4.3: $\delta^{13}\text{C}_{\text{org}}$ and $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ data from Mochras and Yorkshire, and Hg/TOC ratios from Mochras. Line A marks the Pl–To boundary; line B marks the onset of the T-OAE as defined by the lowest appearance of organic-rich shales in Yorkshire, which is broadly coincident with the onset of the $\delta^{13}\text{C}$ negative excursion; line C marks the end of the $\delta^{13}\text{C}$ negative excursion. The grey shaded area marks the stratigraphic width of the $\delta^{13}\text{C}$ negative excursion. Stratigraphic heights are in meters; Stage refers to the Stage in geological time; Zone to biostratigraphic ammonite Zones that subdivide that Stage. Plien. and *spin.* abbreviate Pliensbachian and *spinatum*, respectively. For $\delta^{13}\text{C}$ and Hg/TOC data from Mochras, closed circles illustrate published data, and open circles illustrate new data. The $\delta^{13}\text{C}_{\text{org}}$ Yorkshire data are at too high a resolution to include individual data points. Published data are sourced as follows: $\delta^{13}\text{C}_{\text{org}}$ data from Mochras from Jenkyns *et al.* (2001), and from Yorkshire from Cohen *et al.* (2004), Littler *et al.* (2010), and Kemp *et al.* (2011); Os-isotope data from Yorkshire are from Cohen *et al.* (2004); Hg/TOC data from Mochras are from Percival *et al.* (2015). Preliminary $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ data from the Toarcian of western North America show broadly similar patterns (Them *et al.*, 2015).

These two increases in seawater $^{187}\text{Os}/^{188}\text{Os}$ document two separate pulses of increased global weathering rates during the Pl–To transition and T-OAE, respectively. If the ocean is considered as a single well-mixed reservoir, with continental weathering as the only input of radiogenic Os and alteration of juvenile basalts as the main input of unradiogenic Os, the changes in weathering flux of continental crust required to bring about the observed increases in $^{187}\text{Os}/^{188}\text{Os}$ can be calculated, assuming that mid-ocean ridge activity is constant on geologically short timescales (see Chapter 2, section 2.5). The increase in seawater $^{187}\text{Os}/^{188}\text{Os}$ from ~ 0.4 in the latest Pliensbachian to ~ 0.53 during the Pl–To transition would require a near doubling of continental weathering rates, increasing by a factor of ~ 1.69 . The subsequent rise in seawater $^{187}\text{Os}/^{188}\text{Os}$, from ~ 0.42 to ~ 0.68 , during the T-OAE demands a near tripling of continental weathering rates, increasing by a factor of ~ 2.58 . Moreover, these values are minimum estimates because subaerial weathering of the coevally emplaced Karoo–Ferrar LIP would have contributed additional unradiogenic osmium to the oceans, although the impact of such LIP-derived Os is ambiguous.

The above estimates of weathering rate increases are lower than the 400–800% estimate of Cohen *et al.* (2004). However, the pattern of Mo/U enrichment in samples from Yorkshire indicates particulate shuttling of Mo in a hydrographically restricted basin, in contrast to the more open-marine environment preserved in the Mochras core. Consequently, the increase in $^{187}\text{Os}/^{188}\text{Os}$ at Yorkshire is likely exaggerated due to the particular marine setting at that location. Nonetheless, the two records in tandem confirm that a pronounced and abrupt increase in continental weathering rates coincided precisely with the environmental perturbations that occurred during the T-OAE.

The increases in seawater $^{187}\text{Os}/^{188}\text{Os}$ also correlate with changes in Hg/TOC and $\delta^{13}\text{C}_{\text{org}}$ recorded in the same samples at both the Pl–To boundary and the base of the T-OAE level. Negative $\delta^{13}\text{C}$ and positive Hg/TOC excursions have been previously hypothesised to indicate increased output of isotopically light carbon to the atmosphere and large-scale volcanic activity, respectively (Hesselbo *et al.*, 2000; Percival *et al.*, 2015). The correlation of all three proxies suggests that volcanism and carbon-cycle perturbations were accompanied by increased rates of continental weathering. This conclusion supports previous hypotheses that volcanism triggered a carbon-cycle perturbation, which was eventually alleviated through a feedback of increased silicate weathering as well as organic-carbon burial (summarised in Jenkyns, 2010). Although such a mechanism has previously been proposed for the T-OAE (Cohen *et al.*, 2004), the data presented here indicate that similar processes operated during the Pl–To transition.

The two intervals of perturbed $^{187}\text{Os}/^{188}\text{Os}$, Hg/TOC and $\delta^{13}\text{C}_{\text{org}}$ are separated by the latter part of the *tenuicostatum* Zone, which is thought to have lasted hundreds of thousands of years (Kemp *et al.*, 2011). Consequently, any volcanically related trigger of these perturbations would need to have operated on at least two separate occasions. Burgess *et al.* (2015) record a 600 kyr age difference between Karoo and Ferrar basalts, which could support the notion of episodic LIP volcanism. However, the uncertainties in such measurements, as well as their similarity with the ages of many Karoo basalts (Svensen *et al.*, 2012), means that there is no unambiguous evidence for episodic emplacement of the Karoo–Ferrar LIP. An alternative hypothesis could involve sporadic interaction of LIP basalts with organic-rich sediments causing output of thermogenic carbon and mercury (McElwain *et al.*, 2005; Svensen *et al.*, 2007; Percival *et al.*, 2015).

The increase in seawater $^{187}\text{Os}/^{188}\text{Os}$ recorded during both the Pl–To transition and T-OAE may have been aided by the high-latitude, subaerial emplacement of the Karoo–Ferrar LIP. Intervals associated with low-latitude subaerial LIPs such as the Central Atlantic or Deccan Provinces, or submarine LIPs such as the Ontong-Java or Caribbean Plateaus tend to record predominantly decreased seawater $^{187}\text{Os}/^{188}\text{Os}$, due to the rapid weathering of LIP basalts at low latitudes (Cohen and Coe, 2007), or direct release of unradiogenic Os into the oceans (Bottini *et al.*, 2012; Du Vivier *et al.*, 2014). In contrast, a high-latitude LIP would have experienced less intense weathering compared to continental material from lower latitudes, causing an increased flux of radiogenic Os to dominate the seawater $^{187}\text{Os}/^{188}\text{Os}$ record, as shown here for Mochras and previously for Yorkshire (Cohen *et al.*, 2004). Similar signals of predominantly increased seawater $^{187}\text{Os}/^{188}\text{Os}$ are also recorded from Palaeocene–Eocene sediments that formed contemporaneously with the high-latitude North Atlantic LIP (Dickson *et al.*, 2015). Thus, comparison of Os-isotope records highlights the importance of the setting of LIP emplacement, as well as the magnitude and tempo of volcanism, in controlling the nature of subsequent environmental change.

4.4 Conclusions

This study documents two relatively rapid and transitory increases in the $^{187}\text{Os}/^{188}\text{Os}$ of seawater during latest-Pliensbachian–Early Toarcian time. The $^{187}\text{Os}/^{188}\text{Os}$ increases correlate well with excursions in Hg/TOC and $\delta^{13}\text{C}_{\text{org}}$, thus demonstrating a close coupling between volcanism, weathering, and carbon-cycle perturbations in two distinct Early Jurassic events. The similarity of these events, separated by only a few hundred thousand years, is consistent with a repeating trigger for the cascade of environmental responses, postulated as linked to sequential

emplacement of the Karoo–Ferrar LIP or sporadic release of thermogenic volatiles.

The new observations demonstrate that major environmental perturbations in the

Early Jurassic were episodic, and not solely restricted to the T-OAE.

Chapter 5

Can mercury be used as a tracer of volcanism for all Large Igneous Provinces? Comparing the records of Oceanic Anoxic Event 2 and the end-Cretaceous extinction to other Mesozoic events

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Abstract

Mercury (Hg) is increasingly being used as a sedimentary tracer of Large Igneous Province (LIP) volcanism, and supports hypotheses of a precise coincidence between the formation of several LIPs and Mesozoic mass extinctions and major environmental perturbations. However, numerous questions remain regarding the impact of transportation and depositional processes acting on these sedimentary mercury signals, and the relative importance of different volcanic styles and processes on the global mercury cycle. Here, new mercury records of Cretaceous Ocean Anoxic Event 2 (OAE 2: ~94 Ma) and the latest Cretaceous (~67 to 66.0 Ma) are presented. OAE 2 is associated with the emplacement of multiple submarine LIPs, whereas the latest Cretaceous coincided with subaerial volcanism of the Deccan Traps. The sedimentary mercury records of these two events are compared with each other and with other Mesozoic events to obtain insight into the volcanic contexts required for volcanogenic perturbation of the global mercury cycle. Although Hg anomalies have been documented in records of several Mesozoic events associated with subaerial LIPs that also featured release of additional thermogenic volatiles, neither of OAE 2 or the latest Cretaceous are associated with such LIPs. Mercury records from both events show considerable variation in Hg trends between different locations, which supports previous proposals that certain sedimentary archives, including pure carbonates and very organic-rich shales, are poor recorders of changes in the global Hg inventory. Crucially, there is no dominant signal of sedimentary Hg enrichment during either OAE 2 or the latest Cretaceous, suggesting that LIP volcanism did not cause a global mercury perturbation at those times. These results are in contrast to mercury signals at other Mesozoic events, and suggest that specific volcanic processes associated with LIP emplacement are required to produce major mercury emissions.

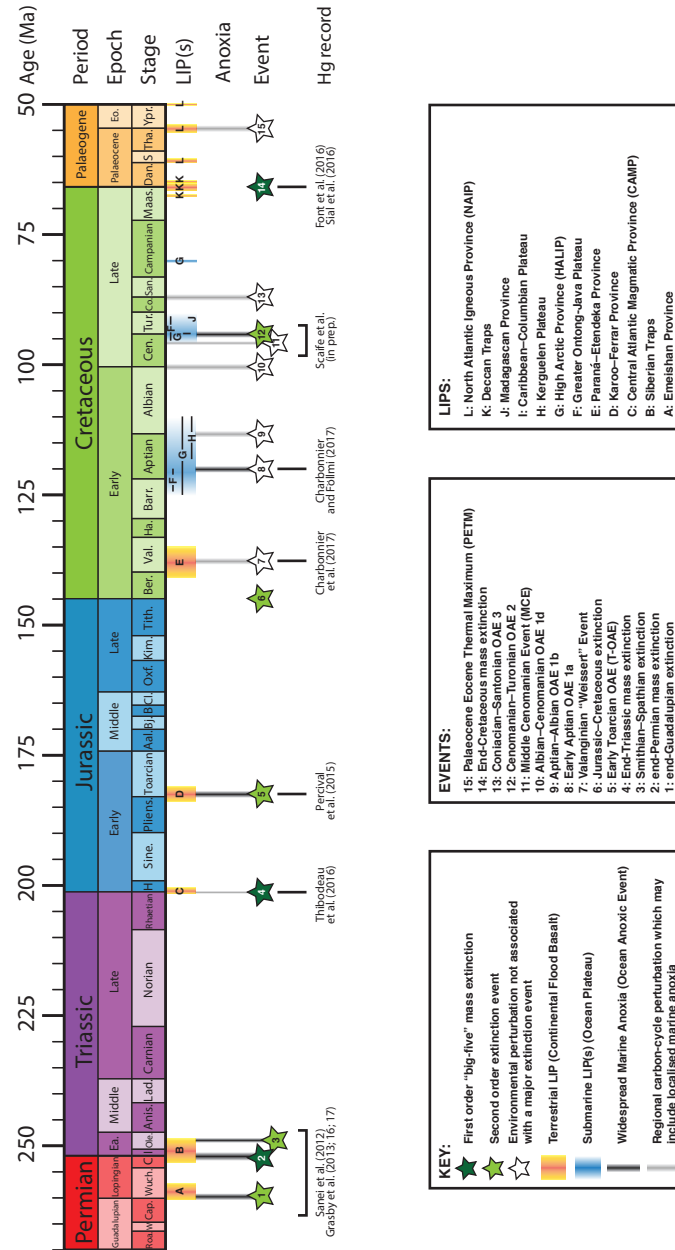


Figure 5.1: An illustration of the Middle Permian to Eocene timescale, showing the respective ages of major Mesozoic environmental perturbations, LIP emplacements, and episodes of marine anoxia and carbon-cycle perturbations (taken from the reviews of Jenkyns, 2010; Bond and Wignall, 2014; Ernst and Youbi, 2017). Previous mercury studies are noted via references under the events. The ages of stage boundaries are taken from the 2016 Geological Timescale (Ogg *et al.*, 2016). Ea. and Eo. signify Early and Eocene, respectively. Abbreviated Stage names are as follows: Roa. = Roadian; W = Wordian; Cap. = Capitanian; Wuch. = Wuchiapingian; C = Changhsingian; I = Induan; Ole. = Olenekian; Anis. = Anisian; Lad. = Ladinian; H = Hettangian; Sine. = Sinemurian; Pliens. = Pliensbachian; Aal. = Aalenian; Bj = Bajocian; B = Bathonian; Cl. = Callovian; Oxf. = Oxfordian; Kim. = Kimmeridgian; Tith. = Tithonian; Ber. = Berriasian; Val. = Valanginian; Ha. = Hauterivian; Barr. = Barremian; Cen. = Cenomanian; Tur. = Turonian; Co. = Coniacian; San. = Santonian; Maas. = Maastrichtian; Dan. = Danian; S. = Selandian; Tha. = Thanetian; Ypr. = Ypresian.

This conclusion is supported by the comparison of Hg records with sedimentary osmium-isotope ratios, another proxy for LIP volcanism and/or primitive basalt-seawater interactions. Both OAE 2 and the latest Cretaceous show a trend towards unradiogenic osmium (Os) isotope values in globally distributed sedimentary records, clearly linking both events to the emplacement of LIPs. The global perturbation of Os isotopes in seawater contrasts the inconsistent and low-magnitude Hg excursions in OAE 2 sediments and indicates that hydrothermal Hg emissions from the submarine LIP had only a local influence on the marine realm, probably due to the near-field influence and short oceanic residence time of mercury. The lack of correlation between Hg and Os-isotope excursions in end-Cretaceous sequences supports evidence from other events that although LIP volcanism can perturb the global mercury cycle, not all such eruptions will do so. It is speculated that several factors could be critical in the impact of LIP eruptions on the global mercury cycle: submarine *versus* subaerial volcanism, volcanic intensity or explosivity, as well as the potential contribution of thermogenic mercury from reactions between magma and enclosing organic-rich sediments. Understanding the role of volcanism-dynamics is crucial for the application of Hg as a sedimentary tracer of LIP volcanism.

5.1. Introduction

Sedimentary mercury (Hg) concentrations have been utilised in a number of studies to link major environmental perturbations with Large Igneous Province (LIP) eruptions (Figure 5.1: e.g. Sanei *et al.*, 2012; Percival *et al.*, 2015; Thibodeau *et al.*, 2016; Font *et al.*, 2016; Charbonnier and Föllmi, 2017; Charbonnier *et al.*, 2017). The use of mercury as a volcanic tracer stems from the known emission of the element from modern volcanoes to the atmosphere and ocean, and the relatively long

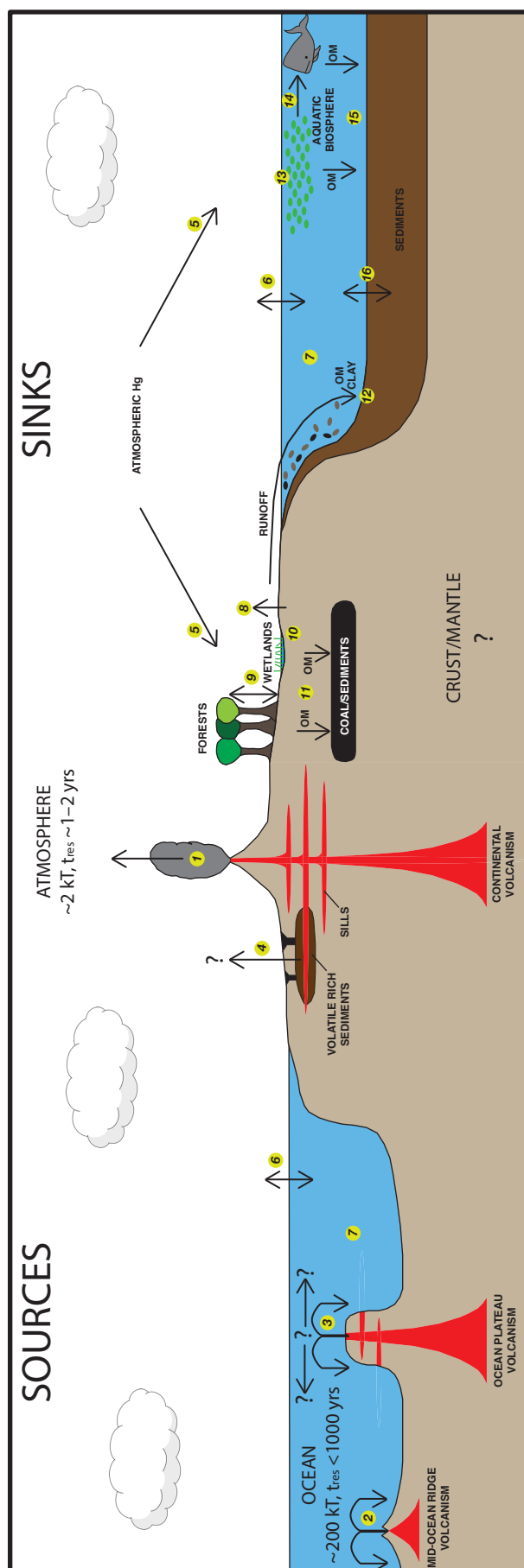


Figure 5.2 (opposite)

residence time of atmospheric mercury allowing it to be distributed globally before being deposited to sediments (Figure 5.2: Slemr *et al.*, 1985; Pyle and Mather, 2003; Lamborg *et al.*, 2006; Bowman *et al.*, 2015). However, the impact of specific volcanic and sedimentological features on mercury emissions and their sedimentary record remains relatively poorly constrained. In this study, new Hg concentration data are presented from sedimentary records of two Mesozoic events associated with LIP eruptions: Cretaceous Ocean Anoxic Event 2 (OAE 2: ~94 Ma), and the end-

Figure 5.2: Simplified illustration of the global mercury cycle, adapted from Percival *et al.* (2015). Processes affecting the source, sink, and transportation of mercury through the ocean–atmosphere system are indicated as follows: **1** – Volcanic emission of mercury, chiefly as inert gaseous elemental mercury (Hg^0) to the atmosphere; **2** – Hydrothermal emission of Hg to the ocean at mid-ocean ridges, rapidly converted to monomethylmercury (MMHg); **3** – Presumed equivalent release of hydrothermal Hg to the ocean from submarine ocean plateau volcanism, similar to that at mid-ocean ridges; **4** – Possible emissions of thermogenic Hg to the atmosphere following heating of organic-rich sediments by intruding sills; **5** – Deposition of atmospheric Hg to land, water, or forest canopy, either as particulate Hg (dry deposition) or soluble oxidised mercury (Hg^{2+}) following interaction between atmospheric Hg^0 and atmospheric oxidising agents such as halogen, nitrile, and hydroxyl radicals (wet deposition); **6** – Air–water interchange of Hg^0 ; **7** – Conversion of mercury species between Hg^0 , Hg^{2+} , MMHg and DMHg (dimethylmercury) through multiple biotic and abiotic reactions (e.g. Fitzgerald *et al.*, 2007; Selin *et al.*, 2009; Bowman *et al.*, 2015; summarised in Munthe *et al.*, 2009); **8** – Reduction of soil Hg to Hg^0 , which is subsequently re-emitted to the atmosphere; **9** – Interchange of mercury between soil and forest canopy through emission of soil Hg and decay of leaves that have taken up Hg; **10** – High abundance of sulphate/iron reducing bacteria in reduced wetland environments promote methylation of Hg^{2+} to organophilic MMHg, which can adsorb onto organic matter; **11** – Deposition of sediments in Hg–OM complexes to soils, peats, or coals; **12** – Riverine runoff (and potentially deposition) into lacustrine or marine environments of detrital Hg bound to either organics or clay minerals; **13** – Uptake of Hg^{2+} or MMHg by aquatic biota; **14** – Bioaccumulation of organophilic MMHg up the food chain; **15** – Deposition of bioaccumulated Hg to sediments as Hg–OM complexes; **16** – Potential remobilisation and release of sedimentary Hg into the aquatic realm. Atmospheric and oceanic residence times of Hg are indicated (Slemr *et al.*, 1985; Gill and Fitzgerald, 1988).

Cretaceous extinction (66.0 Ma). The LIPs associated with these two events have a number of features that contrast with each other, as well as with other Mesozoic LIPs (see section 5.1.1.), making the study of these two events particularly important in determining which volcanic features might be important for mercury emissions. Both events have also been linked to LIP emplacement through excellent sedimentary records of osmium (Os) isotopes (Ravizza and Peucker-Ehrenbrink, 2003; Turgeon and Creaser, 2008; Robinson, 2009; Du Vivier *et al.*, 2014; 2015), allowing comparison of Hg concentrations and Os isotopes as volcanic proxies.

5.1.1. The link between Large Igneous Provinces (LIPs) and Mesozoic events

OAE 2 has been linked with four LIPs: the Caribbean–Columbian Plateau, the High Arctic LIP, the Ontong-Java Plateau, and the Madagascan Province (e.g. Storey *et al.*, 1995; Neal *et al.*, 1997; Snow *et al.*, 2005; Turgeon and Creaser, 2008; Tegner *et al.*, 2011). The latest-Cretaceous (K–Pg: ~67–66 Ma), including the end-Cretaceous extinction, coincided with the emplacement of the Deccan Traps (e.g. Courtillot *et al.*, 1986; Chenet *et al.*, 2007; 2008; 2009; Renne *et al.*, 2015; Schoene *et al.*, 2015). The link between LIPs and Mesozoic environmental perturbations is founded chiefly on a long-known correlation in the ages of individual Mesozoic events and LIPs, based on U–Pb and Ar–Ar geochronology (see Figure 5.1: e.g. Courtillot and Renne, 2003; Bond and Wignall, 2014). LIPs represent the geologically rapid emplacement of enormous quantities of magmatic material, with the main phase of emplacement thought to have typically lasted ~1 Myr (Coffin and Eldholm, 1994). The majority of continental LIP extrusives are believed to have comprised tholeiitic basalts, although evidence for more silicic fractions and/or explosive volcanism has been documented (reviewed in Ross *et al.*, 2005). Indeed, entire LIPs can be predominantly silicic (up

to rhyolitic) in composition, e.g. the Early Jurassic Chon Aike and Early Cretaceous Whitsunday provinces (Bryan and Ernst, 2008; Bryan *et al.*, 2010). LIPs can also be emplaced into either continental or oceanic crust, resulting in some provinces where volcanism was predominantly subaerial (Continental Flood Basalts), and others where eruptions were largely submarine (Oceanic Plateaus). The end-Cretaceous Deccan Traps represent a continental LIP emplaced subaerially, whereas all four LIPs associated with OAE 2 are Oceanic Plateaus, where much of the volcanism would have been submarine. However, Aptian age phreatomagmatic deposits documented from the Ontong-Java Plateau demonstrate that submarine Ocean Plateaus can become emergent and generate subaerial volcanics, (Chambers *et al.*, 2004; Thordarson *et al.*, 2004).

Volatile emissions of LIPs remain poorly constrained, but estimates from petrological analyses suggest figures of at least 13 Mt CO₂ for a typical LIP with a volume of 1 Mkm³ (Self *et al.*, 2005). Geologically rapid emissions of such large quantities of this greenhouse gas are consistent with evidence for warming and/or carbon-cycle perturbations documented in sedimentary records of numerous Mesozoic events (e.g. Li and Keller, 1998a; Voigt *et al.*, 2004; 2006; Schaller *et al.*, 2011; Tobin *et al.*, 2012; Keller *et al.*, 2016). However, if the emissions took place gradually over an entire 1 Myr period of emplacement, such quantities of magmatic carbon would not have significantly perturbed the global carbon cycle (Self *et al.*, 2006; 2014). Moreover, numerous events associated with LIPs also record negative excursions in carbon isotopes ($\delta^{13}\text{C}$) of both organic and inorganic carbon that are too great to have been plausibly produced by magmatic carbon alone (Dickens *et al.*, 1995; Hesselbo *et al.*, 2000; Beerling and Berner, 2002). Consequently, additional sources of volatiles to the ocean-atmosphere system during times of major

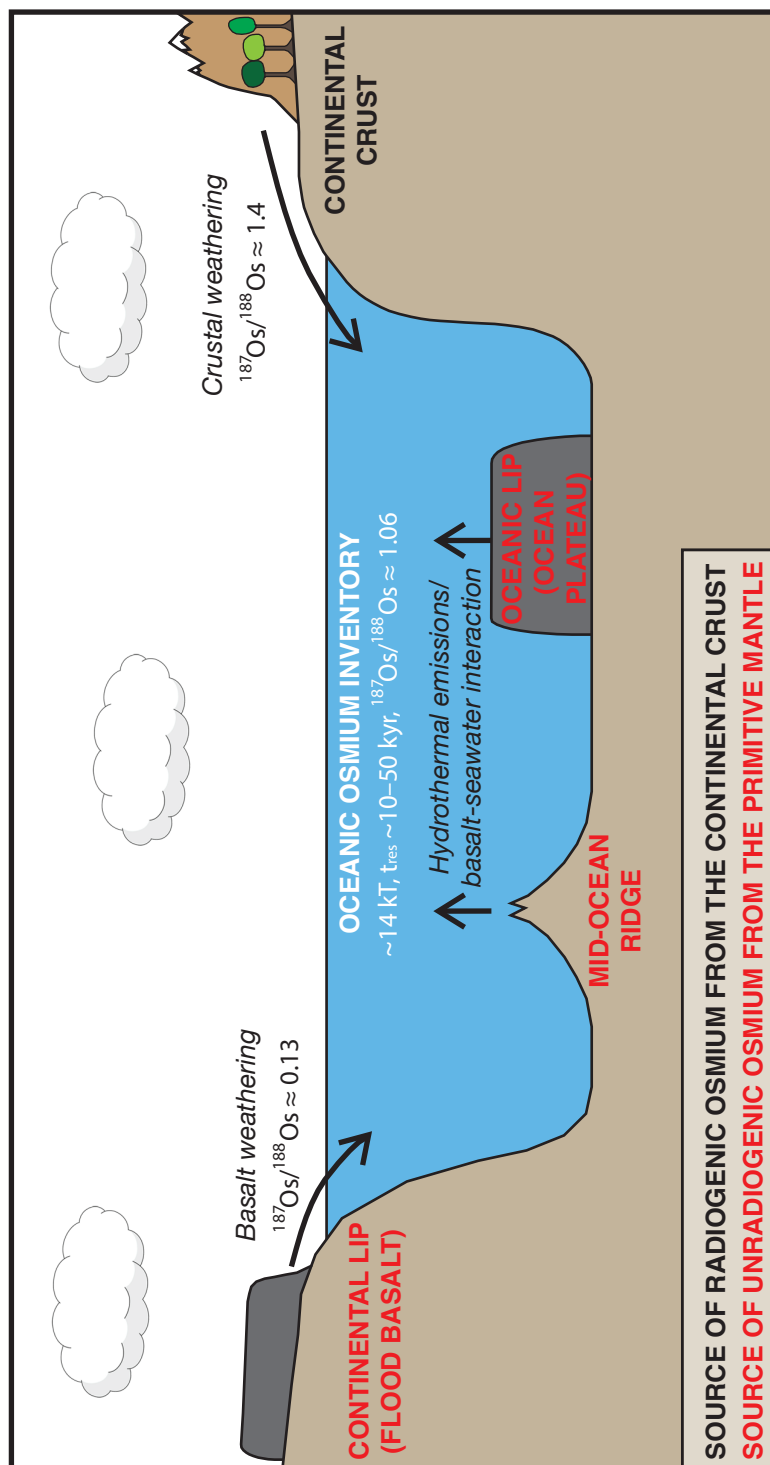


Figure 5.3: Simplified illustration of the inputs of osmium to the global ocean. Radiogenic osmium input is dominated by the flux of osmium from the continental crust. Unradiogenic osmium input is dominated by hydrothermal output from mid-ocean ridges and intra-plate oceanic volcanism, and weathering of subaerial basalts derived from partial melting of the primitive mantle. The relative input of these sources determines the isotopic composition of the oceanic osmium inventory, due to the element being well mixed in the open ocean. The approximate isotopic compositions from each source and oceanic residence time of Os are indicated (reviewed in Peucker-Ehrenbrink and Ravizza, 2000).

environmental perturbations have been proposed. One possible source of (isotopically light) carbon is through melting of methane hydrates (Dickens *et al.*, 1995; Hesselbo *et al.*, 2000). However, it is not clear whether there would have been a sufficiently large hydrate reservoir during the Mesozoic to have substantially perturbed the atmospheric carbon inventory. An alternative isotopically light carbon source could be the release of thermogenic volatiles generated through heating of carbonaceous sediments by intruding magmas during emplacement of a LIP (Svensen *et al.*, 2004). The end-Permian Siberian Traps and Pliensbachian–Toarcian Karoo–Ferrar LIP are two good examples of LIPs believed to have featured such release of additional thermogenic volatiles (McElwain *et al.*, 2005; Svensen *et al.* 2007; 2009). However, neither the end-Cretaceous Deccan Traps nor any of the LIPs associated with OAE 2 are thought to have produced thermogenic volatiles.

As well as a strong temporal association between LIP volcanism and Mesozoic events such as OAE 2 and the end-Cretaceous extinction, a causal link between the two phenomena is indicated by evidence for volcanism in stratigraphic horizons recording the onset of environmental change. As well as mercury concentrations, a number of other geochemical proxies have been utilised to indicate volcanism during OAE 2 and the end-Cretaceous. For example, increased sedimentary abundances of trace metals have been interpreted to result from hydrothermal output from subaqueous LIP volcanism, or weathering of juvenile basalts in a subaerial LIP (e.g. Orth *et al.*, 1993; Snow *et al.*, 2005; Pálffy and Zajzon, 2012; Erba *et al.*, 2015). Numerous isotope systems have also been proposed to be indicative of LIP volcanism, including strontium, lead, neodymium, sulphur, and chromium isotopes (e.g. Jones and Jenkyns, 2001; Kuroda *et al.*, 2007; Zheng *et al.*, 2013; Holmden *et al.*, 2016; Jenkyns *et al.*, 2017). However, the development of many of these proxies remains in

its early stages; many of the proxies have yet to be trialed on multiple records or events, or are known to respond to more than one surface process (e.g. both volcanism and continental weathering). Additionally, strontium has a very long seawater residence time (~1 Myr), making $^{87}\text{Sr}/^{86}\text{Sr}$ ratios less suitable for recording geologically rapid events.

Osmium isotopes ($^{187}\text{Os}/^{188}\text{Os}$) of mudrocks have previously been used the most extensively as stratigraphic markers of LIP volcanism. The $^{187}\text{Os}/^{188}\text{Os}$ composition of the primitive mantle is very unradiogenic, typically <0.15 (Horan *et al.*, 1995; Allègre *et al.*, 1999; Gibson *et al.*, 2016), compared to a much more radiogenic composition of the continental crust, typically ~ 1.4 (Figure 5.3; Peucker-Ehrenbrink and Ravizza, 2000). Thus, weathering of subaerial LIP basalts or hydrothermal activity associated with submarine LIP volcanism would be expected to cause a decrease in the $^{187}\text{Os}/^{188}\text{Os}$ ratios of sediments deposited at that time ($\text{Os}_{(i)}$: Cohen *et al.*, 1999). It is important to note that $\text{Os}_{(i)}$ indicates the calculated $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater at the time the analysed sedimentary rocks were deposited, which can be calculated based on the measured $^{187}\text{Os}/^{188}\text{Os}$ of those sediments today, the age of the rocks, and the content of ^{187}Re in the rock that has decayed to form additional ^{187}Os since deposition. Extensive Os-isotope records have been generated for both the end-Cretaceous and OAE 2, showing a decrease in sedimentary $\text{Os}_{(i)}$ across the globe for both events which is interpreted as evidence for LIP volcanism (Ravizza and Peucker-Ehrenbrink, 2003; Turgeon and Creaser, 2008; Robinson, 2009; Du Vivier *et al.*, 2014; 2015).

5.1.2. *Mercury as a proxy for volcanism*

An advantage of mercury over other proxies is that the element appears to be a uniquely volcanic marker, less impacted by continental weathering than strontium or osmium isotopes, or by marine redox chemistry than many other metals. Figure 5.2 shows a simplified summary of the natural mercury cycle. Hg is emitted as a trace volcanic trace gas in the modern (Pyle and Mather, 2003), and has an atmospheric residence time of up to 0.5–2 years, allowing global distribution (Schroeder and Munthe, 1998). An ice core record of the historical atmosphere from Wyoming has highlighted three episodes of abruptly elevated atmospheric Hg content following major eruptions in the last two centuries (Tambora, Krakatau, and Mount St. Helens: Schuster *et al.*, 2002). Mercury is also emitted from hydrothermal activity of subaqueous volcanism, and appears to be rapidly converted to monomethyl mercury, the dominant measured species of Hg measured within hydrothermal plumes (Lamborg *et al.*, 2006; Bowman *et al.*, 2015). However, hydrothermal mercury has a very limited, near-field, impact on the marine realm at the present day (Bowman *et al.*, 2015), and the element has a shorter oceanic residence time (<1000 yrs: Gill and Fitzgerald, 1988) than the mixing time of the oceans. Thus, Hg sourced from subaqueous volcanism would have a relatively localised impact on surrounding sediments compared to the global influence of mercury emitted to the atmosphere from subaerial volcanism.

The majority of atmospheric mercury is removed via numerous oxidation reactions (Selin, 2009), allowing the resultant Hg^{2+} to be precipitated in aqueous compounds (‘wet’ deposition), with a proportion also removed through particulate deposition (‘dry’ deposition). In the terrestrial realm, both ‘dry’ particulate and ‘wet’ dissolved mercury can be adsorbed by tree canopies or soils, with reduction and re-

emission of mercury in soils allowing for substantial interchange between the two reservoirs (reviewed in Munthe, 2009). Notably, vegetation type can play a significant role in the extent of mercury drawdown in the terrestrial realm, with coniferous vegetation thought to take up more mercury than deciduous species (Obrist *et al.*, 2012). Ultimately, terrestrial mercury may either be deposited into palaeosols or coals, or carried into the aquatic realm as runoff.

In the aquatic realm, mercury can be influenced by both biotic and abiotic processes, several of which result in the conversion of oxidized mercury to monomethyl-mercury or dimethyl-mercury, both in the marine environment and in reducing terrestrial aquatic systems such as lakes and wetlands (Benoit *et al.*, 2001; Ravichandran, 2004). These geochemical species have a considerable affinity for organic matter; thus, Hg is typically transferred into sediments in organo-metal complexes, resulting in a relatively consistent sedimentary Hg/TOC ratio at any one location under stable conditions (e.g. Outridge *et al.*, 2007; Liu *et al.*, 2012; Ruiz *et al.*, 2015). Consequently, sedimentary mercury concentrations are typically normalised against the total organic carbon (TOC) content of the sediment, so that relatively elevated Hg/TOC may point to the Hg content being derived from an external source such as volcanism (Sanei *et al.*, 2012). Additional sinks, in particular those involving reactions of Hg with sulphides or clay minerals, may also influence the deposition of mercury under certain conditions, such as euxinic environments or areas dominated by alluvial runoff (Krupp *et al.* 1988; Benoit *et al.*, 1999; Kongchum *et al.*, 2011; Jin and Liebezeit, 2013).

5.1.3. *Environmental influences on the sedimentary record of atmospheric Hg*

Despite the promise of sedimentary Hg/TOC as a tracer of large-scale volcanism, it has been suggested that specific sedimentological processes might impact the sedimentary Hg archive. In agitated, well-oxygenated environments where there is little organic matter, sulphides, or clays, mercury drawdown is likely to be limited (Mason *et al.*, 2000; Percival *et al.*, 2015). Conversely, very organic-rich sediments that record an abrupt increase in marine anoxia/euxinia may result in TOC contents rising more than available Hg concentrations, overprinting the mercury signal and creating an apparent decrease in Hg/TOC ratios (Percival *et al.*, 2015; Charbonnier and Föllmi, 2017). Sedimentary mercury also appears to have been relatively enriched in terrestrial or near-shore sediments compared to fully marine sediments during latest-Triassic and early Toarcian times, both in terms of background values and in the magnitude of perturbations (Percival *et al.*, 2015; see also Chapter 3).

Recently, the importance of local processes on mercury records has also been hinted by mercury-isotope records. Two end-Permian sedimentary records, both with excursions in Hg/TOC ratios attributed to Siberian Trap volcanism, were found to record significantly different trends in Hg isotopes (Grasby *et al.*, 2017). The marked differences in palaeoenvironment inferred from the two sedimentary records were suggested to be the cause of the differences in observed Hg-isotope trends, given that the mercury was likely originally derived from the same volcanic source (Grasby *et al.*, 2017; Thibodeau *et al.*, 2017).

As well as uncertainties in the depositional processes governing the Hg record, the influence of volcanic source processes on the Hg cycle also remains unclear. Although many LIPs and more recent volcanic eruptions are associated with Hg

enrichments in sedimentary archives, such signals are not universally associated with volcanic activity. Thus, it remains unclear what particular factors associated with volcanism influence the extent to which volcanic eruptions will perturb the global Hg cycle. Such information is crucial in understanding the influence of LIPs on the global Hg inventory, given the large variation in tectonic and volcanic contexts across individual LIPs. Three major features of volcanic source processes that are likely to influence the sedimentary mercury record are discussed here.

Firstly, given the much greater ability for atmospherically-emitted mercury to achieve a widespread distribution than subaqueously emitted Hg, it may be hypothesised that a continental LIP will result in more consistent, widespread, and higher magnitude excursions in sedimentary mercury compared to an oceanic LIP. Secondly, LIPs associated with release of additional thermogenic volatiles (including Hg) from heating of organic-rich lithologies by intruding LIP sills might be more likely to cause a major Hg-cycle perturbation than those unassociated with thermogenic emissions. Finally, LIPs with large numbers of plinian-style eruptions might have achieved a greater distribution of emitted Hg than those without such explosive volcanic events. In the modern environment, explosive eruptions are more likely to result in stratospheric injection of volatiles than effusive volcanism, aiding their widespread distribution. In the aforementioned Wyoming ice core record, all three historical volcanic eruptions coincident with observed elevations in records of atmospheric Hg were explosive. Contrastingly, no change in the documented atmospheric Hg was observed to have followed the large effusive eruptions of Laki (Iceland, 1783), despite the fact that the Laki was far more proximal to Wyoming than two of the three explosive eruptions (Schuster *et al.*, 2002). The absence of a signal of elevated atmospheric Hg following the Laki eruptions is of particular significance

as those eruptions represent what is thought to be the best historical analogy of LIP-style volcanism, albeit at far smaller magnitude.

Gaining insight into which volcanic styles are important for producing major mercury emissions, and which sedimentary processes influence the stratigraphic record of such fluxes to the environment, represents a crucial step in the understanding of the element as a potential proxy of LIP volcanism. Generating and comparing Hg records from multiple records of OAE 2 and the K–Pg that include a range of sedimentary facies will allow the examination of how local processes might influence a sedimentary record of the global mercury inventory. Additionally, the importance of specific volcanic features in producing a volcanogenic perturbation of the global Hg cycle will be tested by comparing the OAE 2 and K–Pg Hg data with mercury records of other major events, spanning a broad range of LIP emplacement styles (submarine: OAE 2; subaerial: K–Pg; subaerial with thermogenics: end-Permian and end-Triassic). Finally, the OAE 2 and K–Pg mercury records will be compared directly to the sedimentary $\text{Os}_{(i)}$ records of the same events, to assess the differences between the two volcanic proxies. Of particular interest is whether: i) there are certain sedimentary facies that can be identified as good archives of atmospheric mercury changes; and ii) all LIP eruptions manifestly produce major Hg emissions, or if the ability to perturb the global Hg cycle depends on factors such as subaerial eruptions (rather than submarine), high eruption intensity or explosivity, or the release of thermogenic volatiles following the intrusion of LIP magmatics.

5.2. Studied events and records

5.2.1. End-Cretaceous Extinction

The end of the Cretaceous (66.0 Ma) saw the close of the Mesozoic Era and witnessed the extinction of up to two thirds of species including, most famously, the non-avian dinosaurs (reviewed in Brusatte *et al.*, 2014). The majority of extinctions appear to have occurred very abruptly at the end of the Cretaceous, although there have been claims for increased extinction rates (alongside climatic degradation) throughout the last few hundred kyr of the Maastrichtian Stage (Li and Keller, 1998b; Abramovich and Keller, 2002; Keller *et al.*, 2016). The key evidence for an abrupt event is the preservation of a thin clay layer at numerous sections around the world, containing abundant spherules and an anomalously high iridium concentration, from which the impact of an extra-terrestrial object has been inferred (Alvarez *et al.*, 1980; Smit, 1999). Such an impact is supported by the presence of a 170 km crater, dated to the Cretaceous–Palaeogene boundary, preserved at Chicxulub, under the Yucatan Peninsula of Mexico (Hildebrand *et al.*, 1991). However, a more gradual event is supported by evidence for climate warming and changes to climate sensitivity through the final 300–400 kyr of the Maastrichtian (e.g. Li and Keller, 1998a; Tobin *et al.*, 2012; Batenburg *et al.*, 2012; 2014).

Latest Cretaceous warming is linked to the main phase of emplacement of the Deccan Traps, dated to have begun at ~66.3 Ma, 300 kyr prior to the K–Pg boundary, approximately coincident with the C30N/C29R palaeomagnetic reversal (e.g. Wellman and McElhinny, 1970; Courtillot *et al.*, 1986; 1988; Duncan and Pyle, 1988; Chenet *et al.*, 2007; 2008; 2009; Jay *et al.*, 2009; Renne *et al.*, 2015; Schoene *et al.*, 2015). Sedimentary osmium-isotope data support an onset of Deccan volcanism significantly before the extinction, with a decrease in $^{187}\text{Os}/^{188}\text{Os}$ ratios interpreted as

caused by weathering of juvenile Deccan basalts correlated with the C30N/C29R boundary in multiple stratigraphic records (Ravizza and Peucker-Ehrenbrink, 2003; Robinson *et al.*, 2009). Although Deccan activity commenced prior to the extinction, there is also evidence of a substantial increase in volcanic intensity coincident with the extinction itself (Renne *et al.*, 2015). The appearance of an excursion in Hg/TOC around the end-Cretaceous extinction horizon at Bidart (France) but not significantly below it, may reflect this increase in intensity (Font *et al.*, 2016). Additional claims for end-Cretaceous Hg/TOC excursions have also been made from a number of other sections across the globe (Sial *et al.*, 2016). However, these excursions do not appear in all records, often do not correlate stratigraphically, and are commonly the result of decreases to TOC abundance rather than increases in Hg concentrations. Crucially, no end-Cretaceous Hg study has interrogated the C30N/C29R boundary, to establish whether the global mercury cycle was perturbed by the onset of the Deccan Trap volcanism, as well as by a potentially more intense eruptive phase during the end-Cretaceous extinction.

Four end-Cretaceous sections were analysed for Hg concentrations and Hg/TOC ratios (Figure 5.4A): Seymour Island (Antarctica), the Hell Creek Formation at East Gilbert Creek (Montana, USA), Zumaia (Spain), and ODP 174AX at Bass River (New Jersey, USA).

5.2.1.1 Seymour Island (Antarctica)

The López de Bertodano Formation of Seymour Island records an extremely expanded and lithologically consistent record of latest Maastrichtian–earliest Palaeogene time, deposited in a back-arc basin (Crame *et al.*, 1991). The facies consist chiefly of very fine (mud–silt) siliciclastics (Macerllari, 1988; Crame *et al.*, 2004),

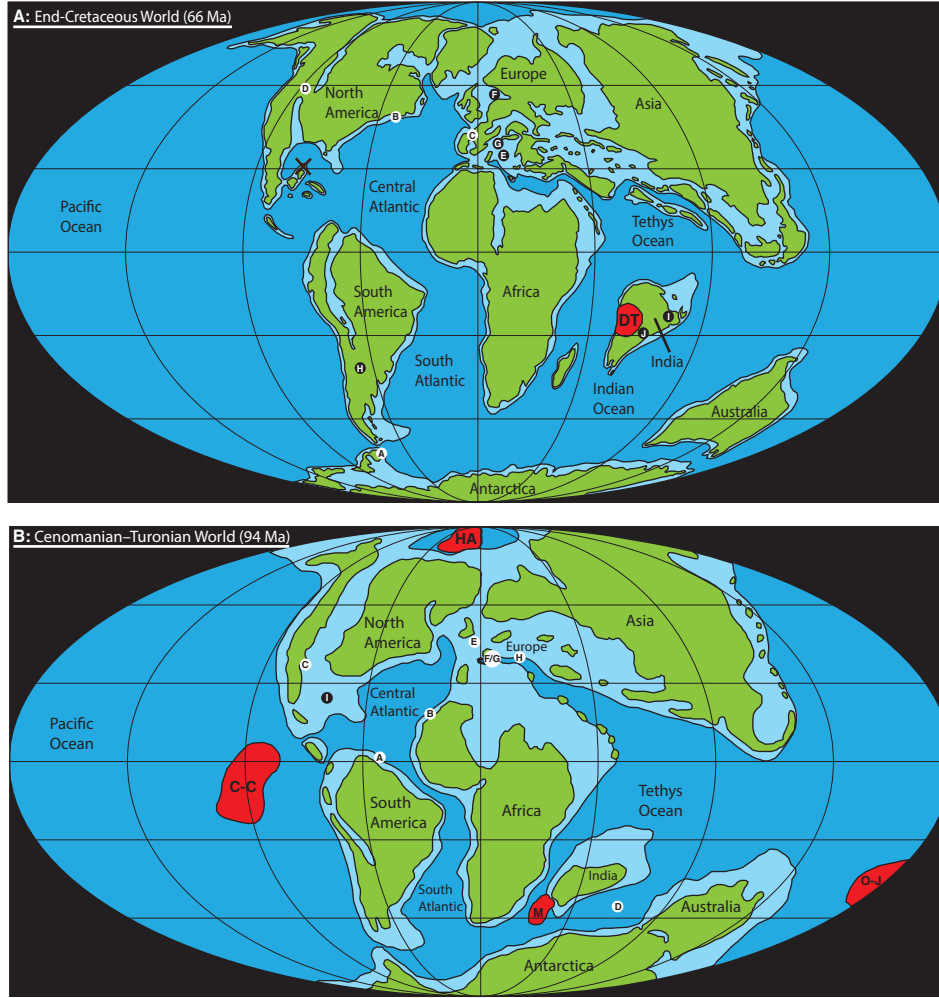


Figure 5.4: Palaeogeographic maps of the end-Cretaceous and Cenomanian–Turonian worlds, indicating the geographical position of LIPs emplaced at those times, and the locations of sedimentary records analysed for mercury in this study (white circles), or previously published studies (black circles). **A:** Palaeogeographic map of the end-Cretaceous world. Sedimentary records studied for mercury are indicated as follows: A – Seymour Island (Antarctica); B – ODP 174AX Bass River (USA); C – Zumaia (Spain: also marks the location of the French Bidart section studied in Font *et al.*, 2016); D – East Gilbert Creek, Montana (USA); E: Botaccione Gorge (Italy); F – Stvens Klint (Denmark); G – Padriciano (Italy); H – Bajada del Jaguel (Argentina); I – Meghalaya (India); J – Jhilmili (India). All of records E–J documented in Sial *et al.* (2016). The positions of the Deccan Traps (DT) and Chicxulub impact crater (X) are also indicated. **B:** Palaeogeographic map of the Cenomanian–Turonian world. Sedimentary records are indicated as follows: A – IODP 1260B (Demerara Rise: also the location of IODP 1258 studied in Scaife *et al.*, in prep.); B – Tarfaya (Morocco); C – Utah composite (USA); D – IODP 1138A (Kerguelen Plateau); E – Eastbourne (UK); F – Pont d’Issole and Vergons (France); G – Clot Chevallier (France); H – Furlo (Italy); I – Maverick Basin (USA) studied by Scaife *et al.* (in prep.). Cenomanian–Turonian Igneous Provinces are indicated as follows: C-C – Caribbean-Columbian Plateau; HA – High Arctic LIP; M – Madagascan Province; O-J – Ontong Java Plateau. Both palaeogeographical reconstructions are based on those of Ron Blakey (<http://cpgeosystems.com>).

with a negligible carbonate content, and low TOC content (0.2–0.4 %wt; Figure 5.5A). An excellent dinoflagellate record, a documented spike in iridium concentration, and an extensive magnetostratigraphy with a well-established C30N/C29R boundary allows good temporal correlation with other latest Cretaceous records (Elliot *et al.*, 1994; Bowman *et al.*, 2012; Tobin *et al.*, 2012). Oxygen-isotope and clumped-isotope data indicate a warming event at the C30N/C29R reversal that has been linked to Deccan volcanic activity (Tobin *et al.*, 2012; Petersen *et al.*, 2016). However, this warming appears to have had limited impact on Antarctic fauna, with no significant change in the taxa recorded below the end-Cretaceous extinction horizon (Witts *et al.*, 2016).

5.2.1.2 ODP174AX (Bass River, New Jersey, USA)

ODP174AX cored Cretaceous–Neogene sediments of Bass River, including the Cretaceous–Palaeogene transition and end-Cretaceous extinction horizon. The Maastrichtian sediments are lithologically homogeneous, typically consisting of glauconitic sands and clays, and containing ~1 %wt TOC (Miller *et al.*, 1998; this study). The K–Pg boundary marks the base of a spherule-rich layer, as well as a spike in iridium concentrations (Olsson *et al.*, 2002). In the uppermost 2 m of the Cretaceous there are also excursions in planktonic foraminifera, $\delta^{18}\text{O}$ and Mg/Ca ratios, all of which are suggestive of warming, interpreted as caused by the emplacement of the Deccan Traps (Olsson *et al.*, 2002). Temporal constraints on the Bass River section are poor, but the *M. prinsii* nannofossil Zone extends to at least 385.5m, indicating that the C29R strata extend to at least that depth on the basis of the first appearance of *M. prinsii* within C29R strata at other locations (Gardin *et al.*, 2012; Thibault *et al.*, 2012). A core-gap at 385.5 m introduces uncertainty, but following the pattern of

warming in oxygen isotopes and comparison to other records (Tobin *et al.*, 2012; Petersen *et al.*, 2016; Birch *et al.*, 2016), the C30N/C29R boundary is positioned at approximately 386 m (see full correlation in Appendix 2A). Consequently, it is likely that the lower samples analysed in this study are from C30N strata, although, in the absence of magnetostratigraphic data from this core, robust conclusions cannot be drawn.

5.2.1.3 Zumaia (Spain)

The Zumaia section on the northern coast of Spain is a reference section for the K–Pg interval. The uppermost Cretaceous sediments consist of reddish-grey to purple marls and marly limestones with a minor amount of intercalated calcareous turbidites. These marine sediments were deposited in a hemipelagic setting in the relatively narrow Basque-Cantabric Basin (Pujalte *et al.*, 1995). The rhythmic alternation of lithologies likely reflects the pacing of late Maastrichtian climate by eccentricity-modulated precession and has been used to refine the geological time scale (Batenburg *et al.*, 2012). The astrochronology provides ages for planktonic foraminifera and calcareous nannofossil events, bulk carbonate carbon-isotope variations, as well as the base of magnetochron C29R, which has been correlated based on individual limestone-marl alternations (Batenburg *et al.*, 2012; 2014). The K–Pg boundary itself is marked by both a clear biostratigraphic change and a spike in sedimentary Ir concentrations within a thin clay layer (Schmitz *et al.*, 1997; Molina *et al.* 2009).

5.2.1.4 East Gilbert Creek (Garfield County, Montana, USA)

New samples were collected for this study from the uppermost sediments of

the Hell Creek Formation at the top of East Gilbert Creek (47°40'03"N; 106°30'27"). The Hell Creek Formation is preserved across Montana, North Dakota, and South Dakota, and provides a terrestrial (fluvial/flood plain) record of the latest-Cretaceous interval, with a number of widespread, stratigraphically continuous coal beds. In the uppermost part of the Hell Creek Formation the two main coal beds are the Null Coal and the Z Coal, with a small coal unit (the IrZ) just below the Z Coal (summarised in Sprain *et al.*, 2014). The IrZ coal has been found to contain an iridium-rich clay, confirming that it marks the end-Cretaceous extinction (Alvarez, 1983; Smit and Van Der Kaars, 1984). Both the Null and IrZ coals contain tephra, that have been Ar–Ar dated to 66.289 ± 0.051 Ma, and 66.043 ± 0.043 Ma, respectively (Sprain *et al.*, 2014). The uppermost Hell Creek Formation also records a negative excursion in carbon isotopes of approximately 2‰, thought to be equivalent with the $\delta^{13}\text{C}$ negative excursion documented at the end-Cretaceous extinction horizon in marine records (Arens and Jahren, 2000; Arens *et al.*, 2014). A previous magnetostratigraphic study placed the C30N/C29R boundary in the Apex Sand, above the Null Coal (LeCain *et al.*, 2014). However, the 66.289 Ma age of the Null Coal matches that of a volcanic ash bed known to have been deposited during C29R from more recent palaeomagnetic studies (Clyde *et al.*, 2016). Consequently, it is assumed that C29R strata likely extend at least down to the Null Coal Unit, and probably lower.

New samples for this study were collected from between 2 m below the Null Coal to 2 m above the Z Coal at East Gilbert Creek, encompassing the uppermost Hell Creek Formation and lowermost Fort Union Member above (see Appendix 2B). These strata also include the K–Pg boundary but, based on the most recent magnetostratigraphic interpretations (Clyde *et al.*, 2016), probably not the C30N/C29R boundary.

5.2.2. OAE 2

The Cenomanian–Turonian boundary (~94 Ma) marks the second largest marine extinction of the Cretaceous, and also records the development of marine anoxia–euxinia across the globe, typically as the abrupt appearance of metre-thick black shale units intercalated between less organic-rich lithologies (reviewed in Jenkyns, 2010). A rapid onset of anoxia is particularly strongly evidenced in Tethyan and North European records, where fine-grained pelagic limestones and chalks show an abrupt transition to black shales before a return to relatively pure carbonates (Schlanger and Jenkyns, 1976). The black shales locally contain abundant organic matter (TOC up to 20–30 %wt), and record a large positive excursion in $\delta^{13}\text{C}$ (up to 4‰), both indicative of increased production and preservation of organic matter, and suggesting very low oxygenation levels (e.g. Tsikos *et al.*, 2004; Erbacher *et al.*, 2005). Widespread marine anoxia at that time is further supported by a range of geochemical proxies, such as molybdenum, iron, manganese, uranium, cerium, and iodine concentrations, and molybdenum, sulphur and iron isotopes, although the degree of anoxia was likely geographically variable (Jenkyns *et al.*, 2007; Jenkyns, 2010; Westermann *et al.*, 2014; Jenkyns *et al.*, 2017).

The date of the Cenomanian–Turonian boundary matches the determined ages of a number of subaqueous LIPs (Storey *et al.*, 1995; Neal *et al.*, 1997; Courtillot and Renne, 2003; Snow *et al.*, 2005; Turgeon and Creaser, 2008; Tegner *et al.*, 2011). Large-scale volcanism during OAE 2 is also shown by an increased abundance of sedimentary trace metals in the interval of the Plenus Cold Event, and a decrease in $^{187}\text{Os}/^{188}\text{Os}$ ratios (Orth *et al.*, 1993; Snow *et al.*, 2005; Turgeon and Creaser, 2008; Eldrett *et al.*, 2014; Du Vivier *et al.*, 2014; 2015; Jenkyns *et al.*, 2017). Palaeotemperature proxies have indicated substantial warming during OAE 2,

proposed as a response to LIP volcanic activity (Voigt *et al.*, 2004; 2006; Forster *et al.*, 2007). However, at least one global cooling and re-oxygenation episode also took place during the OAE, dubbed the Plenus Cold Event (Gale and Christensen, 1996; Jarvis *et al.*, 2011; Jenkyns *et al.*, 2017). A warmer atmosphere would be expected to lead to enhanced rates of continental weathering, which has been supported by calcium and lithium isotopes in sediments (Blättler *et al.*, 2012; Pogge von Strandmann *et al.*, 2013). However, it should be noted that increased continental weathering is not recorded by Os isotopes, suggesting that either the increased weathering included that of LIP basalts, or that volcanic output of Os from LIPs to the ocean inventory overwhelmed any flux of continental radiogenic Os.

Eight sections were analysed for Hg/TOC records from OAE 2 (Figure 5.4B): two from the Atlantic (IODP site 1260B, and Tarfaya, Morocco); three from the margins of the Tethys (Pont d'Issole and Clot Chevallier, France, and Furlo, Italy); and three others (Eastbourne, UK, IODP site 1138 in the Indian Ocean, and a composite terrestrial record from Utah, USA).

5.2.2.1 IODP 1260B (Demerara Rise, South Atlantic)

Site 1260B records a deep pelagic palaeoenvironment on the western side of the Atlantic, dominated by organic-rich shales. A two-metre black shale, correlated with a positive excursion in $\delta^{13}\text{C}_{\text{org}}$, records OAE 2 (Erbacher *et al.*, 2005). Numerous other geochemical studies have been conducted on the 1260B core, including Os, Nd, S, and O isotopes, TEX₈₆, and sedimentary trace-metal concentrations, from which atmospheric warming, changes to ocean redox chemistry, and coeval volcanism have been inferred (Forster *et al.*, 2007; 2008; Turgeon and Creaser, 2008; MacLeod *et al.*, 2008; Hetzel *et al.*, 2009; Martin *et al.*, 2012).

Intriguingly, the decline in sedimentary Os-isotope ratios occurs slightly below the onset of elevated $\delta^{13}\text{C}_{\text{org}}$ values (Turgeon and Creaser, 2008).

5.2.2.2 *Tarfaya (Morocco)*

Tarfaya preserves a somewhat shallower water expanded marine record, predominantly consisting of marls with variable carbonate and organic-matter content (TOC varies between 1–25 %wt: Tsikos *et al.*, 2004). Strong cyclostratigraphic signals are recorded, initially attributed to 20 kyr precession and 40 kyr obliquity forcing (Kuhnt *et al.*, 1997), and reinterpreted as the effect of obliquity and 100 kyr eccentricity (Meyers *et al.*, 2012). An abrupt positive excursion is recorded in the $\delta^{13}\text{C}$ composition of co-existing carbonates and organic matter (Tsikos *et al.*, 2004).

5.2.2.3 *Utah (USA)*

The Dakota Formation in Colorado and Utah records a terrestrial environment on the edge of the Western Interior Seaway (Gustason, 1989), and has long been attributed to the Upper Cenomanian (Averitt, 1962; Peterson, 1969; Laurin and Sageman, 2006). A record of OAE 2 was established by the discovery of a 4‰ positive excursion in the $\delta^{13}\text{C}$ composition of terrestrial organic matter near the top of the Dakota Formation (Barclay *et al.*, 2010), under the assumption that OAE 2 is the only Late Cenomanian event known to produce that great a magnitude excursion in carbon isotopes. Stomatal data from plant fossils in the Dakota Fm. have also been used to reconstruct atmospheric $p\text{CO}_2$ during the Late Cenomanian, with a small overall increase (containing some decreases) documented in strata at the base of the $\delta^{13}\text{C}$ positive excursion, supporting a carbon-cycle perturbation at the time of deposition of these sediments likely coincident with OAE 2 (Barclay *et al.*, 2010).

Importantly, the Utah Dakota Formation represents the only currently known terrestrial record of the ocean-atmosphere perturbations across OAE 2.

5.2.2.4 IODP 1138A (*Kerguelen Plateau, Indian Ocean*)

Site 1138A represents one of the few southern hemisphere records of OAE 2. The site is located on the Kerguelen Plateau, which was largely emplaced on to the Indian Ocean crust during the Early Cretaceous, though with some emplacement in the Late Cretaceous and Cenozoic (Frey *et al.*, 2002; Mohr *et al.*, 2002). The sediments record an exclusively marine environment, with a transition from shallow-marine to deep-marine settings throughout the Late Cretaceous. However, evidence exists for the proximity of land in the form of terrestrial organic matter including pollen, spores and wood fragments (Meyers *et al.*, 2009; Dickson *et al.*, 2017). A positive excursion in $\delta^{13}\text{C}_{\text{org}}$ marks the second half of OAE 2, with foraminiferal and nannofossil biostratigraphy indicating a hiatus that includes the lower part of the event, up to the top of the predicted level of the Plenus Cold Event (Dickson *et al.*, 2017). Elevated TOC abundances generally occur throughout the OAE 2 interval, although the onset of TOC elevation begins half a metre higher than the $\delta^{13}\text{C}$ excursion. The $\delta^{13}\text{C}$ excursion also correlates with increases in trace-metal concentrations and molybdenum-isotope ratios, indicating increased marine anoxia during OAE 2 (Dickson *et al.*, 2017).

5.2.2.5 Eastbourne (*S.W. England, UK*)

The Cenomanian–Turonian succession at Eastbourne consists predominantly of foraminiferal-nannofossil chalk, and OAE 2 is marked by a clear lithological change to the more argillaceous Plenus Marls (Jefferies, 1963; Tsikos *et al.*, 2004).

The Plenus Marls record a broad increase in $\delta^{13}\text{C}_{\text{carb}}$, continuing into the immediately overlying chalk, with a smaller negative excursion superimposed upon it (Gale *et al.*, 1993; Tsikos *et al.*, 2004). $\delta^{18}\text{O}$ data indicate both warming during the onset of OAE 2, and subsequent cooling during the Plenus Cold Event part-way through (Paul *et al.*, 1999; Jenkyns *et al.*, 2017). Calcium and lithium isotopes suggest increased rates of weathering during the Plenus Cold Event, and the likely drawdown of atmospheric CO_2 (Blättler *et al.*, 2011; Pogge von Strandmann *et al.*, 2013). Invasion of a boreal watermass possibly carrying the mafic signature of the Arctic LIP is suggested by the neodymium-isotope record (Zheng *et al.*, 2013).

5.2.2.6 Pont d'Issole and Vergons (S.E. France)

Sediments at the Pont d'Issole and stratigraphically underlying Vergons sections were deposited in the Vocontian Trough, and are dominated by limestone–marl alternations reflecting a fluctuating hemipelagic environment (Grosheny *et al.*, 2006). OAE 2 is recorded at Pont d'Issole by the appearance of laminated black shales, and an order-of-magnitude increase in TOC content from 0.2–0.3 %wt below OAE strata to 2–3 %wt within them (Jarvis *et al.*, 2011). A 2‰ positive excursion is recorded in the $\delta^{13}\text{C}$ compositions of both carbonate and bulk organic matter but, intriguingly, the base of both excursions lies markedly above the base of the black shales (Jarvis *et al.*, 2011). The Plenus Cold Event is also recorded at Pont d'Issole by a relative decrease in $\delta^{13}\text{C}$ values of both organic matter and carbonate in the middle of the positive $\delta^{13}\text{C}$ excursion characteristic of the OAE. As at IODP 1260B, an abrupt decline in sedimentary $\text{Os}_{(i)}$ is recorded below both the base of the black shales and the $\delta^{13}\text{C}$ positive excursion (Du Vivier *et al.*, 2014). However, the more expanded record of the Pont d'Issole/Vergons record highlights the offset between the

shifts in C- and Os-isotope values much more clearly than the record at IODP 1260B, strongly indicating that the onset of submarine volcanism predated OAE 2 (Du Vivier *et al.*, 2014).

5.2.2.7 Clot Chevalier (France)

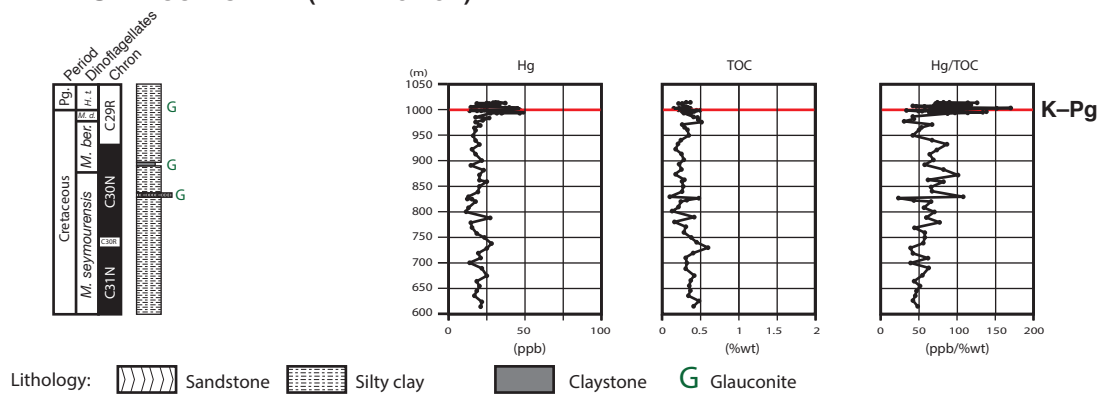
Clot Chevalier also records a pelagic environment from the Vocontian Trough, on the northwestern margin of the Tethys. The record consists of alternating limestones and marlstones, with OAE 2 indicated by the appearance of more organic-rich marls, a broad, positive excursion in $\delta^{13}\text{C}_{\text{carb}}$, and an increase in TOC content to 1–2 %wt within the organic rich-marls, compared to 0.1–0.2 %wt in the limestones above and below (Falzoni *et al.*, 2015). The positive excursion in $\delta^{13}\text{C}_{\text{carb}}$, like that of Pont d’Issole, is punctuated by multiple small negative excursions.

5.2.2.8 Furlo (Italy)

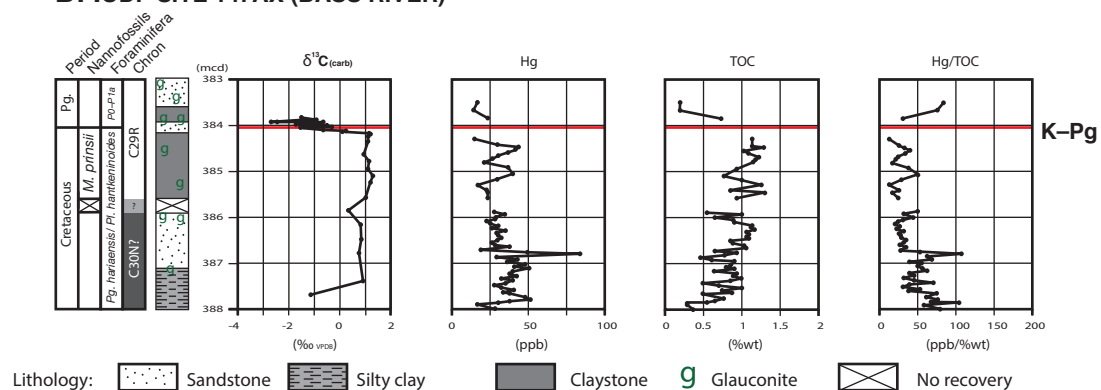
The Furlo section (Umbria-Marche Apennines) was deposited on southern margin of the Tethys, and chiefly consists of regularly bedded pelagic limestones and marls with thin to very thin (<1–10 cm) sporadic layers of heterogeneous cherts and organic-rich shales, which are sometimes discontinuous. A much thicker (>1 m) band of organic-rich shales records the Bonarelli Level, marking OAE 2 and documenting a positive excursion in $\delta^{13}\text{C}_{\text{org}}$. Like site 1260B, numerous other geochemical studies have been conducted on samples from Furlo, with nitrogen-, iron-, and osmium- and molybdenum-isotope data all showing perturbations at the Bonarelli Level, supporting increased volcanism and marine anoxia at that location during OAE 2 (Jenkyns *et al.*, 2007; Turgeon and Creaser, 2008; Du Vivier *et al.*, 2014; Westermann *et al.*, 2014).

CHAPTER 5

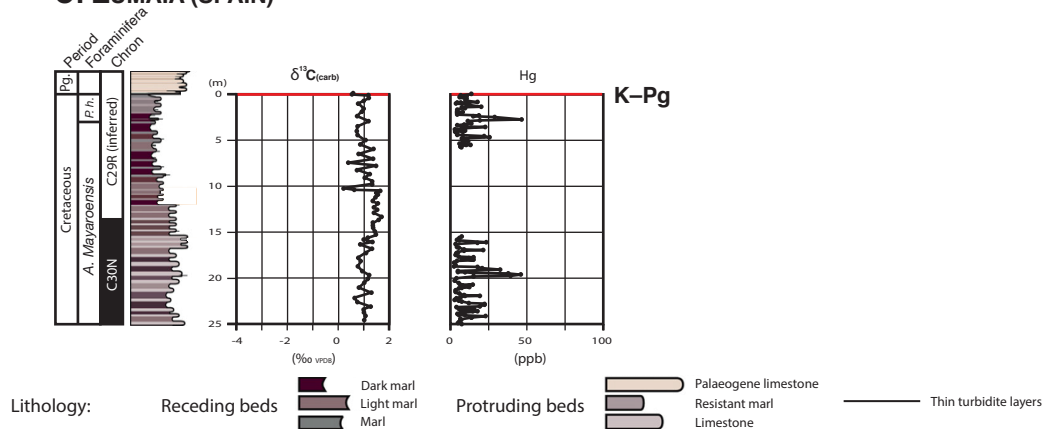
A: SEYMOUR ISLAND (ANTARCTICA)



B: IODP SITE 147AX (BASS RIVER)



C: ZUMAIA (SPAIN)



D: MONTANA (USA)

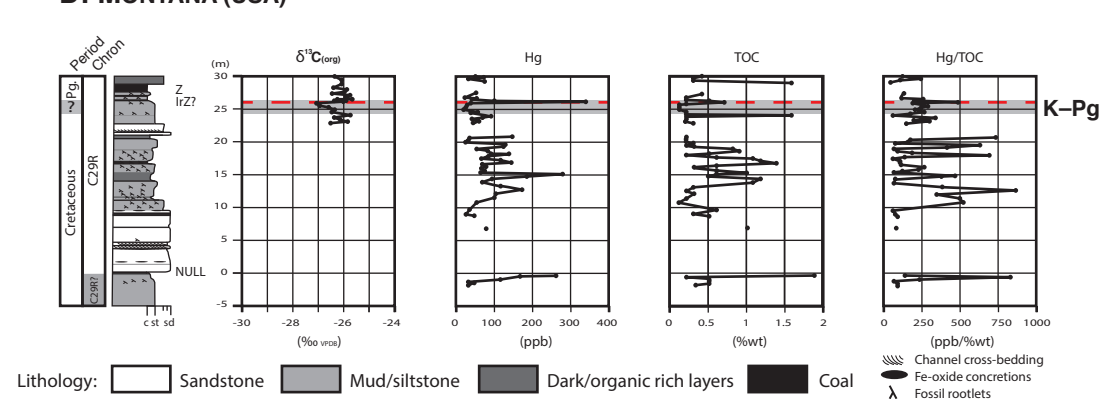


Figure 5.5 (opposite)

5.3. Methods

Mercury analysis was performed on the RA-915 Portable Mercury Analyzer with PYRO-915 Pyrolyzer, Lumex, at the University of Oxford, based on the methods described in Chapter 2 (section 2.1.1.). New TOC abundance data were measured using either a Strohlein Coulomat 702 (methodology in Jenkyns, 1988) or Rock-Eval VI (following the methods in Espitalié *et al.*, 1977) at the University of Oxford (see Chapter 2, section 2.1.2. for full details of TOC analysis). New end-Cretaceous carbon-isotope data were generated on samples from East Gilbert Creek (Montana). See Chapter 2 (section 2.4.) for full details of carbon-isotope analysis.

Carbon-isotope, TOC, Hg, and Hg/TOC data for each section are displayed in Figure 5.5 (end-Cretaceous) and Figure 5.6 (OAE 2), along with lithological and, where possible, biostratigraphic data. The presence or absence of mercury excursions in sedimentary records of both events (and other Mesozoic events) are also summarised in Table 5.1. See Appendices 3E–F for full data.

Figure 5.5: Raw data plots for $\delta^{13}\text{C}$, Hg and TOC abundances, and Hg/TOC ratios, from the 4 sedimentary records of the K–Pg transition investigated in this study. Note the expanded Hg/TOC scale for Montana. The bold red line indicates the stratigraphic position of the K–Pg boundary at Seymour Island, Bass River, and Zumaia. The grey shading with dashed red line marks the stratigraphic uncertainty of the K–Pg boundary at Montana (the dashed red line marks the stratigraphic position of the assumed IrZ coal that marks the K–Pg boundary elsewhere in Montana). All stratigraphic heights are in metres. Lithological data are sourced as follows: Seymour Island from Witts *et al.* (2015); Bass River adapted from Miller *et al.* (1998); Zumaia from Batenburg *et al.* (2012); Montana from this study. Biostratigraphic data are sourced as follows: Seymour Island from Witts *et al.* (2015); Bass River from Miller *et al.* (1998) and Esmeray-Senlet *et al.* (2015); Zumaia from Batenburg *et al.* (2012). Magnetostratigraphic data for Seymour Island is sourced from Tobin *et al.* (2012); and for Zumaia from Batenburg *et al.* (2012). Magnetostratigraphic data for Montana is inferred from data in Clyde *et al.* (2016: see also section 2.1.4 in this study). Bass River magnetostratigraphic data are inferred in this study (see section 2.1.2). Carbon isotope data are sourced as follows: Bass River from Esmeray-Senlet *et al.* (2015); Zumaia from Batenburg *et al.* (2012); Montana from this study.

5.4. Results

5.4.1. End-Cretaceous results

A clear increase in Hg/TOC is observed at the end-Cretaceous extinction horizon at Seymour Island (Figure 5.5A), similar to that documented at Bidart by Font *et al.* (2016). However, throughout the rest of the strata that record C29R, Hg and Hg/TOC values show no increase compared to below the base of C29R. In uppermost Cretaceous strata from Bass River, peaks in Hg concentrations and Hg/TOC are observed, though of low magnitude (Figure 5.5B). Samples from the extinction horizon itself were not available. Higher Hg/TOC is observed above the extinction horizon, and towards the base of the record (below 386.5m), but these higher values result from decreased TOC rather than increased Hg. Numerous peaks in Hg are recorded through the uppermost Cretaceous strata at Zumaia, in both C29R strata and C30N strata (Figure 5.5C). However, the Hg peaks in C29R strata are not of a higher magnitude than those in C30N strata, suggesting that both sets of Hg peaks arise from local processes rather than Deccan volcanism. There is also no obvious excursion at the extinction horizon. The Montanan record from East Gilbert Creek shows numerous high-magnitude excursions in Hg concentrations and Hg/TOC ratios throughout the record of chron C29R, including a peak around the extinction horizon (Figure 5.5D).

It is apparent from these, and previously published, results that the uppermost Cretaceous mercury record shows substantial variation between individual localities (Tables 5.1 and 5.2). A clear increase in Hg/TOC is observed at the K–Pg boundary section at Seymour Island, similar to that documented at Bidart by Font *et al.* (2016). Peaks in Hg and/or Hg/TOC are also recorded at the extinction horizons at East

Gilbert Creek, Bottaccione Gorge and Stevens Klint (Sial *et al.*, 2016; this study), although it should be noted that both the Bottaccione Gorge and Stevens Klint Hg peaks coincide with profound changes in lithology from carbonates to clays. Most of the other latest Cretaceous archives studied for mercury lack a record of the K–Pg boundary, due to either hiatus or a lack of sampling.

The mercury record from C29R strata significantly below the extinction horizon boundary is very inconsistent. Some records document isolated Hg/TOC peaks in C29R strata (Seymour Island, Bass River, Padriciano and Um Sohrynkw), but others show no signal (Bidart), or a signal likely dominated by local processes (Zumaia). Multiple Hg/TOC peaks are documented in C29R strata from Montana, but without a C30R record from that location, it is not clear whether such anomalies in sedimentary Hg/TOC are a feature of that palaeoenvironment, or whether they arose specifically from Deccan volcanism. There is good evidence for local volcanics proximal to both the Seymour Island and Montana records (e.g. Crame *et al.*, 1991; Swisher *et al.*, 1993), providing a potential alternative source of volcanic mercury to the environment besides the Deccan Traps.

Most importantly, no single record yet shows a clear increase in Hg/TOC throughout C29R strata (i.e. during the initiation of the main phase of Deccan volcanism) compared to C30N strata (pre-Deccan).

5.4.2. OAE 2 results

A small increase in Hg/TOC (from 10–20 ppb/%wt) is recorded at the base of OAE 2 strata from IODP Site 1260B (Figure 5.6A). This low-magnitude excursion is similar to those recorded at IODP 1258 and in the Maverick Basin (southern Western Interior Seaway: USA) by Scaife *et al.* (*in preparation*). Elevated Hg/TOC is also

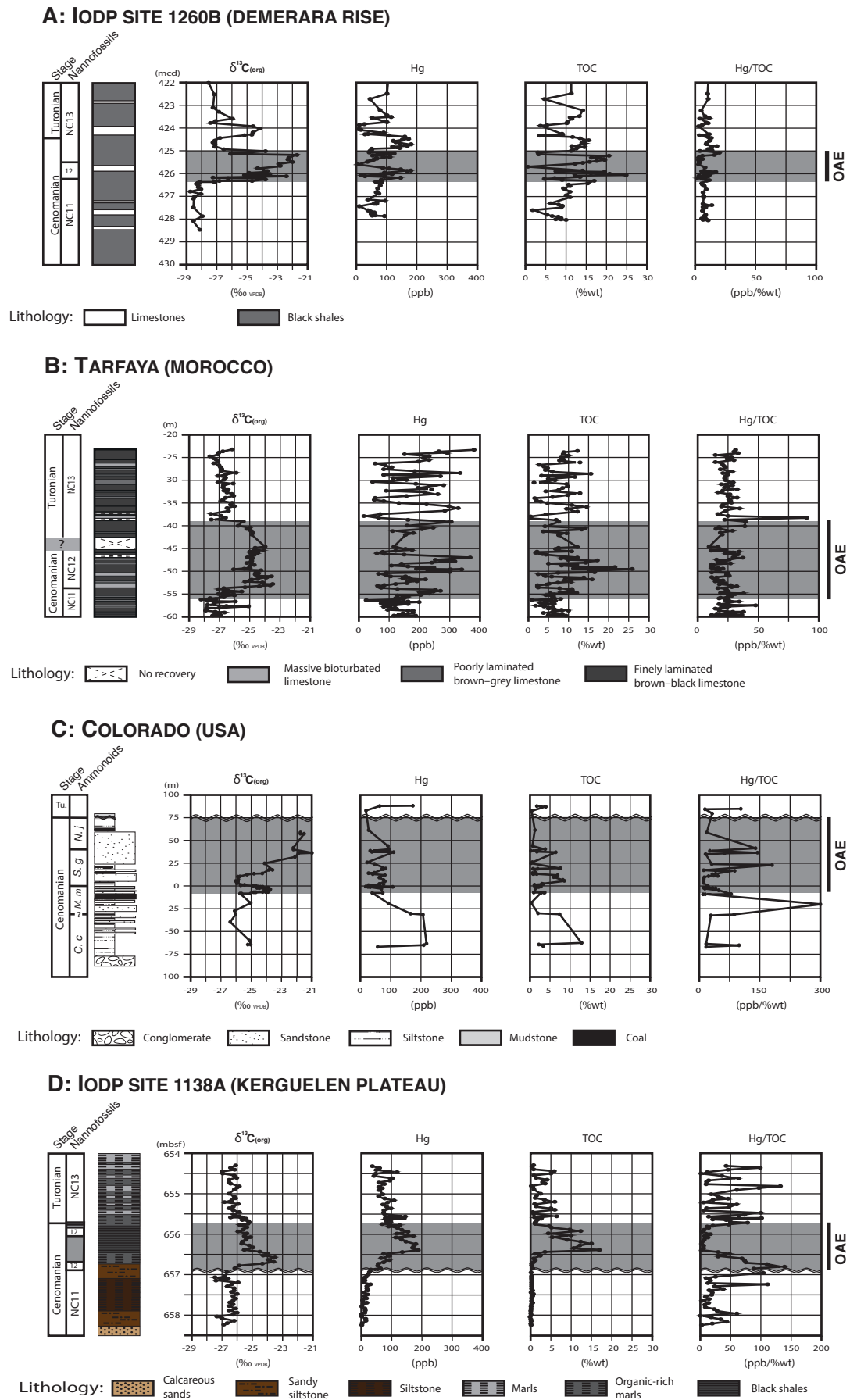
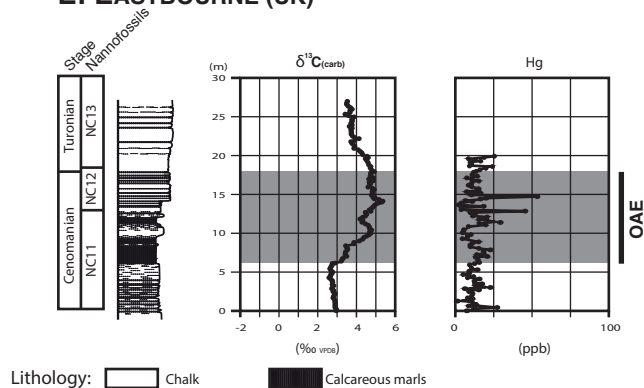


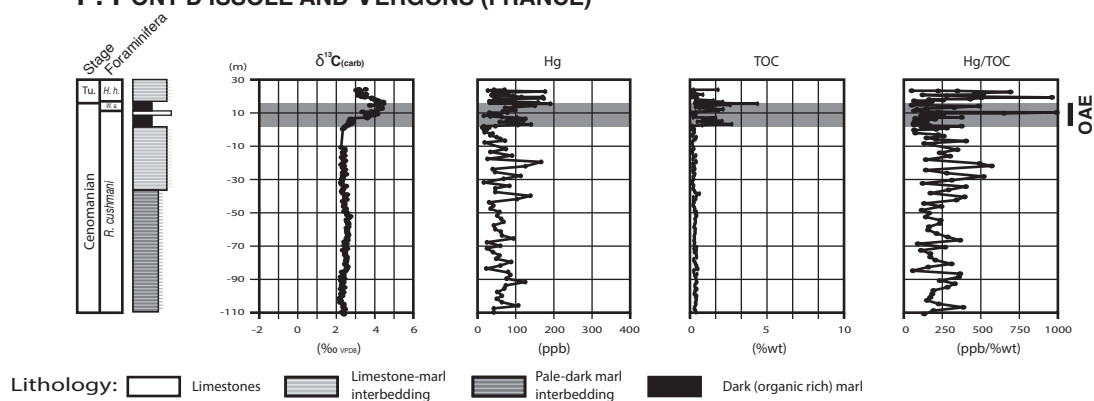
Figure 5.6 (overleaf)

recorded in OAE 2 strata at IODP 1138A (Figure 5.6C), but because the onset of the OAE is not recorded at that location, the temporal relationship between the mercury perturbation and initiation of widespread anoxia is not clear. Aside from these records, there is no good evidence for significant perturbations of the global mercury cycle during OAE 2. Some records do document sporadic Hg/TOC peaks in sediments deposited during OAE 2 (e.g. Utah, Pont d'Issole, and Clot Chevallier: Figure 5.6) but these peaks correlate with a decreased TOC content rather than with elevated Hg content. Actual sedimentary Hg concentrations of OAE 2 strata are not significantly higher than concentrations in sediments deposited prior to the OAE. Minor increases in Hg concentrations are observed in the Plenus Marls that record OAE 2 at Eastbourne, but there is insufficient TOC against which the mercury can be reasonably normalised, and it is possible that the slight increase in Hg content arises from the change in lithology from chalks to more clay-rich marls (Figure 5.6E). None of the Tethyan records of Pont d'Issole, Furlo, and Clot Chevalier show an increase in Hg/TOC ratios based on elevated Hg (as opposed to reduced TOC) in OAE 2 strata (Figure 5.6F–H). There is also no clear increase in sedimentary Hg/TOC at Tarfaya (Figure 5.6B). Significantly, there is no good record of perturbed atmospheric mercury in the terrestrial deposits from Utah (Figure 5.6D).

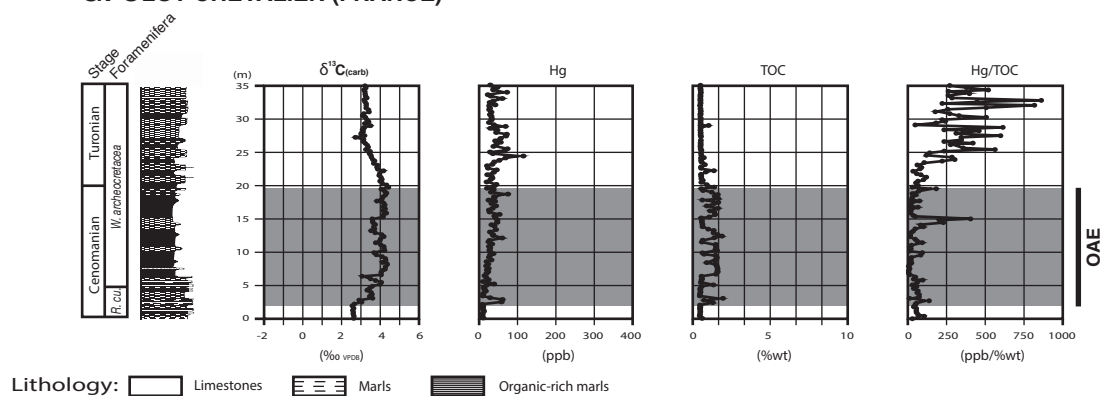
E: EASTBOURNE (UK)



F: PONT D'ISSELE AND VERGONS (FRANCE)



G: CLOT CHEVALIER (FRANCE)



H: FURLO (ITALY)

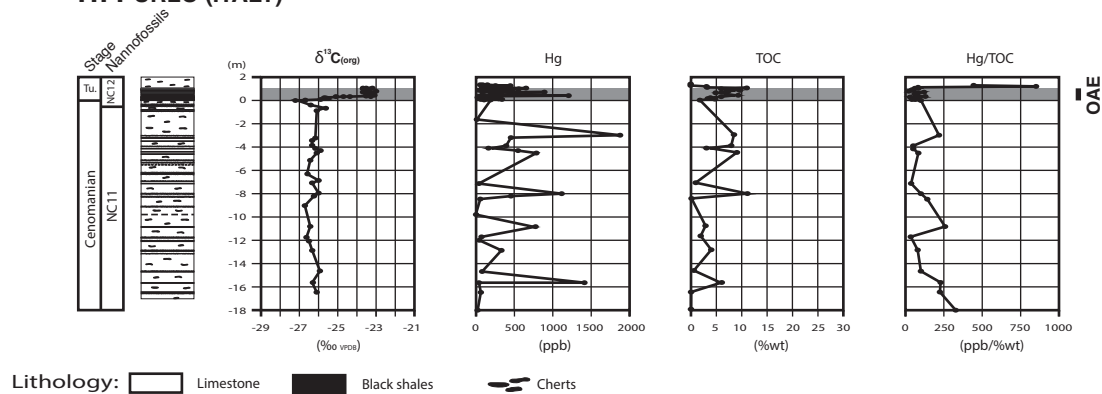


Figure 5.6 (opposite)

5.5. DISCUSSION

5.5.1. The impact of the depositional environment on the mercury record

5.5.1.1 Links between mercury records and sedimentary facies

As stated in section 5.1.3, sedimentary records of the global mercury inventory likely vary depending on factors such as lithological changes, and the nature of the palaeoenvironment recorded by those sediments. The low mercury concentrations observed at Velebit (T-OAE: Percival *et al.*, 2015), Eastbourne (OAE 2: Figure 5.6E), Zumaia, Bottaccione Gorge and Stvens Klint (all K–Pg: Sial *et al.*, 2016; and Figure

Figure 5.6: Raw data plots for $\delta^{13}\text{C}$, Hg and TOC abundances, and Hg/TOC ratios, from the 8 sedimentary records of OAE 2 investigated in this study. Note the changed scales for Hg concentrations for Eastbourne and Furlo, for TOC content for Pont d’Issoles and Vergons and Clot Chevalier, and variable scales for Hg/TOC ratios. Grey shaded areas indicate the stratigraphic extent of the OAE as indicated by the positive excursion in carbon isotopes, typically beginning at the base of more organic-rich lithologies. All stratigraphic depths are in metres. Tu., *R. cu.*, *W. a.*, *H. h.*, *C. c.*, *M. m.*, *S. g.*, and *N. j.*, and 12 indicate the Turonian Stage, *R. cushmani*, *W. archaeocretaca*, and *H. helvetica* foraminiferal Zones, *C. canitaurinum*, *M. masbyense*, *S. gracile*, and *N. juddii* ammonoid Zones, and NC12 calcareous nannofossil Zone, respectively. Stratigraphic logs are sourced as follows: IODP 1260B from Forster *et al.* (2007); Tarfaya and Eastbourne from Tsikos *et al.* (2004); Colorado from Barclay *et al.* (2010); IODP 1138A from this study; Clot Chevalier from Falzoni *et al.* (2016); Furlo from Jenkyns *et al.* (2007). Biostratigraphy is sourced as follows: IODP 1260B based on the correlations of Erbacher *et al.* (2005), and Hardas and Mutterlose (2006); Tarfaya and Eastbourne from Tsikos *et al.* (2004); Colorado from Barclay *et al.* (2010); IODP 1138A from Dickson *et al.* (2017); Pont d’Issole and Vergons from Jarvis *et al.* (2011); Clot Chevalier from Falzoni *et al.* (2016); Furlo from Tsikos *et al.* (2004), and Lanci *et al.* (2010). Carbon-isotope data are sourced as follows: IODP 1260B from Forster *et al.* (2007); Tarfaya and Eastbourne from Tsikos *et al.* (2004); Colorado from Barclay *et al.* (2010); IODP 1138A from Dickson *et al.* (2017); Clot Chevalier from Falzoni *et al.* (2016); Furlo from Jenkyns *et al.* (2007). Tarfaya TOC data are from Tsikos *et al.* (2004); IODP 1138A TOC data are from Dickson *et al.* (2017). Clot Chevallier TOC data are from Andy Gale (*personal communication*); Pont d’Issole TOC and carbon-isotope data are from Jarvis *et al.* (2011) or from Ian Jarvis (*personal communication*).

Event	Age (Ma)	Large Igneous Province(s)	LIP Location	Subaerial or Submarine	Global coverage of Hg records:	Proximity of sedimentary record to LIP volcanism					
						<500 km	500–2000 km	2000–5000 km	>5000 km	Marine	Terrestrial
PETM	55	North Atlantic Province	High latitude: Greenland and NW Europe	SUBAERIAL	N/A						
K–Pg	66	Deccan Traps	Mid latitude: India	SUBAERIAL	GLOBAL DISTRIBUTION: Europe, N. America, S. America, India, Antarctica	Meghalaya Jhimili	Biot, Botaccione, Svens Klint, Padriciano, Seymour Island, Bass River, Zumaia, Bayuda del Jaguel				Montana
OAE 2	94	Caribbean–Columbian, High Arctic LIP, Madagascar Plateau, Ontong–Java Plateau, Kerguelen Plateau?	widespread	SUBMARINE	GLOBAL DISTRIBUTION: Europe, N. America, Central Atlantic, Indian Ocean		Maverick Basin, Kerguelen Plateau	Demerara Rise	Colorado	Eastbourne, Pont d'Issole, Clot Chevalier, Tarfaya, Furlo	
OAE 1a	121	Ontong–Java Plateau	Low latitude: West Pacific	PREDOMINANTLY SUBMARINE (with some subaerial)	LIMITED TO TETHYAN REALM:					La Bédoule*, Glaise, Roter Sattel*	
Valanginian	134	Paraná–Etendeka	Mid latitude: Africa and S. America	SUBAERIAL	LIMITED TO TETHYAN REALM: France, Switzerland, and southern Poland					Angles, Orpierre, Wawal, Breggia	
T-OAE	183	Karoo–Ferrar	High latitude: Africa and Antarctica	SUBAERIAL	WIDESPREAD DISTRIBUTION: Europe, S. America		Arroyo Lapa			Hawsker Bottoms*, Kanche, S. Africa, Bombaim, Moehlis, Veldbit	
TJ	201	Central Atlantic Magmatic Province (CAMP)	Low latitude: Africa, N. America, S. America, Europe	SUBAERIAL	GLOBAL DISTRIBUTION: N. America, Europe, S. America, Africa	Partridge Island, Igounane	Kuhjoch, St Audries Bay	Arroyo Malo, New York Canyon	Astartekløft		
PT	252	Siberian Traps	High latitude: Russia	SUBAERIAL	WIDESPREAD DISTRIBUTION: Arctic, China		Buchanan Lake, Spitsbergen			Meishan	

Table 5.1: Recorded mercury anomalies vs proximity to LIP volcanism (opposite)

5.5C) confirm that mercury deposition and preservation appears to be limited in well-oxygenated environments where organics and sulphides are absent. At Zumaia, Hg concentrations follow those of Al_2O_3 , suggesting that mercury content in that archive is lithologically controlled, with the peaks resulting from local processes likely revolving around changes in terrestrial runoff, with mercury bound on to clay minerals (Figure 5.7). As noted above, the Hg peaks at Bottaccione Gorge and Stvens Klint also coincide with a marked increase in clay content (Sial *et al.*, 2016). Therefore, it is possible that the Hg peaks at Eastbourne, Bottaccione Gorge, and Stvens Klint all arose through increased clay deposition rather than volcanism, although it cannot be ruled out that the mercury bound on to clays was derived from volcanic sources. Regardless, pure carbonate sediments appear to be poor recorders of mercury availability in the environment (Table 5.2).

Relatively organic-rich lithologies appear to be more suited to recording mercury trends. However, relatively consistent organic-matter content is desirable

Table 5.1: Table summarising the presence or absence of a clear excursion in Hg concentrations and Hg/TOC ratios with respect to the approximate distance of individual sedimentary records from LIP volcanism erupting coincident with deposition of those sediments. General review of LIP characteristics in Bryan and Ferrari (2013) and Self *et al.* (2014). Hg and sedimentary record location information sourced as follows: K–Pg: Font *et al.* (2016); Sial *et al.* (2016); and this study; OAE 2: Scaife *et al.* (*in preparation*); and this study; OAE 1a: Charbonnier and Föllmi (2017); Valanginian: Charbonnier *et al.* (2017); T-OAE: Percival *et al.* (2015); TJ: Thibodeau *et al.* (2016); see also Chapter 3; PT: Sanei *et al.* (2012); Grasby *et al.* (2013; 2016; 2017). Green text signifies a clear excursion in Hg concentrations and Hg/TOC ratios; red text signifies a mercury record that does not show an excursion, one impacted by very low/very high TOC content, or shows apparent peaks in Hg/TOC that do not correlate with the strata that record the respective event. *NB:* Hawsker Bottoms records a clear Hg/TOC excursion at the Pliensbachian–Toarcian boundary, but not in T-OAE strata. La Bédoule and Rotter Sattel do show peaks in Hg/TOC in OAE 1a strata, but these peaks are not significantly clear compared to background strata below.

Event	Age (Ma)	Large Igneous Province(s)	LIP Location	Subaerial or Submarine	RELATIVELY CONSISTENT REDOX THROUGH EVENT						Anoxic/euxinic environment	Oxygenated environment where anoxia abruptly develops
					Terrestrial: (e.g. lacustrine, fluvio-lacustrine, deltaic)	Coastal/shoreface	Nearshore shallow marine	Hemipelagic	Pelagic	Oxygenated carbonate reef		
PETM	55	North Atlantic Province	High latitude: Greenland and NW Europe	SUBAERIAL								
K-Pg	66	Deccan Traps	Mid latitude: India	SUBAERIAL	Montana Meghalaya Jhimli		Bidart Seymour Island Bass River Zumaia Bajada del Jaquel		Bottaccione Stevens Klint			
OAE 2	94	Caribbean–Columbian High Arctic LIP Madagascar Plateau Ontong–Java Plateau Kerguelen Plateau?	widespread	SUBMARINE	Colorado			Maverick Basin*			Demerara Rise	Pont d'Issolle Clot Chevalier Tarfaya Furo Kerguelen Plateau
OAE 1a	121	Ontong–Java Plateau	Low latitude: West Pacific	PREDOMINANTLY SUBMARINE (with some subaerial)								La Bédoule* Glaise Roter Sattel*
Valanginian	134	Paraná–Etendeka	Mid latitude: Africa and S. America	SUBAERIAL				Angles Orpierre Wawal	Breggia			
T-OAE	183	Karoo–Ferrar	High latitude: Africa and Antarctica	SUBAERIAL		Bornholm	Arroyo Lapa Mochras	Peniche		Velebit		Hawsker Bottoms* Sancene
TJ	201	Central Atlantic Magmatic Province (CAMP)	Low latitude: Africa, N. America, S. America, Europe	SUBAERIAL	Partridge Island Astartekløft Igounane		New York Canyon St Audries Bay Arroyo Malo	Kuhjoch				
PT	252	Siberian Traps	High latitude: Russia	SUBAERIAL			Meishan		Buchanan Lake Spitsbergen			

Table 5.2: Recorded mercury anomalies vs specific sedimentary facies (opposite)

throughout the stratigraphy because of the potential to overprint any Hg/TOC ratio through unusually high TOC values (Percival *et al.*, 2015; Charbonnier and Föllmi, 2017). Records of OAEs, where burial of organic matter typically increased in most environments, are therefore particularly prone to this phenomenon (Table 5.2), with examples of overprinting known from both the T-OAE (Hawsker Bottoms and Sancerre: Percival *et al.*, 2015), and OAE 1a (Roter Sattel: Charbonnier and Föllmi, 2017). The same *proviso* would apply to clay content. The OAE 2 record from Tarfaya may be impacted by TOC overprinting, as Hg concentrations do rise in OAE 2 strata, but in concert with elevated TOC content (Figure 5.6B). Furthermore, a possible explanation for the absence of a Hg/TOC increase at Pont d’Issole (Figure 5.6F) is the 10-fold increase in TOC in OAE 2 strata that could mask any excess mercury. However, Hg concentrations do not significantly increase in the black shales compared to the marls below, despite the great increase in organic matter. Thus, the data suggest that a lack of an increase in the Hg concentration of the sediments, rather than a change in TOC, is the reason for the absence of an excursion Hg/TOC at Pont

Table 5.2: Table summarising the presence or absence of a clear excursion in Hg concentrations and Hg/TOC ratios in specific sedimentary facies for each major Mesozoic event. General review of LIP characteristics in Bryan and Ferrari (2013) and Self *et al.* (2014). Hg and facies information sourced as follows: K–Pg: Font *et al.* (2016); Sial *et al.* (2016); and this study; OAE 2: Scaife *et al.* (*in preparation*); and this study; OAE 1a: Charbonnier and Föllmi (2017); Valanginian: Charbonnier *et al.* (2017); T-OAE: Percival *et al.* (2015); TJ: Thibodeau *et al.* (2016); see also Chapter 3; PT: Sanei *et al.* (2012); Grasby *et al.* (2013; 2016; 2017). Green text signifies a clear excursion in Hg concentrations and Hg/TOC ratios; red text signifies a mercury record that does not show an excursion, or shows one impacted by very low/very high TOC content, or shows apparent peaks in Hg/TOC that do not correlate with the strata that record the respective event. *NB:* Hawsker Bottoms records a clear Hg/TOC excursion at the Pliensbachian–Toarcian boundary, but not in T-OAE strata. La Bédoule and Rotter Sattel do show peaks in Hg/TOC in OAE 1a strata, but these peaks are not significantly clear compared to background strata below.

d'Issole. These examples highlight the importance of presenting time series of both Hg concentrations as well as the normalised values when considering Hg excursions.

The end-Cretaceous data show that terrestrial deposits appear to record markedly higher magnitude Hg/TOC ratios than do marine sediments, as has also been observed for the Triassic and Toarcian events (Table 5.2, Percival *et al.*, 2015; see also Chapter 3). For the K–Pg, Hg/TOC peaks in Montana are of a much greater magnitude than in any other K–Pg record, despite having TOC values comparable to those in sedimentary samples from both Seymour Island and the Bass River core (Figure 5.5). The trend of high Hg/TOC values in continental sediments suggests that mercury is more efficiently taken up, retained, or preserved on land compared to the marine realm. This phenomenon might reflect processes such as direct adsorption of atmospheric Hg by the tree canopy. Alternatively, terrestrial organic matter may have a greater affinity for mercury than other types of organic matter. In addition, many terrestrial sediments are also clay-rich, which may further enhance the burial potential of mercury in such environments.

Based on this study and previous work (Table 5.2), it is clear that the type of sedimentary facies appears to play a major role in determining the suitability of those sediments for recording perturbations to the mercury cycle. Carbonate records lacking organic matter or clays are likely to be poor mercury archives. Sediments with consistent organic/clay content are more likely to be suitable. However, a record with abrupt and profound lithological changes reflecting a major change in the palaeoenvironment (such as the onset of marine anoxia) can present challenges in terms of its suitability as a mercury record due to the likelihood of Hg/TOC ratios being overprinted by a large increase in TOC content. Finally, terrestrial records appear to show higher magnitude changes in sedimentary Hg than do marine

sediments, hence showing greater potential to detect the occurrence (or otherwise) of atmospheric Hg perturbations.

5.5.1.2 Geographical disparity in mercury records

It is not clear whether mercury trends from closely-spaced sections within a single sedimentary basin would be expected to vary due to different input fluxes, or to be similar due to mixing of aquatic mercury within that basin. Subtle variations in sedimentary mercury records of the same deposition age in the same sedimentary basin have previously been observed (Vocontian Basin: Charbonnier *et al.*, 2017; Maverick Basin: Scaife *et al.*, *in preparation*), suggesting that mercury records may indeed differ within a single deposition area. Zumaia and Bidart sediments were deposited very close to each other in the Basque-Cantabric Basin (Pujalte *et al.*, 1995; Font *et al.*, 2011). However, where Hg concentrations at Zumaia show very cyclical trends throughout the Cretaceous, the Bidart Hg trends show no Cretaceous cyclicity, with low values up to the documented increase just below the boundary (Figure 5.7). Moreover, Hg contents in sediments from Zumaia follow changes in lithology and Al₂O₃ content, indicating that the variations in Hg burial resulted from changes in clay deposition. No such match between trends of Hg and Al₂O₃ content is recorded at Bidart (Font *et al.*, 2016). This contrast implies that the influx of Hg at Zumaia was dominated by local processes, and thus did not record the global Hg-cycle perturbation documented in the latest-Cretaceous strata at Bidart. However, unless the stratigraphic sequences at Bidart and Zumaia record fundamentally different palaeoenvironments, despite their close proximity, it is unclear why this should be the case. Regardless, the discrepancy between the two datasets clearly points to the

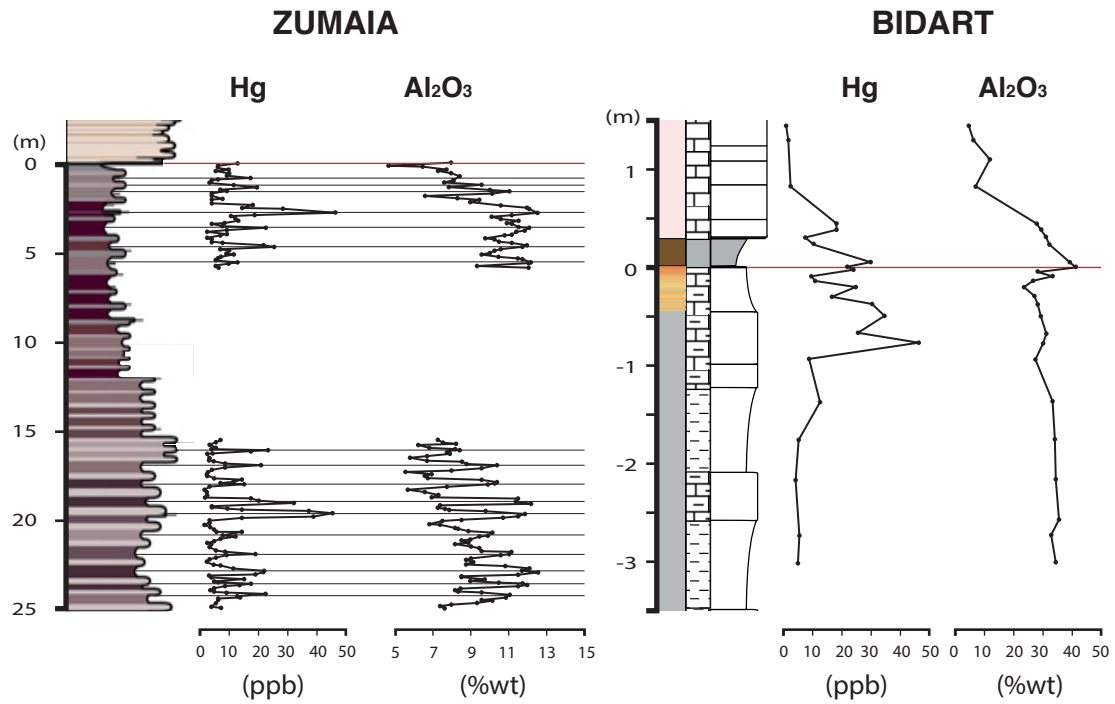


Figure 5.7: Lithology, Hg concentration, and Al₂O₃ content for the proximal records of Zumaia and Bidart (Basque-Cantabric Basin). The red lines indicate the stratigraphic position of the end-Cretaceous extinction horizon at each section. The black lines for Zumaia highlight the correlation between peaks in Hg and Al₂O₃ content. Lithological and Al₂O₃ data for Zumaia is from Batenburg *et al.* (2012); Hg data from this study. All Bidart data is sourced from Font *et al.* (2016).

potential for two nearby localities in the same basin to record markedly different sedimentary mercury trends.

As well as varying locally, there is the potential for sedimentary mercury content to vary in markedly dispersed geographical areas, even at times assumed to be of relative volcanic quiescence. Comparing the magnitude of sedimentary Hg concentrations and Hg/TOC ratios in Atlantic and Tethyan sedimentary records of the Late Cenomanian and OAE 2 may highlight such geographical variation in Hg drawdown at those times (Figure 5.8). In the Tethyan records of Pont d'Issole and Furlo, upper Cenomanian and OAE 2 strata have Hg/TOC ratios averaging 100–200 ppb/%wt or more. In contrast, both Hg concentrations and Hg/TOC ratios in time-equivalent strata from the Iona Core, (from the Maverick Basin in the southern Western Interior Seaway) and Demerara Rise rarely rise above 100 ppb or 100 ppb/%wt, and are typically much lower. It is possible that such variation may arise lithologically, or as a result of low TOC content, but total Hg concentrations at Furlo are also much higher than any other location, despite the analysed samples being black shales like those deposited at Demerara Rise. The black shales at the Pont d'Issole OAE 2 level (Vocontian Trough) also have much higher Hg concentrations and Hg/TOC ratios than any level in the Iona core despite Pont d'Issole and Vergons sediments typically having a lower TOC content than those of the Iona core. If the variation in sedimentary mercury content between the Atlantic and Tethyan regions does not arise lithologically, it is likely that the watermasses in those two regions contained different Hg concentrations. Possible sources of additional mercury to the Tethys could be persistent hydrothermal activity from local Tethyan oceanic volcanism, or continental runoff of mercury from the nearby terrestrial realm. Alternatively, mercury analyses of the modern oceans have shown that deep-water

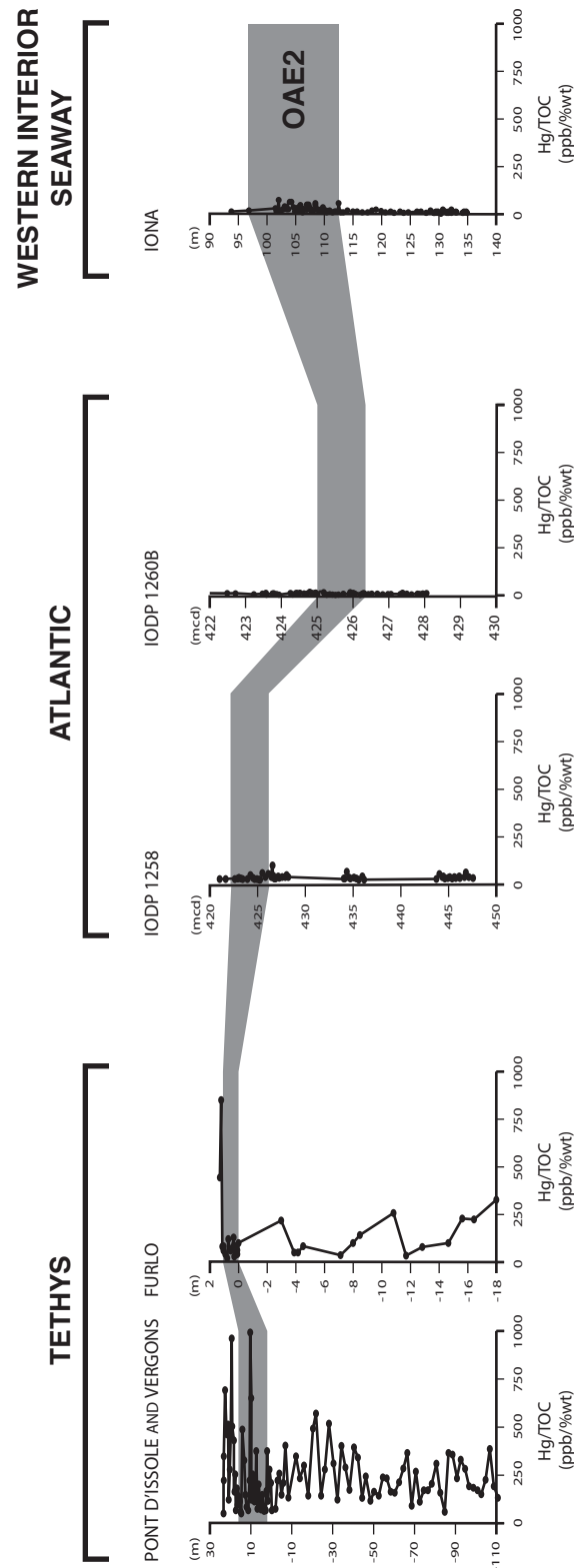


Figure 5.8: Comparison of the magnitude of Hg/TOC ratios in sediments from the Tethyan (Pont d'Issole and Vergons, and Furlo), Atlantic (IODP sites 1258 and 1260B), and Western Interior Seaway (Iona). All stratigraphic heights are in metres. Grey shading indicates the stratigraphic extent of OAE 2 at each location on the basis of carbon-isotope data. Hg/TOC data from IODP 1258 and Iona are sourced from Scaife *et al.* (*in preparation*); all other data are from this study.

bodies can have markedly variable mercury contents depending on their age (Bowman *et al.*, 2015), and thus the elevated Hg content in Tethyan sediments compared those of the Atlantic or Western Interior Seaway may result from the global ocean circulation of mercury. Regardless of the exact cause, it is likely that the geographic discrepancy in sedimentary mercury contents arises from a non-volcanic-related variability in the mercury contents of their associated oceanic watermasses.

In conclusion, it appears that palaeogeographic setting can be a major influence on the Hg content of sediments. Combined with the varying lithological suitability of sedimentary archives as recorders of global Hg, there is a high potential for local processes to influence and/or overprint any global mercury signal. Thus, analysing numerous sedimentary records of various palaeoenvironments, with a wide geographic coverage, may be of paramount importance in investigating changes to the global mercury inventory.

5.5.2. The impact of volcanic context on the mercury emissions of a LIP

As stated in section 5.4, the mercury records from both OAE 2 and the K–Pg document considerable geographical variability. For OAE 2, small excursions in Hg/TOC ratios are documented in OAE 2 records from the southern Western Interior Seaway, the proto-North Atlantic, and the Kerguelen Plateau, but no clear excursions are observed in Hg concentrations or Hg/TOC ratios in the Tethyan or boreal European realms, or in the North American terrestrial environment (Scaife *et al.*, *in preparation*; Figure 5.6 and Table 5.1: this study).

Likewise, uppermost Cretaceous strata from around the world show very inconsistent Hg/TOC trends, with significant variations across all records, some of which likely arise from lithological changes (Font *et al.*, 2016; Sial *et al.*, 2016; Figure

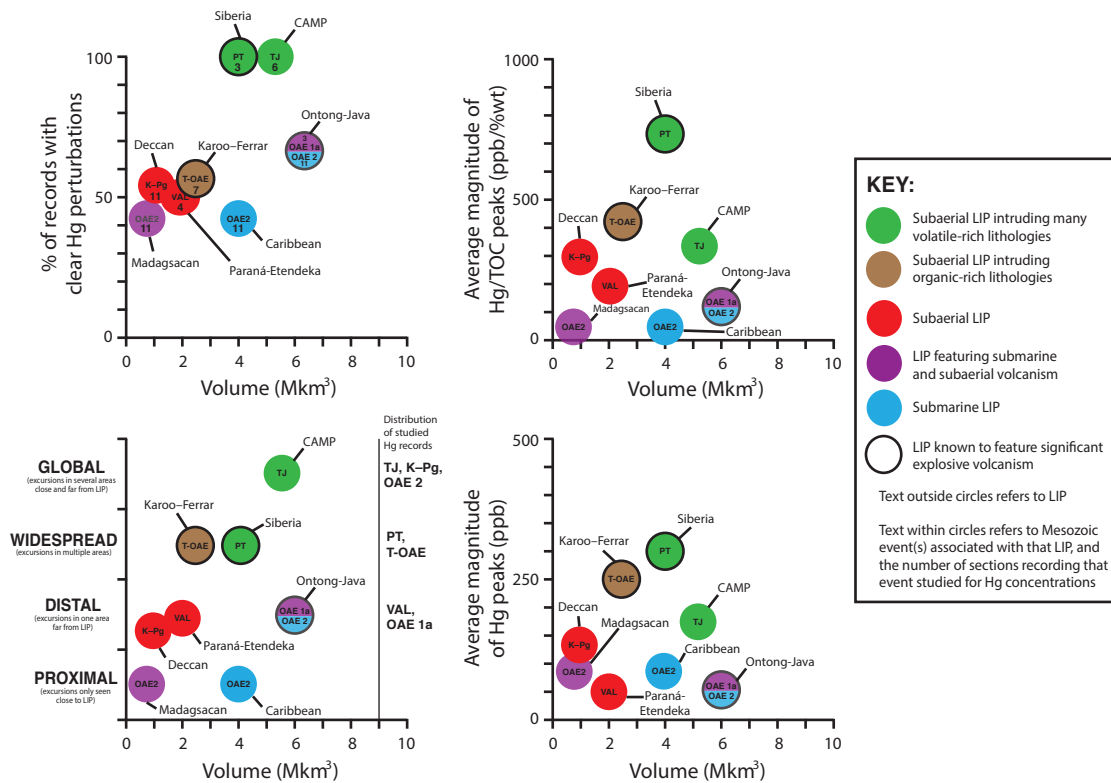


Figure 5.9: Plots showing the relationship of LIP volume with: the consistency of Hg excursions (i.e. for the T-OAE, 7 sections have been studied for Hg, but only 4 show clear Hg/TOC perturbations); the magnitude of observed excursions in sedimentary Hg concentrations; the magnitude of observed excursions in sedimentary Hg/TOC ratios; and the distribution of documented sedimentary Hg excursions with respect to LIP volcanism (see also Table 5.1). The subaerial vs submarine nature of LIP volcanism, presence vs absence of evidence for significant explosive eruptions, and the country rock intruded, are also shown for each LIP. The distribution plot shows the distribution of clear sedimentary enrichment compared to the LIP, with the total distribution of all sections analysed for mercury also shown (i.e. a global distribution of OAE 2 records have been analysed for mercury, but Hg enrichments are only recorded in records proximal to a LIP). The plots are based on data from the LIP reviews of Ganino and Arndt (2009); Bond and Wignall (2014); and Marzoli *et al.* (2004: CAMP only), and the Hg records of Sanei *et al.* (2012); Grasby *et al.* (2013; 2016; 2017); Percival *et al.* (2015); Font *et al.* (2016); Sial *et al.* (2016); Thibodeau *et al.* (2016); Charbonnier and Föllmi (2017); Charbonnier *et al.* (2017); Scaife *et al.* (*in preparation*); and this study.

5.5 and Table 5.1: this study). The strongest case for a clear Hg/TOC excursion is at or just below the end-Cretaceous extinction horizon, although even that does not appear in all records. There is no sedimentary Hg enrichment throughout C29R strata compared to C30N strata that would be consistent with a perturbed Hg cycle during the first 300 kyr of the main phase of Deccan volcanism.

The Hg/TOC records for all major Mesozoic events studied to date (including the records of OAE 2 and the K–Pg presented in this study) are summarised in Tables 5.1 and 5.3. Records of the end-Permian and end-Triassic extinctions document clear excursions in Hg/TOC beginning at the respective extinction horizons, and do so consistently in multiple geographically widespread sedimentary records (Sanei *et al.*, 2012; Grasby *et al.*, 2013; 2016; 2017; Thibodeau *et al.*, 2016; see also Chapter 3). Hg/TOC excursions are also documented in a number of widespread records of the T-OAE, although some T-OAE records appear to be impacted by local processes (Percival *et al.*, 2015). Records of OAE 1a and the Valanginian Event are currently limited to the Tethyan realm (Charbonnier and Föllmi, 2017; Charbonnier *et al.*, 2017). Although Hg/TOC perturbations do appear in strata that record both events, they are not consistent across all records, and for OAE 1a they appear to be of rather small magnitude, potentially due to muting by excess organic-matter content (see section 5.5.1.1 and Table 5.2). Figure 5.9 illustrates the relationship between LIP volume and the consistency, distribution, and magnitude, of associated sedimentary Hg enrichments, with evidence for major explosive eruptions and/or intrusion of volatile-rich country rocks also indicated. Although each of these relationships may be biased by the number and distribution of sedimentary records studied for mercury concentrations, and the nature of the sedimentary archives studied, there is a clear pattern indicating that sedimentary records of the end-Permian, end-Triassic, and

Early Toarcian currently document the most widespread, consistently observed, high magnitude excursions in sedimentary Hg. However, further work is needed to expand the mercury records of other events in order to confirm this pattern.

Why records of the end-Permian and end-Triassic (and potentially Toarcian) events show such consistent and clear Hg/TOC excursions compared to other events is intriguing. It is likely that the diverse igneous contexts of each LIP associated with an individual event impacted the degree of mercury emissions and their impact on the atmosphere. The atmospheric dispersal of LIP mercury emissions might be increased through explosive volcanism that could inject greater quantities of Hg into the stratosphere rather than the troposphere. Both the Siberian Traps and the Karoo–Ferrar LIP in particular are known to include substantial areas of explosive-volcanism-derived igneous rocks (Ross *et al.*, 2005; McClintock and White, 2006; Burgess and Bowring, 2015). Most other Mesozoic LIPs do not appear to preserve significant volumes of explosive igneous material, although the true fraction of explosive *vs* effusive volcanism is poorly documented for most LIPs (Ross *et al.*, 2005). Additionally, the dynamics of either effusive or explosive LIP eruptions are not well understood, and it may be that effusive eruptions could have injected volatiles into the stratosphere as efficiently as explosive ones (Glaze *et al.*, 2017). Further work is needed on LIP lithologies and processes to investigate the impact of explosive *vs* effusive eruptions. Alternatively, subaerial LIPs are expected to have been more efficient at emitting volcanic volatiles to the atmosphere than submarine examples. The size of LIP emplacement may also be an important factor. Whilst this is poorly constrained for many LIPs, the Siberian Traps and CAMP were by far the largest continental LIPs of the Mesozoic (Bond and Wignall, 2014). The Ontong-Java Plateau is thought to have been larger, but it was a submarine LIP in which most volcanism

likely happened subaqueously, potentially limiting the impact of its mercury emissions, although some subaerial volcanics are known from that LIP (Chambers *et al.*, 2004; Thordarson *et al.*, 2004). Finally, thermogenic emissions associated with LIP emplacement may also have played a role. The Karoo–Ferrar is not an exceptionally large continental LIP, and yet is associated with the T-OAE, which gives one of the better records of a perturbed Hg cycle. However, the Karoo–Ferrar is one of only four LIPs that have been strongly associated with thermogenic emissions. Two others of those four are the Siberian Traps and CAMP (Svensen *et al.*, 2009), which are also associated with excellent records of a perturbed Hg cycle; the fourth being the North Atlantic Province that is associated with the Palaeocene–Eocene Thermal Maximum, for which no Hg records have yet been published.

The importance of subaerial vs submarine LIP volcanism on the impact of a LIP on the mercury cycle is supported by the low magnitude or absence of Hg excursions observed in strata recording OAE 1a and OAE 2 compared to many other events (Figure 5.9). However, both the Deccan Traps and Paraná–Etendeka were subaerial LIPs, so the discrepancy between the clarity of Valanginian and end-Cretaceous Hg/TOC anomalies and those of the end-Permian and end-Triassic cannot be explained solely in that way. It is noteworthy that the most consistent, widespread, high magnitude excursions in Hg and Hg/TOC are seen in records of the end-Permian, end-Triassic, and T-OAE, which coincided with the Siberian Traps, CAMP, and Karoo–Ferrar LIP, respectively (Figure 5.9). Volcanism at all of these LIPs would have been predominantly subaerial; all of them have been associated with release of thermogenic volatiles, and two of them with significant explosive volcanism. Thus they likely had all the characteristics required to easily perturb the global mercury

cycle. However, the appearance of Hg/TOC spikes in strata recording other events indicates that other LIPs were still capable of perturbing the mercury cycle to a degree.

5.5.3. *Comparisons between trends in mercury concentrations and osmium isotopes*

To evaluate how mercury emissions evolved over the eruptive history of a LIP, Hg/TOC ratios are compared with other proxies for LIP volcanism, such as decreases in sedimentary $Os_{(i)}$ to very unradiogenic values (Table 5.3). Such comparisons might allow further insight into what style of LIP volcanism was in operation at the time of major mercury emissions. Abrupt declines in sedimentary $Os_{(i)}$ are documented in strata that record numerous Mesozoic events, including the end-Permian, end-Triassic, and end-Cretaceous mass extinctions, and OAEs 1a and 2 (Table 5.3; Cohen and Coe, 2002; 2007; Ravizza and Peucker-Ehrenbrink, 2003; Turgeon and Creaser, 2008; Robinson, 2009; Tejada *et al.*, 2009; Kuroda *et al.*, 2010; Bottini *et al.*, 2012; Schoepfer *et al.*, 2013; Du Vivier *et al.*, 2014; 2015 Georgiev *et al.*, 2015). These are thought to result from one or more of hydrothermal emissions, basalt-seawater interactions, or weathering of continental LIP basalts.

5.5.3.1 *Submarine volcanism*

Osmium-isotope and Hg/TOC records are documented for both OAE 1a and OAE 2, the two events associated with submarine LIP volcanism (Jenkyns, 2010). For OAE 2, the inconsistent nature of the Hg/TOC record strongly indicates that any perturbation to the mercury cycle only occurred locally to certain areas, with positive excursions limited to the proto-North Atlantic and Kerguelen Plateau areas (Scaife *et al.*, *in preparation*; this study, Figure 5.6). Since atmospheric Hg emissions are expected to be globally distributed, a non-global Hg-cycle perturbation suggests that

the main source of mercury to the environment was submarine. This conclusion is consistent with the absence of a Hg/TOC excursion in the terrestrial OAE 2 record of Utah, as well as with the predominantly oceanic emplacement of the LIPs coinciding with OAE 2, where the majority of volcanism would presumably have been submarine (Courtillot and Renne, 2003). In contrast, the osmium-isotope signal of volcanism and/or basalt-seawater interactions during OAE 2 is clearly recorded in sedimentary archives from around the world, indicating a global perturbation of the marine osmium inventory (Turgeon and Creaser, 2008; Du Vivier *et al.*, 2014; 2015).

The contrast in geographical extent of Hg- and Os-anomalies is consistent with osmium's modern oceanic residence time of 10–50 kyr, long enough to be well mixed throughout the global ocean (Peucker-Ehrenbrink and Ravizza, 2000). Mercury has a much shorter oceanic residence time of <1000 yr (Gill and Fitzgerald, 1988), and hydrothermal Hg emissions are known to only have a near-field influence (Bowman *et al.*, 2015). Consistent with this, the only locations where Hg/TOC increases are documented in OAE 2 strata are relatively proximal to oceanic LIPs associated with the OAE (Table 5.1): the Caribbean Plateau (Maverick Basin and Demerara Rise), and the Madagascan LIP (Kerguelen Plateau). Such a pattern suggests that mercury can act only as a local tracer of submarine volcanism, in contrast with osmium isotopes, which can record a global signature of submarine volcanism.

The Hg/TOC excursions observed in sediments from the Maverick Basin and Demerara Rise begin at the base of the positive excursion in $\delta^{13}\text{C}$ that characterises OAE 2. The onset of OAE 2 and the excursion in Hg/TOC are missing from the Kerguelen Plateau record, and thus their temporal relationship cannot be constrained here. By contrast, the $\text{Os}_{(i)}$ decline is known to begin in strata noticeably below those

Event	Age (Ma)	Large Igneous Province(s)	LIP Location	Subaerial or Submarine	Evidence of thermogenic emissions?	C-isotope excursion	Hg/TOC excursion	Os _(i) record	Os _(i) vs Hg/TOC comparison
PETM	55	North Atlantic Province	High latitude: Greenland and NW Europe	SUBAERIAL	YES	Up to 8 ‰ NEGATIVE defines event, with a very abrupt onset. Excursion much smaller in marine carbonates.	NONE PUBLISHED	Predominant INCREASE in values to radiogenic	N/A
K-Pg	66	Deccan Traps	Mid latitude: India	SUBAERIAL	NO	1–2 ‰ NEGATIVE at the KPg boundary	11 RECORDS, 5 with INCREASES at KPgB, 5 with peaks in C29R, NO evidence of consistent increase throughout C29R	DECREASED values to unradiogenic throughout C29R chron	Hg spikes inconsistent and Hg anomalies not present throughout C29R, unlike Os _(i) anomalies. Suggests weathering of Deccan basalts that were not all producing major mercury emissions, but major volcanic event at the KPg boundary.
OAE 2	94	Caribbean–Columbian High Arctic LIP Madagascan Plateau Ontong–Java Plateau Kerguelen Plateau?	widespread	SUBMARINE	NO	Up to 4 ‰ POSITIVE across OAE 2 (with smaller negatives superimposed on that positive)	11 RECORDS, 4 with INCREASES (all low magnitude). Increases not seen globally (increases also seen at precursor MCE)	Abrupt DECREASE in values to unradiogenic 10s of kYrs prior to OAE	Os _(i) decline observed globally, Hg anomalies only locally. Os _(i) decline also precedes Hg excursions. Suggests mainly submarine volcanism, with geographically restricted Hg output less able to impact ocean inventory than Os output.
OAE 1a	121	Ontong–Java Plateau High Arctic LIP?	Low latitude: West Pacific High latitude: Arctic	PREDOMINANTLY SUBMARINE (with some subaerial) SUBAERIAL	NO YES	Up to 3 ‰ NEGATIVE at the onset of OAE 1a, followed by a 2 ‰ POSITIVE excursion	3 RECORDS, all show INCREASES (2 are low magnitude)	DECREASE in values to unradiogenic but with short INCREASE at onset of OAE	Both Os _(i) and Hg anomalies appear to begin at onset of OAE 1a (albeit with no single record with both proxies yet). Suggests volcanism with subaerial component, but coincident submarine volcanism as well. Consistent with known LIPs from that time.
Valanginian	134	Paraná–Etendeka	Mid latitude: Africa and S. America	SUBAERIAL	NO	Protracted 2–3 ‰ POSITIVE excursion through much of Valanginian (also with less abrupt onset than for other events)	4 RECORDS, at least 2 clear INCREASES. But the increases are only seen at the onset of the event (not throughout).	NONE PUBLISHED	N/A
T-OAE	183	Karoo–Ferrar	High latitude: Africa and Antarctica	SUBAERIAL	YES	Up to 6 ‰ NEGATIVE (smaller in carbonates). Sometimes observed within a smaller overarching positive	7 RECORDS, 4 INCREASES (with 2 other increases likely muted by high TOC). 3 increases also noted at the precursor PI–To event	INCREASE to radiogenic values during both T-OAE and PI–To precursor event	Hg increases coincide (or very slightly precede) Os _(i) increases at both the T-OAE and PI–To events. Suggests volcanism geologically rapidly triggered weathering through climate feedback.
TJ	201	Central Atlantic Magmatic Province (CAMP)	Low latitude: Africa, N. America, S. America, Europe	SUBAERIAL	YES?	Up to 9 ‰ NEGATIVE (but sometimes much smaller magnitude) at extinction horizon, values remain low considerably above.	7 RECORDS, 6 clear INCREASES beginning at the extinction horizon (the other record was also likely deposited prior to the event)	DECREASE to unradiogenic values throughout the Triassic–Jurassic transition	Precise onset of Os _(i) decline poorly temporally constrained, inhibiting ability to correlate Hg and Os anomalies. But anomalies in both proxies appear to be present throughout the Triassic–Jurassic transition (including the end-Triassic extinction event).
PT	252	Siberian Traps	High latitude: Russia	SUBAERIAL	YES	3–4 ‰ NEGATIVE at extinction horizon, values remain low considerably above.	4 RECORDS, 4 INCREASES beginning at the extinction horizon	Small DECREASES in values to unradiogenic values starting prior to the event	Hg increases begin at the extinction horizon, Os _(i) decreases begin below that horizon. Suggests earliest Siberian volcanism did not produce major mercury emissions (but resulting basalts were still weathered).

Table 5.3: Mercury vs osmium-isotopes as indicators of volcanism (opposite)

that document the onset of the $\delta^{13}\text{C}$ excursion in most records (Du Vivier *et al.*, 2014; 2015), indicating that the marine osmium perturbation began prior to the OAE (by up to 80 kyr). IODP 1260B is the only site where anomalies in both Hg/TOC and $\text{Os}_{(i)}$ have been documented, with the onset of Hg/TOC elevation clearly documented above the initial decrease in sedimentary $\text{Os}_{(i)}$ (Figure 5.10). Taken together, these trends suggest that hydrothermal osmium output was occurring prior to the mercury perturbation, which is also assumed to originate from hydrothermal sources. This non-correlative trend of the two volcanic proxies may indicate that hydrothermal mercury and osmium are released diachronously by submarine volcanism, but it is difficult to conceive why this should be the case. An alternative explanation is that redox changes during OAE 2 may have impacted mercury transport and deposition compared to the

Table 5.3: Table summarising each major Mesozoic event (as well as the end-Permian and Palaeocene–Eocene Thermal Maximum), the details of Large Igneous Provinces associated with each event, and the sedimentary mercury and osmium signals in strata that record each event. Overall summaries of Mesozoic events found in Wignall (2005), Jenkyns (2010), and Bond and Grasby (2016). General review of LIP characteristics in Bryan and Ferrari (2013) and Self *et al.* (2014), with evidence for thermogenic emissions summarised in Svensen *et al.* (2004; 2007; 2009), and Ganino and Arndt (2009). Carbon-isotope information sourced as follows: PT: Korte and Kozur (2010); TJ: Bartolini *et al.* (2012); T-OAE, OAE 1a, and OAE 2: Jenkyns (2010); Valanginian: Charbonnier *et al.* (2017); K–Pg: Zachos and Arthur (1986); PETM: McInerney and Wing (2011). Hg information sourced as follows: K–Pg: Font *et al.* (2016); Sial *et al.* (2016); and this study; OAE 2: Scaife *et al.* (*in preparation*); and this study; OAE 1a: Charbonnier and Föllmi (2017); Valanginian: Charbonnier *et al.* (2017); T-OAE: Percival *et al.* (2015); TJ: Thibodeau *et al.* (2016); see also Chapter 3; PT: Sanei *et al.* (2012); Grasby *et al.* (2013; 2016; 2017). Os-isotope information sourced as follows: PETM: Ravizza *et al.* (2001); Dickson *et al.* (2015); K–Pg: Ravizza and Peucker-Ehrenbrink (2003); Robinson *et al.* (2009); OAE 2: Turgeon and Creaser (2008); Du Vivier *et al.* (2014; 2015); OAE 1a: Tejada *et al.* (2009); Bottini *et al.* (2012); T-OAE: Cohen *et al.* (2004); see also Chapter 4; TJ: Cohen and Coe (2002; 2007); Kuroda *et al.* (2010); PT: Schoepfer *et al.* (2013); Georgiev *et al.* (2015).

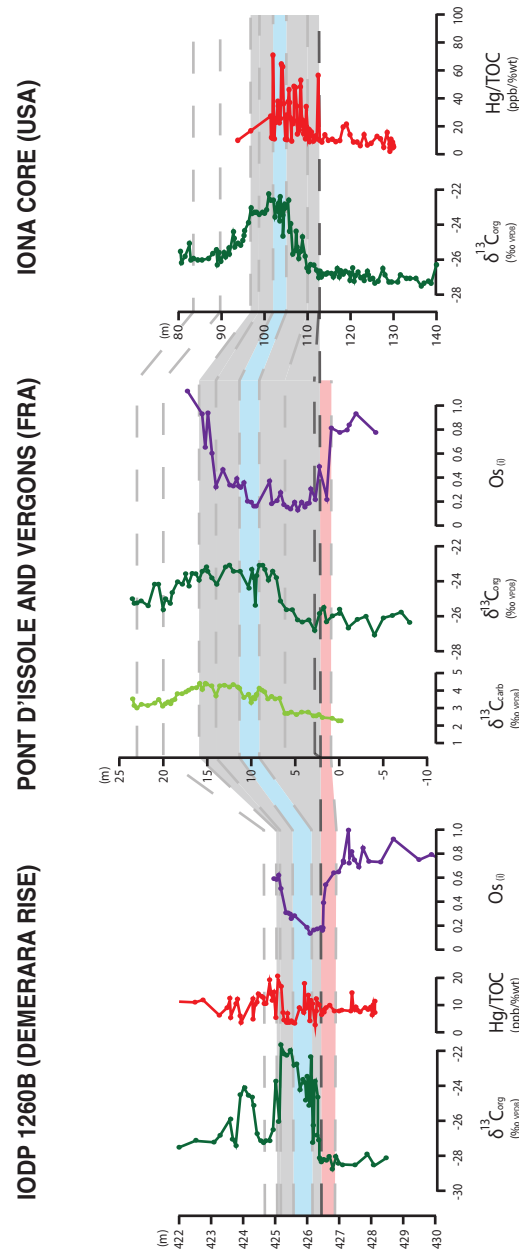


Figure 5.10: Correlation of carbon- and osmium-isotope data and Hg/TOC ratios from IODP 1260B, Pont d'Issole and Vergons, and the Iona core. All stratigraphic heights are in metres; note the variable Hg/TOC scales. Grey shading indicates the stratigraphic extent of OAE 2, based on carbon isotopes; the bold dashed line indicates the horizon marking the onset of OAE 2 (the double line at Pont d'Issole indicates the diachronous increases in carbon-isotope values and TOC content, either of which could mark the onset of the OAE). Blue shading indicates the stratigraphic extent of the Plenus Cold Event. Red shading indicates the stratigraphic gap between the onset horizon of OAE 2, and the base of the decrease in $Os_{(i)}$. Carbon-isotope data are sourced as follows: IODP 1260B from Forster *et al.* (2007); Pont d'Issole and Vergons from Jarvis *et al.* (2011); Iona from Eldrett *et al.* (2014). Osmium-isotope data are sourced as follows: IODP 1260B from Turgeon and Creaser (2008); Pont d'Issole and Vergons from Du Vivier *et al.* (2014). Hg/TOC data from Iona is sourced from Scaife *et al.* (*in preparation*); all other data are from this study.

modern. However, the Maverick Basin became more oxygenated during the OAE, whereas Demerara Rise sediments record increased marine anoxia at that time (Erbacher *et al.*, 2005; Eldrett *et al.*, 2014), but both record the mercury perturbation (Scaife *et al.*, *in preparation*; this study, Figure 5.6A). This relationship would not be expected if mercury deposition was controlled by marine redox changes.

A more plausible answer may hinge on mercury only recording submarine volcanism locally, whilst a change in the osmium-isotope composition of seawater would be reflected globally. Consequently, oceanic LIP volcanism occurring at any location prior to OAE 2 would have caused the globally documented seawater $Os_{(i)}$ decrease. However, a mercury perturbation would only have been recorded at a location once volcanism began proximally to that location. Therefore, it is possible that the mercury perturbations recorded at Demerara Rise and in the Maverick Basin were caused by the beginning of (local) Caribbean Plateau volcanism coincident with the onset of OAE 2, but that one of the other Cenomanian LIPs had already been active for 10s of kyr prior to that point, causing the preceding flux of unradiogenic osmium to the global ocean. A further caveat to this hypothesis is the potential change in ocean circulation at the onset of OAE 2, as inferred from neodymium isotopes (Zheng *et al.*, 2013). Such a change in ocean currents might, during OAE 2, have carried volcanic mercury from an active LIP to an area where there had been no influx of volcanic mercury prior to that time. Thus an apparent input of mercury to that area would be recorded in sediments deposited at the time of circulation change, even if LIP volcanism had actually begun 10s of kyr earlier (and been recorded by a fall in seawater $Os_{(i)}$). Additional studies of mercury in sedimentary records of OAE 2 close to Cenomanian LIPs are needed to confirm such a hypothesis of hydrothermal Hg being limited to near-field sites.

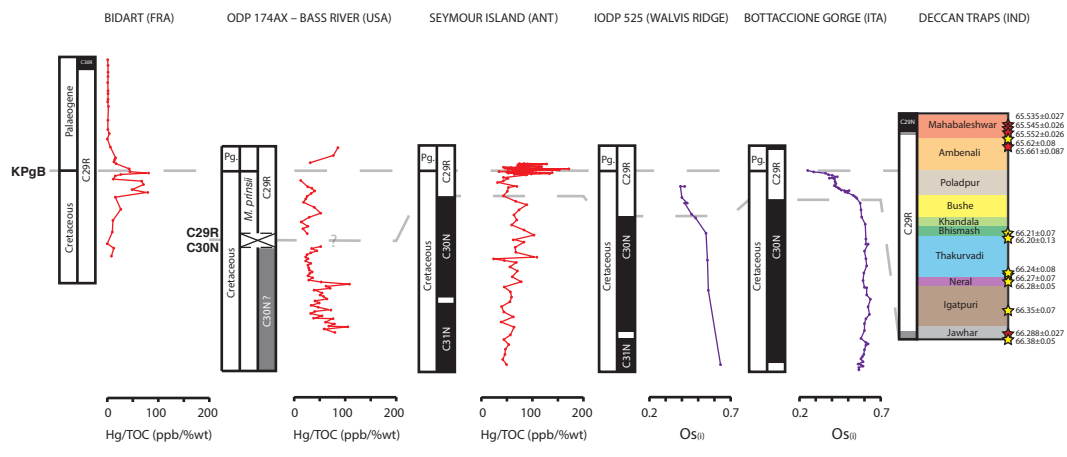
The conclusion that hydrothermal mercury can only record relatively proximal submarine volcanism has important implications for the volcanic processes that took place during OAE 1a. There is a clear decline in $Os_{(i)}$ values across the base of strata that record OAE 1a, proposed to result from hydrothermal emissions of the Ontong-Java Plateau (Table 5.3; Tejada *et al.*, 2009; Bottini *et al.*, 2012). However, Tethyan sedimentary archives also record elevated Hg/TOC during that event, albeit of smaller magnitude than Hg/TOC excursions associated with most other Mesozoic events (Table 5.1; Charbonnier and Föllmi, 2017). No LIP volcanism is documented proximal to the Tethys during the Aptian. However, whilst the majority of Ontong-Java Plateau volcanism is thought to have been submarine, subaerial (phreatomagmatic) volcanism is documented in the geological record of that Province (Chambers *et al.*, 2004; Thordarson *et al.*, 2004). Thus, some Ontong-Java volcanism may have emitted mercury to the atmosphere, potentially reconciling a mercury perturbation with a largely submarine distal LIP. Additionally, it has been suggested that High Arctic LIP magmatics of Aptian age intruded organic-rich sediments to produce additional thermogenic volatiles (Polteau *et al.*, 2016). Therefore, the documented mercury perturbations during OAE 1a might have been produced by subaerial volcanism on the Ontong-Java Plateau, or by High Arctic volcanism and the potentially associated release of thermogenic volatiles, rather than subaqueous Ontong-Java volcanism and associated hydrothermal mercury emissions (Table 5.3). Mercury studies of additional OAE 1a records from outside the Tethys, ideally including terrestrial archives, sections closer to the Ontong-Java Plateau, and records where $Os_{(i)}$ studies have been carried out, are needed to confirm the relationships between Aptian LIPs and sedimentary Hg enrichment during OAE 1a.

5.5.3.2 Subaerial volcanism

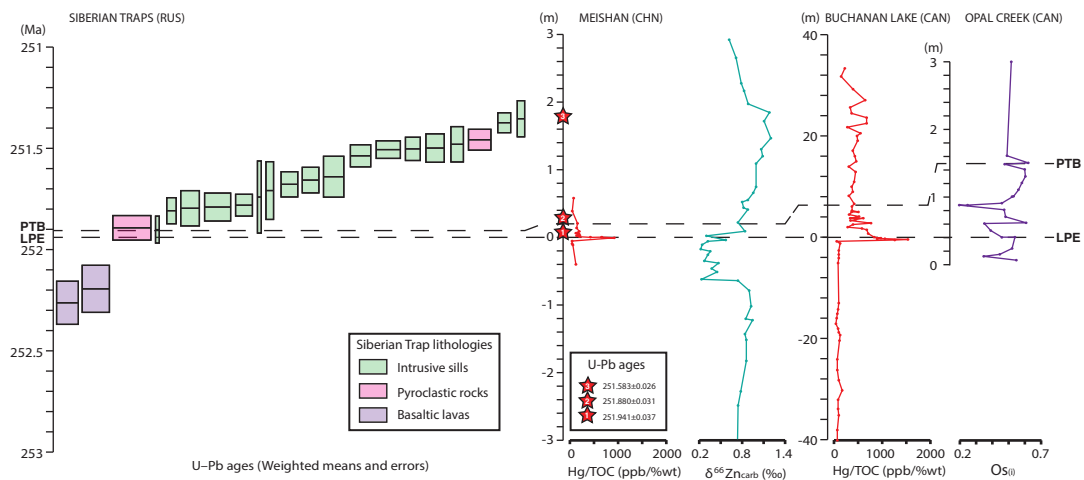
A comparison between mercury and osmium records has not previously been attempted for an event associated with a continental LIP, except for the T-OAE, where the osmium isotopes indicate increased continental weathering rates rather than LIP volcanism (see Chapter 4). The end-Cretaceous has the best sedimentary osmium-isotope record from sediments deposited coevally with the emplacement of a continental LIP (Ravizza and Peucker-Ehrenbrink, 2003; Robinson, 2009). In uppermost Cretaceous strata, there is a recorded decrease in sedimentary $Os_{(i)}$ that begins at the C30N/C29R boundary (Figure 5.11A; Table 5.3), interpreted to reflect the onset of large-scale eruption and weathering of Deccan basalts (Ravizza and Peucker-Ehrenbrink, 2003; Robinson, 2009). However, there is no clear record of sedimentary Hg enrichment during C29R compared to C30N at any of the locations analysed for mercury in this study (Figure 5.5), and previous studies have not analysed strata recording the C30N/C29R reversal (Font *et al.*, 2016; Sial *et al.*, 2016). Even the most convincing end-Cretaceous Hg/TOC spike, recorded at the K–Pg boundary itself, is not observed at all locations, and in any case would have postdated the C30N/C29R reversal by 300–400 kyr (Font *et al.* 2016; this study). Thus, comparisons of end-Cretaceous Hg/TOC and $Os_{(i)}$ data suggest that the Deccan basalts were being erupted and weathered without a major impact on the global mercury cycle for much of their history (Figure 5.11A; Table 5.3). Consequently, it is more plausible that most Deccan basalts did not emit sufficient mercury to perturb the global Hg cycle, with the possible exception of those erupted immediately before the end-Cretaceous extinction.

CHAPTER 5

A: Deccan Traps (End-Cretaceous)



B: Siberian Traps (End-Permian)



C: Paraná–Etendeka Provinces (Early Valanginian)

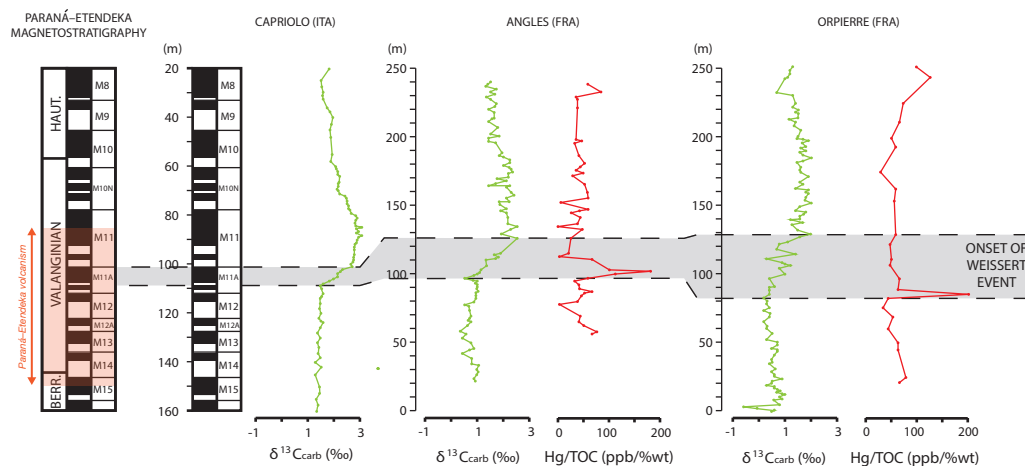


Figure 5.11 (opposite)

End-Permian sedimentary $\text{Os}_{(i)}$ data are only published from one locality. A series of decreases and increases are documented throughout the Permian–Triassic transition, with the first decrease occurring in strata below the end-Permian extinction horizon (Schoepfer *et al.*, 2013; Georgiev *et al.*, 2015). By contrast, in all three studied records of end-Permian sedimentary mercury, Hg/TOC ratios increase abruptly at the extinction horizon, and remain elevated higher up the stratigraphic sequence, but are

Figure 5.11: Temporal correlation of mercury records with other indicators of Large Igneous Province volcanism. **A:** Correlated end-Cretaceous records of Hg/TOC and $\text{Os}_{(i)}$ data. Temporal correlation achieved using palaeomagnetic records of the sedimentary successions and also Deccan basalts, as well as Deccan geochronological dating. $\text{Os}_{(i)}$ data are from Robinson *et al.* (2009). Hg/TOC data are from Bidart sourced from Font *et al.* (2016); all other Hg/TOC data from this study. The Deccan basalt formations and ages shown are from the Western Gnats, following Schoene *et al.* (2015) and Renne *et al.* (2015). The end-Cretaceous extinction horizon (marked KPgB) and C30N/C29R chron reversal are indicated. Biostratigraphic data at Bass River sourced from Miller *et al.* (1998). Magnetostratigraphic data are sourced as follows: Bidart from Galbrun and Gardin (2004); Bass River inferred in this study (see section 2.1.2); Seymour Island from Tobin *et al.* (2012); IODP 525 and Bottaccione Gorge from Robinson *et al.* (2009); Deccan Traps from Chenet *et al.* (2009). **B:** Correlated end-Permian records of Hg/TOC, $\text{Os}_{(i)}$, and zinc-isotope data. Correlation achieved using the indicated end-Permian extinction (marked LPE) horizon and Permian–Triassic boundary (marked PTB). Further correlation with the Siberian Traps achieved using radioisotopic geochronology (Burgess and Bowring, 2015). U–Pb data are sourced as follows: Siberian Traps from Burgess and Bowring (2015); Meishan from Burgess *et al.* (2014). Hg/TOC data are sourced as follows: Meishan from Grasby *et al.* (2017: *corrected following personal communication with Steve Grasby*); Buchuan Lake from Sanei *et al.* (2012). Meishan zinc-isotope data are from Liu *et al.* (2017). Opal Creek $\text{Os}_{(i)}$ data are from Georgiev *et al.* (2015). **C:** Temporal correlation of Valanginian Hg/TOC records with the record of emplacement of the Paraná-Etendeka LIP. Correlation achieved on the basis of carbon-isotope stratigraphy and magnetostratigraphy. The magnetostratigraphic history of the Paraná-Etendeka is from Dodd *et al.* (2015). All Capriolo data are from Channell *et al.* (1993). Other carbon-isotope data are sourced as follows: Angles from Duchamp-Alphonse *et al.* (2007); Orpierre from Charbonnier *et al.* (2013). Hg/TOC data are from Charbonnier *et al.* (2017).

low below the extinction horizon (Sanei *et al.*, 2012; Grasby *et al.*, 2013; 2016; 2017). Consequently, the end-Permian data suggest that the osmium inventory was perturbed by volcanism before the global Hg cycle during that event, similarly to the latest Cretaceous (Figure 5.11B; Table 5.3).

Stratigraphic comparisons between the osmium and mercury records of most other events associated with continental LIPs are more problematic (Table 5.3). There are currently no osmium-isotope data from Valanginian sedimentary records. The end-Triassic records of osmium isotopes are either poorly constrained stratigraphically, or do not record the onset of the $Os_{(i)}$ decrease at a high enough resolution to make a meaningful correlation (Cohen and Coe, 2002; Kuroda *et al.*, 2010). As stated above, Toarcian mercury and osmium have been correlated in one record, but indicate that the oceanic osmium inventory was dominated by weathering of the continental crust during the T-OAE, not weathering of LIP basalts (see Chapter 4). Thus, interpreting a direct volcanic history from Toarcian osmium isotopes is not possible.

When the Hg/TOC and $Os_{(i)}$ comparisons from records of the end-Permian, end-Cretaceous, and OAE 2 events are taken together, it seems that the marine osmium inventory will be perturbed by LIP volcanism (whether submarine or subaerial) from the onset. By contrast, the global mercury cycle may not be perturbed until much later, if at all. Submarine LIP volcanism may only be capable of producing a localised mercury perturbation, whereas subaerial LIP volcanism can cause a global perturbation of the mercury cycle, but will not necessarily do so throughout its entire eruptive history.

5.5.4. *The link between style of LIP volcanism and mercury emissions*

The conclusion that volcanism from the end-Permian Siberian Traps and end-Cretaceous Deccan Traps did not perturb the mercury cycle throughout the entirety of their emplacement is further supported by other sedimentary proxies for volcanism, as well as the basalt geochronology of the LIPs themselves (Figure 5.11). A similar comparison can be made for the Paraná-Etendeka LIP.

For the end-Cretaceous, both palaeomagnetic studies and U–Pb and Ar–Ar dating of Deccan basalts indicate an onset of the main phase of volcanism during the C30N/C29R reversal, 300kyr prior to the end-Cretaceous extinction (Figure 5.11A; e.g. Chenet *et al.*, 2009; Renne *et al.*, 2015; Schoene *et al.*, 2015). Thus, Deccan basalt geochronology supports the conclusion from combined sedimentary Os_(i) and Hg/TOC trends that for much of its history, Deccan volcanism did not perturb the global Hg cycle, and that major mercury emissions may only have begun during the most intense phase of Deccan volcanism just prior to and during the end-Cretaceous extinction (Renne *et al.*, 2015; Font *et al.*, 2016; Sial *et al.*, 2016).

The relative brevity of mercury perturbations observed in lower Valanginian sediments associated with the Paraná-Etendeka Province may provide a further example of LIP activity lacking major mercury emissions. Elevated sedimentary Hg/TOC is recorded only at the onset of the Valanginian ‘Weissert’ Event, indicating a short spell of mercury release from LIP volcanism (Charbonnier *et al.*, 2017). However, palaeomagnetic studies of Paraná-Etendeka basalts indicate a much more prolonged emplacement history of compared to most other LIPs (4–5 Myr), which might explain why the Valanginian ‘Weissert’ Event had a somewhat lesser environmental impact compared to other LIPs (Dodd *et al.*, 2015). The magnetostratigraphy of the Paraná-Etendeka allows its eruptive history to be

compared directly with the Valanginian stratigraphic record, highlighting that the Hg-cycle perturbation documented in Valanginian strata did not occur throughout the entirety of the Paraná-Etendeka's eruptive history (Figure 5.11C).

For the end-Permian, sedimentary zinc-isotope compositions show a marked change below the end-Permian extinction horizon, which has been attributed to weathering of Siberian Trap basalts, supporting the interpretation of a decline in sedimentary $Os_{(i)}$ values in uppermost Permian strata (Figure 5.11B; Liu *et al.*, 2017). Furthermore, radioisotopic dating of Siberian igneous rocks and ash beds throughout the sedimentary record of the end-Permian extinction at Meishan (China) has illustrated that Siberian Trap basalts were already being extruded prior to the extinction (Figure 5.11B; Burgess *et al.*, 2014; Burgess and Bowring, 2015). Thus, Siberian Trap volcanism commenced before the end-Permian extinction, but without perturbing the global Hg cycle, as suggested by the absence of Hg enrichment or elevated Hg/TOC below the extinction horizon (Sanei *et al.*, 2012; Grasby *et al.*, 2016; 2017).

The temporal relationship between end-Permian events and Siberian Trap volcanism is particularly intriguing, as it may highlight specific volcanic processes that might influence the global Hg cycle. The radioisotopic dating of Siberian Trap igneous units has shown that the extinction coincided with large explosive eruptions, as well as with major sill intrusions that might have allowed for release of thermogenic volatiles (Figure 5.11B; Burgess and Bowring, 2015). Therefore, the precise coincidence between elevated Hg/TOC ratios during the end-Permian extinction and explosive eruptions and intrusive sills might indicate that explosive eruptions and thermogenic volatile release were crucial for the perturbation of the mercury cycle during the end-Permian extinction. However, further work is needed to clarify the

degree of explosive *vs* effusive eruptions in other LIPs, and the degree of mercury loss from sediments within metamorphic aureoles, before such a hypothesis can be confirmed. However, the importance of explosive eruptions and thermogenic emissions for the impact of Siberian Trap volcanism on the mercury cycle is consistent with the conclusions of section 5.5.2 (see also Figure 5.9). Of key importance is that the most widespread, high magnitude, enrichments in sedimentary Hg are observed in records of events associated with LIPs that are subaerial and feature one or both of thermogenic emissions and explosive volcanism. As neither of these volcanogenic features have been strongly associated with the Deccan Traps or Paraná-Etendeka LIP, the Hg/TOC peaks associated with those provinces may have been caused during a particularly intense phase of volcanism, when magmatic/volatile flux was at its highest. This is certainly thought to be the case for the end-Cretaceous mercury peak (Font *et al.*, 2016).

5.6. Conclusions

Comparing of new and previously published mercury data from multiple records of multiple events provides new insights into the possible controls on mercury as a sedimentary proxy of distant volcanism. Different facies vary in their suitability as recorders of global mercury trends, depending on what palaeoenvironment that they record. Terrestrial environments record very pronounced mercury signals, whereas relatively pure carbonates appear to be less suitable archives of mercury input, particularly if they give way to organic-rich sediments, which potentially allow overprinting of any Hg/TOC signal by excess TOC. Sedimentary mercury concentrations can show both regional and global disparity, likely resulting from different Hg fluxes to individual locations either through local sedimentary or

volcanic processes. It is clear that numerous surface processes can influence the deposition of mercury in sediments at any one location, demonstrating the need to evaluate multiple records from locations around the globe.

Comparing mercury records from multiple Mesozoic events highlights the contrast between the clear sedimentary Hg/TOC perturbations documented in records of the end-Permian and end-Triassic extinctions, and the more geographically variable records of Hg/TOC trends observed in records of other events, including OAE 2 and the K–Pg. This contrast is suggested to plausibly result from differences in the volcanic contexts of the LIPs associated with each event.

Additional understanding of the importance of volcanic style during Mesozoic events has been gained by comparing sedimentary mercury records with those of osmium isotopes, another proxy for volcanic activity or at least some form of basalt–seawater interaction. OAE 2 shows a stark contrast in records of the two proxies, with a global record of decreased $Os_{(i)}$ values, whereas Hg/TOC excursions are only recorded at a few locations proximal to LIPs and appear higher in the stratigraphy than the base of the $Os_{(i)}$ anomaly. This pattern suggests that mercury emitted from submarine volcanism operates only as a relatively local tracer, whereas hydrothermal osmium can leave a global signature of volcanic processes. This local *vs* global disparity in the two proxies for submarine volcanism may play an important role in explaining the non-correlative Hg/TOC and $Os_{(i)}$ signals of volcanism during OAE 2. Comparisons of end-Cretaceous Hg/TOC and $Os_{(i)}$ data, where $Os_{(i)}$ anomalies begin markedly lower in the stratigraphic record than Hg/TOC anomalies, further indicate that not all LIP eruptions manifestly result in major perturbations to the global mercury cycle. This conclusion is further supported by Hg/TOC and $Os_{(i)}$ comparisons of end-Permian strata, as well other geochemical proxies of volcanism and

geochronological studies of LIP basalts. Several possible factors may determine the potential impact of LIP eruptions on the global mercury cycle: the subaerial *vs* submarine nature of volcanism, and one or more of an unusually high (relative to normal LIP volcanism) magmatic flux, substantive explosive volcanism, and the likelihood of additional thermogenic emissions. Future work is needed to determine precisely what volcanic features have the greatest influence on the scale and distribution of mercury emissions from LIP volcanism.

Chapter 6

Conclusions and future work

6.1. Summary of results

The data generated towards this work clearly demonstrate that mercury shows promise as a sedimentary tracer of volcanism, but also highlight the considerable influence of volcanic and sedimentary context on its use as a volcanic proxy. These results are repeated below in reference to the four key questions laid out at the beginning of this thesis (Chapter 1, section 1.4.), along with the conclusions that can be drawn from this work towards answering these questions.

1) How does the emplacement characteristics of the LIP volcanism affect the presence or otherwise of a global perturbation to the global Hg cycle?

Chapter 3 showed six new mercury records from latest-Triassic to earliest-Jurassic strata. In the five records where the end-Triassic extinction horizon is preserved, a large enrichment in sedimentary Hg was documented at that stratigraphic level, matching the previous record of Thibodeau *et al.* (2016). Additional distinct mercury peaks were also observed in stratigraphically higher sediments at multiple locations, consistent with the previously proposed pulsed emplacement of the latest Triassic Central Atlantic Magmatic Province. Thus, end-Triassic sediments provide a good record of mercury as a proxy for volcanism.

In contrast to the promising end-Triassic mercury record, the sedimentary Hg/TOC trends presented in Chapter 5 for OAE 2 and the end-Cretaceous extinction showed considerable inconsistency across multiple sedimentary records. Of the eight OAE 2 records analysed, only two showed

a small increase in Hg/TOC in strata recording that event, both relatively proximal to coevally erupting submarine LIPs. This geographical trend is consistent with the findings of Scaife *et al.* (*in preparation*), who also document low magnitude Hg/TOC increases in OAE 2 strata deposited proximally to LIPs. Significantly, no clear signal in Hg/TOC is observed in the terrestrial record of OAE 2, indicating that any mercury perturbation did not majorly impact the atmosphere, and therefore was likely only sourced from submarine (hydrothermal) emissions. The four end-Cretaceous records also showed no clear mercury enrichment in sediments deposited coevally with latest-Cretaceous Deccan volcanism (during magnetochron C29R) compared to in sediments deposited prior to the Deccan (C30N). A possible mercury spike may appear at or just below the end-Cretaceous extinction horizon, matching the findings from Font *et al.* (2016) and Sial *et al.* (2016), although it is of a smaller magnitude than the end-Triassic excursion, or those of the end-Permian and early Toarcian (see Chapter 5, section 5.5.2.). This extinction took place 300 kyr after Deccan magmatic activity began (Schoene *et al.*, 2015), and thus this extinction horizon Hg peak cannot mark the onset of volcanism, although the most intense phase of Deccan volcanism is thought to have occurred at that time (Renne *et al.*, 2015).

In conclusion, there is a clear mercury excursion in the record of the end-Triassic proposed to be associated with the Central Atlantic Magmatic Province in sedimentary records from numerous continents, but there is no such conclusive signal of the end-Cretaceous Deccan Traps, or the Cenomanian submarine LIPs linked to OAE 2. It is concluded that subaerial LIPs are more likely to cause a global Hg-cycle perturbation than a

submarine LIP, particularly if they feature the intrusion of volatile-rich lithologies to generate additional thermogenic mercury emissions.

2) Do recorded Hg enrichments concur with other indications of the timing of LIP emplacement, strengthening the case for Hg/TOC peaks resulting from LIP volcanism?

Chapter 3 showed six records (including that previously published by Thibodeau *et al.*, 2016) of elevated sedimentary mercury correlative with the negative excursion in $\delta^{13}\text{C}$ at the end-Triassic extinction horizon. The previously established correlation between this $\delta^{13}\text{C}$ excursion and the lowest known CAMP basalt thus allows the Hg/TOC peak at the extinction horizon to be stratigraphically tied to that specific episode of volcanism (Deenen *et al.*, 2010; Blackburn *et al.*, 2013). Further geochronological work is needed to similarly tie the stratigraphically higher pulses of Hg/TOC to other CAMP units. Nonetheless, this correlation between a LIP basalt unit and a Hg/TOC peak greatly strengthens the case for episodes of LIP volcanism contributing towards perturbations of the global Hg cycle.

Chapter 5 showed a major contrast in Hg/TOC and osmium (Os) isotopes as sedimentary proxies of LIP volcanism, with Hg trends very inconsistent across sedimentary records of OAE 2 and the K–Pg, whilst Os-isotope records of both events show clear trends towards unradiogenic values across the globe, clearly indicating the onset of LIP volcanism (Ravizza and Peucker-Ehrenbrink, 2003; Turgeon and Creaser, 2008; Robinson, 2009; Du Vivier *et al.*, 2014; 2015). Moreover, where Hg/TOC peaks do appear in

OAE 2 or KPg records, they do so stratigraphically above the shift in Os-isotopes to unradiogenic values, confirming that LIP volcanism began prior to any perturbation in the global Hg cycle. These contrasts between mercury and osmium records for both OAE 2 and the KPg highlights the fact that not all LIP eruptions, even if subaerial, perturb the global mercury cycle such that it will be recorded in the sedimentary record, and a specific volcanic context may be required for major emissions of mercury. This result is supported by comparing mercury with other indicators of volcanism from records of the end-Permian and Valanginian events.

In conclusion, for the end-Triassic extinction, a direct tie between a CAMP basalt and Hg peaks can be established and indicates that the volcanic episode that gave rise to that basalt likely contributed towards the documented global Hg-cycle perturbation. For OAE 2 and the K–Pg however, there is no good match between Hg/TOC and Os-isotope records, suggesting that for those events, Hg/TOC peaks cannot be clearly correlated with volcanic episodes, and indicating that not all LIP eruptions are manifestly associated with Hg perturbations.

3) Can mercury be used in multiproxy studies to investigate the temporal relationship between volcanism and other surface processes during major events?

Chapter 3 documented a clear stratigraphic correlation in TJ strata from Astartekløft between sedimentary Hg enrichment and previously published $p\text{CO}_2$ reconstructions based on stomatal indices (Steinthorsdottir

et al., 2011). This correlation shows that the atmospheric mercury and carbon inventories were perturbed geologically simultaneously, likely through emissions of both gases either volcanically or from thermogenic sources produced by intrusion of LIP sills into organic-rich country rocks.

Chapter 4 showed a correlation between elevated sedimentary Hg/TOC, a negative excursion in $\delta^{13}\text{C}$, and a shift in Os-isotopes to radiogenic values. These changes are interpreted to reflect increased volcanism, a major flux of (isotopically light) carbon to the atmosphere, and enhanced continental weathering. Interestingly, the changes in sedimentary Os-isotope compositions begin stratigraphically slightly above those of Hg/TOC and $\delta^{13}\text{C}$, and also end stratigraphically higher, potentially indicating that enhanced weathering lagged the increases in volcanic eruptions and atmospheric carbon content. However, it cannot be ruled out that the apparent lag results from the longer residence time of osmium in the ocean–atmosphere system compared to mercury and carbon.

Therefore, it is concluded that there is a good correlation between records of increased volcanism and perturbations to the carbon cycle, at least for both the end-Triassic and Early Toarcian events. The additional link with enhanced weathering for the T-OAE also supports this process as an important feedback mechanism to counter the increased atmospheric carbon brought about by volcanogenic processes, as previously proposed by Cohen *et al.* (2004) and Jenkyns (2010).

4) How do sedimentary and local transport processes impact particular palaeoenvironments as potential archives of changes in the global Hg cycle?

Chapter 5 explored the possible influences of local sedimentary processes on mercury records. It was established that particular palaeoenvironments might be much more suitable archives of changes to the mercury cycle than others, and that mercury fluxes to sediments may vary considerably in different locations, even without volcanic forcing. Very well oxidised environments without organics or clays present are poor mercury archives. Similarly, records with major lithological variations, for example resulting from interdeposited sands and shales in a deltaic environment, or sudden changes in marine redox leading to enhanced organic-matter burial, represent poor mercury archives, due to the likelihood of very high/very low TOC overprinting/exaggerating Hg concentrations. Terrestrial/near terrestrial environments appear to be the best recorders of changes in atmospheric mercury, potentially due to the ability of trees and soils to take up atmospheric mercury directly.

In conclusion, it is shown that local sedimentary processes and lithological variations can have a profound impact on whether a perturbation to the global Hg cycle will be recorded in the sedimentary record. Use of an appropriate sedimentary archive is critical for mercury studies.

6.2. Conclusions

The studies laid out in this work highlight that mercury shows considerable promise as a sedimentary tracer of volcanic activity, particularly when utilised in multiproxy analyses where LIP volcanism can be tied to other surface processes.

The globally observed end-Triassic mercury perturbation and its tie with the lowest known CAMP basalts demonstrates in an unprecedented manner the potential of the element as a proxy for volcanism. The further correlation between mercury as an indicator of volcanism and osmium isotopes as a weathering proxy in records of the T-OAE suggests that LIP volcanism can be temporally related directly with perturbations of other surface processes on planet Earth.

However, it is also apparent from this work that whilst mercury appears to provide a strong marker for LIP volcanism during the end-Triassic, and other events such as the end-Permian (Sanei *et al.*, 2012; Grasby *et al.*, 2013; 2016; 2017) and T-OAE (Percival *et al.*, 2015), it is a far less reliable indicator of LIP volcanism during multiple Cretaceous events, and in particular OAE 2. The differences in volcanic style on the LIPs associated with these events may play a major role in determining the ability for a Large Igneous Province to cause a perturbation in atmospheric mercury. It is also worth noting that multiple LIPs appear to cause a mercury excursion during only part of their emplacement history, rather than throughout the entire duration of emplacement (see Chapter 5, section 5.5.4.). Consequently, the subaerial or submarine nature of a LIP, as well as its eruptive rate, fraction of explosive *vs* effusive eruptions, and potential to generate thermogenic volatiles, may be very important in the impact of that LIP on the global Hg cycle throughout its eruptive history.

Additionally, even if LIP volcanism does cause a global Hg-cycle perturbation, the recording of this mercury excursion in the sedimentary realm may depend on a specific palaeoenvironment, as well as an absence of major changes in factors such as the specific lithology of the sedimentary record. It should be noted that lithological stability in the records of interest is relatively unlikely due to the major environmental flux often associated with periods of LIP emplacement.

6.3. Future work

Clearly, considerable work is needed to expand all Mesozoic records associated with LIPs to cover a global distribution, particularly for OAE 1a and OAE 2, which were associated with submarine LIPs that likely had only a local influence on the oceanic mercury inventory. On a broader scale, extending the mercury records of major events into the Palaeozoic and Cenozoic remains desirable, particularly for the Botomian (~510 Ma), Frasnian–Famennian (~376 Ma), and Palaeocene–Eocene (~55 Ma) events, which have all been proposed as associated with LIP volcanism (e.g. Courtillot and Renne, 2003; Courtillot *et al.*, 2010; Kravchinsky, 2012).

Comparison of Hg concentrations and Os-isotopes at individual records is also desirable for more events, particularly for those where trends to unradiogenic Os-isotope compositions are recorded (e.g. the end-Triassic), where the Os-isotope records thus record volcanic activity or weathering of primitive basalts, rather than increased weathering of the generic continental crust. Of particular interest is the Early Aptian OAE 1a, an event coincident with a predominantly submarine LIP (the Ontong-Java Plateau) that became subaerial (Chambers *et al.*, 2004; Thordarson *et al.*, 2004), potentially changing its efficiency in distributing mercury globally, and

an event also potentially coincident with the release of thermogenic volatiles by intrusive magmatics related to the High Arctic LIP (Polteau *et al.*, 2016). Thus, since hydrothermal mercury should not majorly perturb the global ocean, comparing the mercury and osmium records from Late Barremian to Early Aptian sediments may give an insight into the temporal relationships between submarine LIP volcanism, subaerial LIP volcanism, and thermogenic emissions.

Additional exploration of the influence of sedimentary processes on mercury records would be useful. As an example, it is known that organic matter is the major sink of mercury to sediments, with clays also contributing to this drawdown process in certain environments (Charbonnier and Föllmi, 2017). However, it remains unclear as to which species might dominate Hg drawdown in environments where both are present, an ambiguity which makes the decision regarding normalisation of Hg concentrations by either organic or aluminium content more difficult to justify. Moreover, it is likely that certain types of organic matter, and certain types of clay mineral, represent more efficient adsorbers of mercury. Terrestrial organic matter might be particularly good at mercury uptake based on the high mercury content observed in terrestrial sedimentary records (Percival *et al.*, 2015; see also Chapter 5, section 5.5.1.), whilst the clay mineral smectite has been previously shown to have a better correlation with mercury adsorption than many other clay types (Kongchum *et al.*, 2011). Determining to what extent sedimentary mercury content can be influenced by the type of clays or organics is therefore important when interpreting any data.

Finally, given the apparent dependence on specific volcanogenic features in impacting the global mercury cycle, further research into how volcanogenic mercury emissions take place would be intriguing. Precise sedimentary and igneous

geochronology would potentially enable sedimentary Hg/TOC peaks to be tied to more LIP units, and potentially to specific igneous units (with either effusive or explosive histories), particularly for the end-Triassic and CAMP, but also for other events and LIPs. Constraining the degassing history of volcanic mercury at modern volcanoes would aid in determining whether petrological analysis of igneous rocks can be used to estimate mercury output from LIP magmatism. Finally, studying the mercury trends in aureoles of organic-rich strata baked by LIP intrusives may give an important insight into whether thermogenic emissions of mercury could have been significant. It is noteworthy that the three events with the best mercury records (the end-Permian, end-Triassic, and Early Toarcian) have all been associated with thermogenic volatile emissions (Svensen *et al.*, 2007; 2009; 2012).

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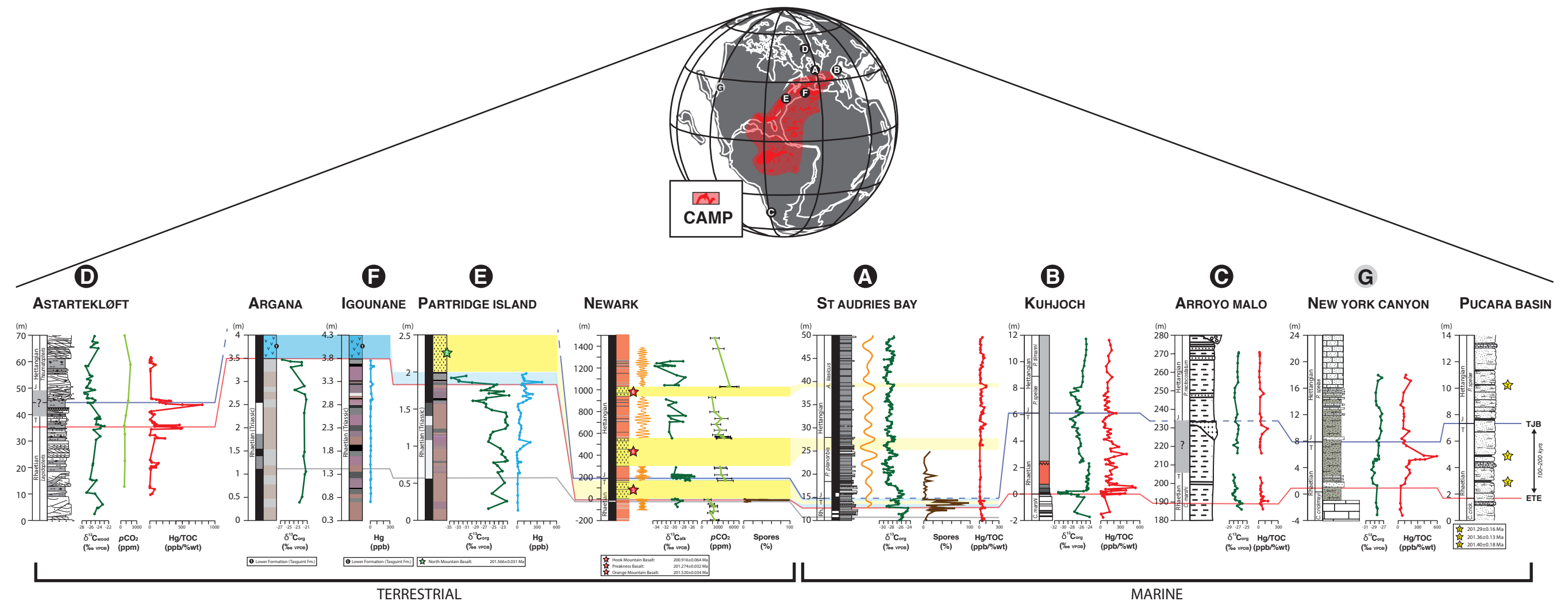
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Appendix 1

Chapter 3 Supplementary Figures

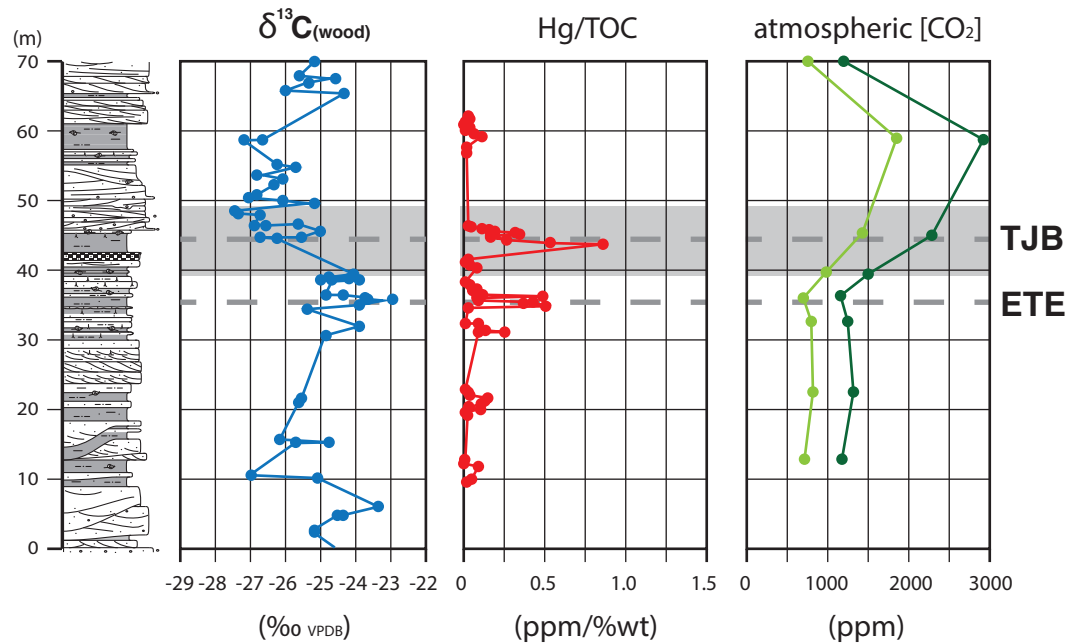
- A Stratigraphic correlation of the Triassic–Jurassic transition**
- B End-Triassic terrestrial mercury and carbon record
(Astartekløft, Greenland)**

Chapter 3 Supplementary Figure A: Stratigraphic correlation of the Triassic–Jurassic transition



Astartekløft lithology and carbon-isotope data from Hesselbo *et al.* (2002); CO_2 data from Steinthorsdottir *et al.* (2011); Hg/TOC data new for this study. Argana lithology and carbon isotope data from Deenen *et al.* (2010), paleomagnetic data from Deenen *et al.* (2011b). Igounane lithology and Hg data new for this study. Partridge Island palaeomagnetic data are from Deenen *et al.* (2011a); lithology, carbon-isotope, and Hg data are new for this study, radioisotopic date from Blackburn *et al.* (2013). Newark lithology and CO_2 data from Schaller *et al.* (2011); astrochronology from Kent and Olsen (1999); carbon-isotope data from Whiteside *et al.* (2010); stratigraphic relationships of spore and palaeomagnetic data are summarised in Blackburn *et al.* (2013); radioisotopic dates of Newark basalts from Blackburn *et al.* (2013). St. Audries Bay lithology and astrochronology data from Ruhl *et al.* (2010a) and Xu *et al.* (2017); carbon-isotope data from Hesselbo *et al.* (2002) and Ruhl *et al.* (2010a); spore data from Bonis *et al.* (2010); Hg/TOC data are new for this study; correlation of Argana and Newark CAMP basalts at each location and St Audries Bay based on the correlation in Whiteside *et al.* (2010). Kuhjoch lithology and carbon-isotope data from Ruhl *et al.* (2009); Hg/TOC data are new for this study. Arroyo Malo lithology from Riccardi *et al.* (2004), carbon-isotope and Hg/TOC data are new for this study. New York Canyon lithology, carbon-isotope, and Hg/TOC data are from Thibodeau *et al.* (2016). Pucara Basin lithology and radiometric dates are from Schoene *et al.* (2010). The red line marks the end-Triassic extinction horizon; the blue line marks the Triassic–Jurassic boundary; the grey line marks the base of the double palaeomagnetic reversal just below the Triassic–Jurassic boundary. Based on radioisotopic dates from the Newark, Fundy, Argana, and Pucara basins (Schoene *et al.*, 2010; Blackburn *et al.*, 2013), and astronomical time scales from Newark and St Audries Bay (Kent and Olsen, 1999; Xu *et al.*, 2017) the end-Triassic extinction and beginning of the Jurassic Period are estimated as separated by approximately 100–200 kyrs.

**Chapter 3 Supplementary Figure B:
End-Triassic terrestrial mercury and
carbon record (Astartekløft, Greenland)**



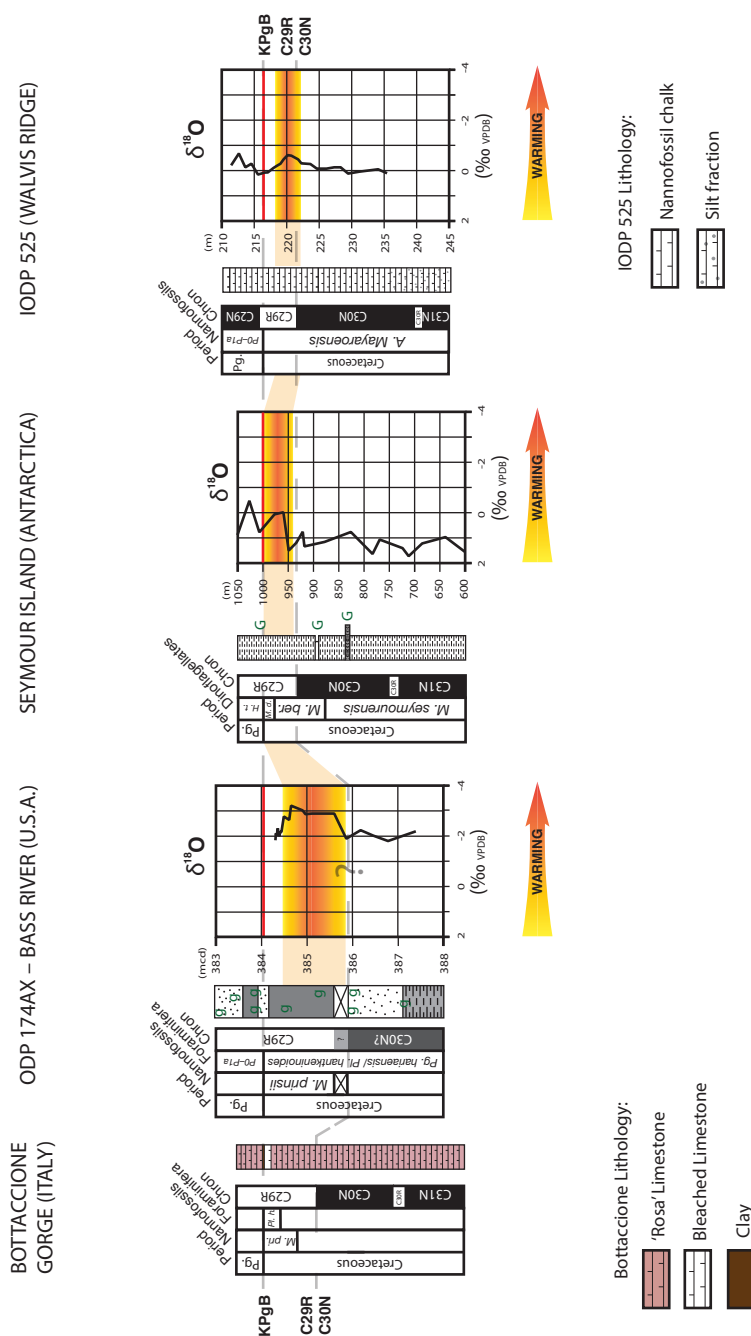
Astartekløft lithology and carbon-isotope data from Hesselbo *et al.* (2002); CO_2 data from Steinthorsdottir *et al.* (2011); Hg/TOC data new for this study.

Appendix 2

Chapter 5 Supplementary Figures

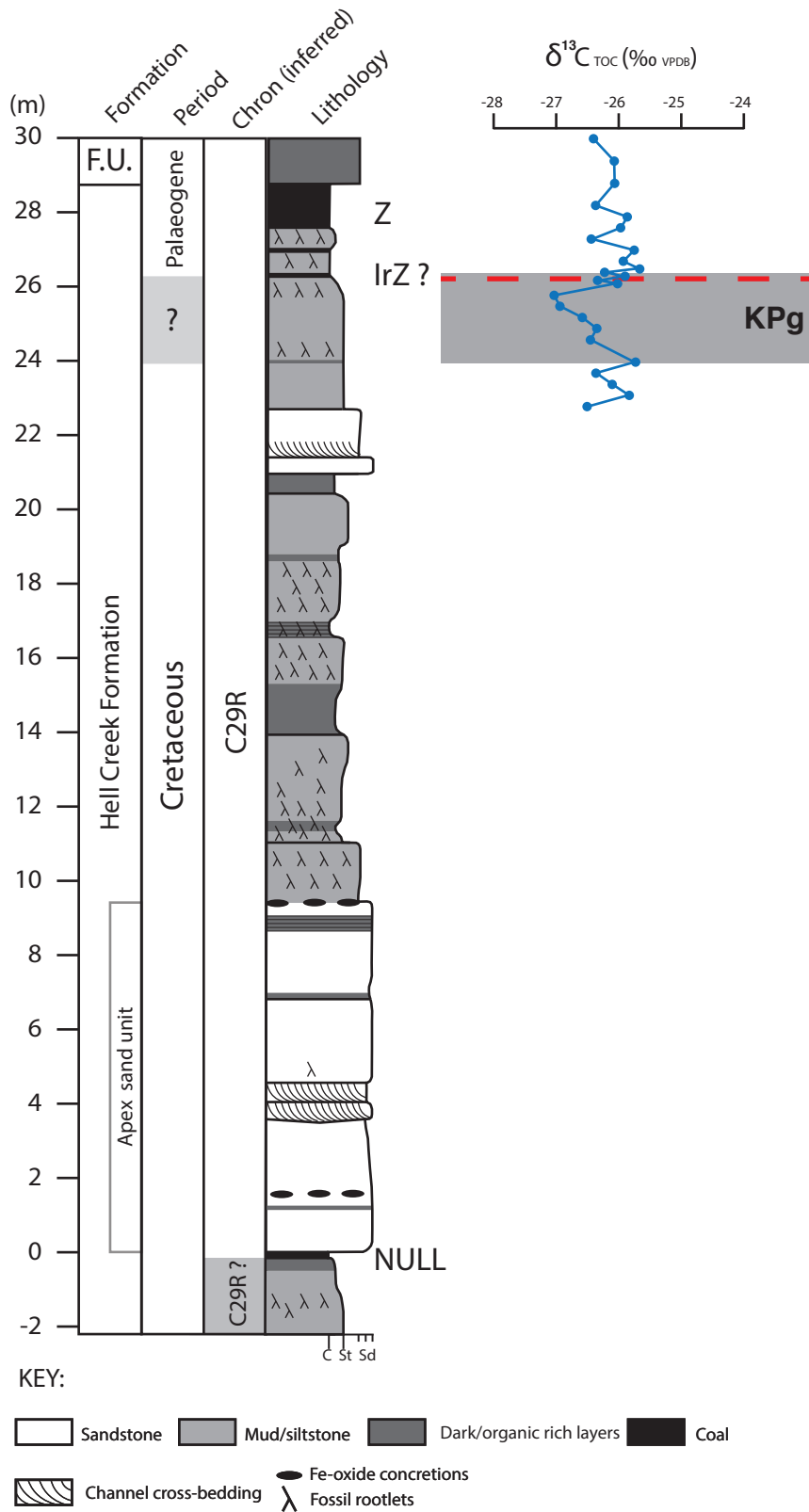
- A Oxygen-isotope correlation of C30N/C29R boundary at Bass River**
- B East Gilbert Creek (Montana) stratigraphic log of new of section**

Chapter 5 Supplementary Figure A: Oxygen-isotope correlation of C30N/C29R boundary at Bass River



Botaccione Gorge biostratigraphy from Gardin *et al.* (2012); Bass River lithology and biostratigraphy from Miller *et al.* (1998) and Esmeray-Senlet *et al.* (2015); Seymour Island lithology and biostratigraphy from Witts *et al.* (2015); Walvis Ridge lithology and biostratigraphy from Moore *et al.* (1983). Oxygen isotope trend lines based on data from Olsson *et al.* (2002: Bass River); Tobin *et al.* (2012: Seymour Island); and Birch *et al.* (2016: Walvis Ridge). Botaccione Gorge palaeomagnetic data from Gardin *et al.* (2012); Seymour Island palaeomagnetic data from Tobin *et al.* (2012); Walvis ridge palaeomagnetic data from Robinson *et al.* (2009). The KPg boundary and C30N/C29R boundaries are indicated. Bass River magnetostratigraphy reconstructed on the basis of the relationship between the C30N/C29R boundary and changes in nannofossil species and oxygen-isotope compositions recorded at these locations.

Chapter 5 Supplementary Figure B: East Gilbert Creek (Montana) stratigraphic log of new section



Magnetostratigraphy inferred from data in Clyde et al. (2016). “F.U.” denotes “Fort Union Member”. NULL, IrZ, and Z indicate the stratigraphic position of their respective coal units.

Appendix 3

Data tables

- A TJ data: d13C, TOC, Hg, and Hg/TOC**
- B T-OAE data: Age corrected Rhenium–Osmium analyses by
N-TIMS**
- C T-OAE data: Molybdenum and Uranium enrichment**
- D T-OAE data: d13C, Hg, TOC, and Hg/TOC**
- E OAE2 data: TOC, Hg, and Hg/TOC**
- F KPg data: d13C, TOC, Hg, and Hg/TOC**

Data tables A: TJ data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**St Audries Bay***TOC data from Hesselbo et al. (2002), Ruhl et al (2010a), or unpublished*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
SA 177	49.5	21	0.43	48.730
SA 173	49.1	40	2.16	18.553
SA 169	48.6	73	6.30	11.588
SA 165	48.1	42	3.03	13.881
SA 163	47.8	70	2.44	28.703
SA 159	47.3	72	3.91	18.433
SA 155	46.9	90	4.78	18.843
SA 153	46.7	45	2.11	21.292
SA 149	46.2	23	1.00	23.087
SA 145	45.7	21	0.33	63.398
SA 143	45.4	31	0.50	61.751
SA 141	45.2	30	0.39	76.671
SA 139	45.0	42	0.64	66.138
SA 131	44.2	44	0.90	49.102
SA 129	44.0	38	0.78	48.769
SA 125	43.5	42	1.53	27.364
SA 123	43.3	53	1.03	51.449
SA 119	42.8	108	4.66	23.163
SA 117	42.6	58	6.82	8.504
SA 113	42.0	85	4.60	18.482
SA 109	41.4	90	9.49	9.487
SA 105	40.9	63	3.26	19.311
SA 103	40.6	72	2.92	24.683
SA 101	40.2	91	6.10	14.918
SA 97	39.7	59	3.13	18.858
SA 93	39.1	32	0.30	107.283
SA 91	38.8	45	0.45	100.450
SA 87	38.3	23	0.91	25.340
SA 83	37.8	28	0.76	36.991
SA 81	37.5	65	2.60	24.957
SA 79	37.2	42	2.20	19.095
SA 77	36.8	46	1.20	38.298
SA 73	36.4	66	3.17	20.820
SA 71	36.2	114	4.74	24.067
SA 69	35.9	171.5	6.78	25.300
SA 65	35.5	24	0.73	32.683

Data tables A: TJ data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**St Audries Bay***TOC data from Hesselbo et al. (2002), Ruhl et al (2010a), or unpublished*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
SA 63	35.3	32	0.78	41.070
SA 59	34.8	39	1.96	19.946
SA 55	34.4	46	0.61	75.660
SA 51	33.8	40	0.68	59.148
SA 49	33.4	85	2.39	35.627
SA 47B	33.0	38	0.62	61.474
SA 47A	33.0	24	0.62	38.826
SA 45	32.6	44	2.24	19.627
SA 43	32.3	44	2.46	17.905
SA 41	32.0	76	4.45	17.063
SA 39	31.8	55	4.58	12.010
SA 37	31.6	45	3.40	13.220
SA 33	30.9	56	0.59	94.653
SA 31	30.5	45	0.66	68.327
SA 29	30.2	35	1.51	23.142
SA 27	29.9	34	0.63	53.975
SA 25	29.6	47	4.11	11.423
SA 23	29.2	26	1.20	21.652
SA 19	28.3	19	0.93	20.442
SA 15	27.5	13	0.42	30.924
SA 13	27.2	24	0.94	25.416
SA 11	26.9	97	5.79	16.759
SA 9	26.7	66	5.81	11.356
SB-41	26.5	114	7.3	15.561
SA 7	26.5	80	6.37	12.557
SA 5	26.3	59	1.15	51.415
SA 3	26.2	42	3.15	13.350
SB-39	22.9	56	5.1	11.068
SB-37	21.7	57	5.6	10.231
SB-34	19.3	37	1.7	21.655
SB-33	18.9	78	5.8	13.555
SB-30	17.3	67	7.5	8.895
SB-28	16.3	55	4.8	11.471
SB-26	15.2	27	3.2	8.423
SB-24	14.9	35	2.6	13.403
SB-22	14.4	68	5.4	12.708

Data tables A: TJ data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**St Audries Bay***TOC data from Hesselbo et al. (2002), Ruhl et al (2010a), or unpublished*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
SAB 129	14.3	34	0.48	70.833
SAB 128	14.2	0	0.29	0.000
SB-20	14.2	44		
SAB 126	14	5.9	0.26	22.692
SB-18	13.7	10	0.7	14.610
SB-17	13.7	28	0.7	40.582
SB-16	13.6	19	0.8	24.639
SB-15	13.0	39	0.7	53.778
SB-13	12.9	51	0.8	60.956
SB-12	12.8	42	0.9	45.329
SB-10	12.8	50	0.6	86.871
SB-8	12.7	1.9		
SB-7	12.6	15	0.4	37.101
SB-5	12.6	12	0.3	44.117
SB-4	12.5	11		
SB-3	12.5	1.9	0.1	17.517
SAB 100	11.4	46	1.42	32.394
SAB 97	11.1	48	1.17	41.026
SAB 94	10.8	38	0.9	42.222
SAB 92	10.6	21	0.47	44.681
SAB 90	10.4	57	0.76	75.000
SAB 88	10.2	47	1.22	38.525
SAB 62	10	28	0.61	45.902

Data tables A: TJ data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Kuhjoch***TOC data from Ruhl et al (2010b)*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
S74	11.65	21	0.17	123.529
S73	11.25	29	0.20	145.000
S72	10.85	30	0.18	166.667
S71	10.45	20	0.18	111.111
S70	10.05	21	0.16	131.250
S69	9.65	16	0.19	84.211
S68	9.25	16	0.17	94.118
S67	8.85	29	0.17	170.588
S66	8.45	17	0.17	100.000
S65	8.05	20	0.19	105.263
S64	7.9	28	0.27	103.704
S63	7.75	16	0.15	106.667
S62	7.6	25	0.36	69.444
S61	7.45	17	0.37	45.946
S60	7.3	17	0.16	106.250
S59	7.15	18	0.28	64.286
S58	7	22	0.18	122.222
S57	6.85	19	0.21	90.476
S56	6.7	15	0.24	62.500
S55	6.55	18	0.16	112.500
S54	6.4	13	0.18	72.222
S53	6.25	23	0.19	121.053
S52	6.1	37	0.16	231.250
S51	5.95	25	0.20	125.000
S50	5.8	19	0.24	79.167
S49	5.65	21	0.37	56.757
S48	5.5	11	0.38	28.947
S47	5.35	13	0.20	65.000
S46	5.2	17	0.25	68.000
S45	5.05	20	0.33	60.606
S45	5.05	17	0.33	51.515
S44	4.9	28	0.19	147.368
S43B	4.75	26	0.25	104.000
S42	4.6	31	0.21	147.619
S41	4.45	23	0.22	104.545
S40	4.3	31	0.24	129.167

Data tables A: TJ data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Kuhjoch***TOC data from Ruhl et al (2010b)*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
S39	4.15	19	0.35	54.286
S38	4	31	0.19	163.158
S37	3.8	31	0.17	182.353
S36	3.6	46	0.17	270.588
S35	3.45	26	0.18	144.444
S34	3.25	28	0.18	155.556
S33	3.05	66	0.17	388.235
S32	2.85	36	0.18	200.000
S31	2.65	10	0.15	66.667
S30	2.55	24	0.20	120.000
S29	2.45	25	0.18	138.889
S28	2.36	48	0.26	184.615
S27	2.3	17	0.21	80.952
S26	2.05	33	0.14	235.714
S25	1.8	28	0.20	140.000
S24	1.5	21	0.13	161.538
S23	1.4	14	0.18	77.778
S22	1.3	27	0.17	158.824
S21	1.2	21	0.13	161.538
S20	1.1	19	0.18	105.556
S19	1	15	0.18	83.333
S18	0.9	20	0.18	111.111
S17	0.8	29	0.12	241.667
S16	0.7	13	0.10	130.000
S15	0.6	53	0.11	481.818
S14	0.5	47	0.09	522.222
S13	0.4	29	0.40	72.500
S12	0.35	28	0.11	254.545
S11	0.34	34	0.09	377.778
S10	0.25	23	0.15	153.333
S9	0.2	13	0.16	81.250
S8	0.15	2.7	0.37	7.297
S7	0.08	6.4	0.37	17.297
S6	0.07	36	0.71	50.704
S5	0.06	555	1.52	365.132
S4	0.02	429	1.50	286.000

Data tables A: TJ data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Kuhjoch***TOC data from Ruhl et al (2010b)*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
S3	0.005	225	8.77	25.656
S2	-0.01	81	3.82	21.204
S1	-0.04	35	1.05	33.333
K1	-0.06	11	0.49	22.449
K2	-0.18	13	0.27	48.148
K3	-0.21	47	0.84	55.952
K4	-1.33	43	0.32	134.375
K5	-1.46	3.5	1.46	2.397
K6A	-1.72	23	0.62	36.898
K6B	-1.72	20	0.62	32.086

Data tables A: TJ data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Arroyo Malo***All data are new for Chapter 3*

Sample	Height (m)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	Hg (ppb)	TOC (%wt)	Hg/TOC
RA1	263.3	-26.88	7.7	0.74	10.4054
RA2	262.3	-26.992	17.5	1.16	15.0862
RA3	261.3	-27.054	11.2	0.85	13.1765
RA4	257.3	-27.099	15.5	0.93	16.6667
RA5	252.8	-27.18	5	0.86	5.8140
RA6	249.8	-27.126	9	1.46	6.1644
RA7	246.8	-27.008	8.1	0.66	12.2727
RA8	243.8	-27.764	13	0.8	16.2500
RA9	240.8	-27.735	41.5	0.55	75.4545
RA10	238.8	-27.852	33	1.55	21.2903
RA11	229.8	-27.178	6.3	0.41	15.3659
RA12	227.8	-27.513	20	0.54	37.0370
RA13	225.8	-27.672	36	1.47	24.4898
RA14	223.8	-26.954	46.5	1.12	41.5179
RA15	221.8	-26.926	45	0.32	140.6250
RA16	218.9	-27.128	21.5	0.43	50.0000
RA17	215.9	-27.414	17.5	0.73	23.9726
RA18	214.4	-27.069	12.5	0.57	21.9298
RA19	212.9	-28.032	19	0.94	20.2128
RA20	211.4	-27.104	7.2	0.41	17.5610
RA21	208.5	-27.187	18.5	0.47	39.3617
RA22	196.6	-28.127	37.5		
RA23	195.1	-27.785	17	0.82	20.7317
RA24	193.6	-28.055	39		
RA25	192.1	-27.807	37	0.73	50.6849
RA26	190.6	-27.627	21	0.73	28.7671
RA27	189.1	-27.186	25.5	0.97	26.2887
RA28	188.4	-27.728	20.5	0.8	25.6250
RA29	187.7	-27.669	28.5	0.74	38.5135
RA30	186.9	-28.005	24.5	0.9	27.2222
RA31	186.2	-28.324	26	1.06	24.5283
RA32	185.4	-28.193	40	1.12	35.7143
RA33	184.7	-27.649	53.5	0.73	73.2877
RA34	183.9	-27.735	54.5	0.86	63.3721
RA35	183.2	-27.6	48.5	1.15	42.1739
RA36	182.5	-26.617	45	0.31	145.1613

Data tables A: TJ data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Arroyo Malo***All data are new for Chapter 3*

Sample	Height (m)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	Hg (ppb)	TOC (%wt)	Hg/TOC
RA37	181.7	-26.725	19	0.54	35.1852
RA38	181	-26.088	20.5	0.9	22.7778
RA39	180.2	-27.272	60	1.48	40.5405
RA42	178	-26.246	21	0.33	63.6364

Data tables A: TJ data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Astartekløft***All data are new for Chapter 3*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
ASTB 277	62.1	31.5	1.09	28.8991
ASTB 275	61.7	44	1.17	37.6068
ASTB 273	61.3	58.5	4.89	11.9632
ASTB 271	60.9	46.5	5.77	8.0589
ASTB 269	60.5	40	0.89	44.9438
ASTB 267	60.1	18	1.25	14.4000
ASTB 265	59.7	27.5	0.45	61.1111
ASTB 263	59.3	34.5	0.31	111.2903
ASTB 255	57.7	14	0.72	19.4444
ASTB 251	56.9	9.1	0.52	17.5000
ASTB 215	49.7		12.5	
ASTB 214	49.5		19	
ASTB 213	49.3		45	
ASTB 212	49.1		14	
ASTB 211	48.9		25	
ASTB 210	48.7		19.5	
ASTB 209	48.5		14.5	
ASTB 208	48.3		30	
ASTB 207	48.1		20.5	
ASTB 206	47.9		17	
ASTB 205	47.7		28.5	
ASTB 204	47.5		83.5	
ASTB 203	47.3		53	
ASTB 202	47.1		63.5	
ASTB 201	46.9		135.5	
ASTB 200	46.7		71	
ASTB 199	46.5	34	1.3	26.1538
ASTB 198	46.3	33.5	0.7	47.8571
ASTB 197	46.1	57	0.5	114.0000
ASTB 196	45.9	46	0.3	153.3333
ASTB 195	45.7	57.5	0.3	191.6667
ASTB 194	45.5	126	0.4	315.0000
ASTB 193	45.3	135.5	0.4	338.7500
ASTB 192	45.1	85.5	0.5	171.0000
ASTB 191	44.9	81.5	0.4	203.7500
ASTB 190	44.7	66	0.4	165.0000

Data tables A: TJ data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Astartekløft***All data are new for Chapter 3*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
ASTB 189	44.5	34.5	0.2	172.5000
ASTB 188	44.3	52.5	0.2	262.5000
ASTB 187	44.1	52.5	0.1	525.0000
ASTB 186	43.9	85	0.1	850.0000
ASTB 175	41.7	32.5	1.1	29.5455
ASTB 174	41.5	84	5.5	15.2727
ASTB 173	41.3	54	8.7	6.2069
ASTB 171	40.9	81	3.4	23.8235
ASTB 170	40.7	84	2.7	31.1111
ASTB 169	40.5	46	0.8	57.5000
ASTB 168	40.3	41	0.5	82.0000
ASTB 167	40.1		44	
ASTB 166	39.9		33.5	
ASTB 165	39.7		50.5	
ASTB 164	39.5		344.5	
ASTB 163	39.3		13	
ASTB 162	39.1		9	
ASTB 161	38.9		19.5	
ASTB 160	38.7		105.5	
ASTB 159	38.5	19	2	9.5000
ASTB 158	38.3	8.4	0.6	14.0000
ASTB 157	38.1	45.5	1.1	41.3636
ASTB 156	37.9	51.5	1.9	27.1053
ASTB 152	37.1	39.5	0.7	56.4286
ASTB 151	36.9	18.5	0.2	92.5000
ASTB 150	36.7	20	0.2	100.0000
ASTB 149	36.5	23.5	0.2	117.5000
ASTB 148	36.3	48.5	0.1	485.0000
ASTB 147	36.1	17	0.2	85.0000
ASTB 146	35.9	56	0.3	186.6667
ASTB 144	35.5	84.5	0.2	422.5000
ASTB 143	35.3	73	0.2	365.0000
ASTB 142	35.1	103.5	0.2	517.5000
ASTB 141	34.9	200.5	0.4	501.2500
ASTB 140	34.7	20	0.7	28.5714
ASTB 130	32.7	57	5.6	10.1786

Data tables A: TJ data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Astartekløft***All data are new for Chapter 3*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
ASTB 129	32.5	53.5	5.3	10.0943
ASTB 128	32.3	36.5	0.4	91.2500
ASTB 124	31.5	13.5	0.1	135.0000
ASTB 123	31.3	10	0.1	100.0000
ASTB 122	31.1	50	0.2	250.0000
ASTB 81	22.9	15.5	1.1	14.0909
ASTB 79	22.5	11.5	0.4	28.7500
ASTB 77	22.1	9.5	0.25	38.0000
ASTB 71	20.9	24	0.22	109.0909
ASTB 69	20.5	23	0.69	33.3333
ASTB 67	20.1	17	0.16	106.2500
ASTB 65	19.7	16.5	1.09	15.1376
ASTB 63	19.3	9.1	0.37	24.5946
ASTB 31	12.9	9.9	1.84	5.3804
ASTB 30	12.7	6	7.93	0.7566
ASTB 28	12.3	8.5	2.02	4.2079
ASTB 26	11.9	15.5	0.17	91.1765
ASTB 17	10.1	20	0.44	45.4545
ASTB 15	9.7	23.5	1	23.5000

Data tables A: TJ data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Partridge Island**

All data are new for Chapter 3. Italicised samples were collected on a different day to non-italicised.

Sample	Depth (cm)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	Hg (ppb)	TOC (%wt)
PI 1	2		137.5	0.25
PI 2	5	-31.64	80.5	0.01
PI 3	9	-34.51	86.5	0.05
PI 4	12		111.5	0.02
PI 5	13	-32.99	103	0.04
PI 6	16	-33.09	108	0.02
PI 7	19	-30.46	337	0.12
PI 8	22	-25.63	78	0.04
PI 9	24	-26.25	63	0.02
PI 10	28	-27.00	117	0.09
PI 11	32	-28.71	138	0.08
PI 12	36	-24.30	108	0.03
PI 13	40	-27.19	132	0.02
PI 14	43	-23.24	232.5	0.11
PI 15	47	-27.69	92.5	0.34
PI 16	51	-27.77	207.5	0.28
PI 17	55	-30.34	143	0.09
PI 18	59	-28.17	88.5	0.01
<i>PI 16</i>	43	-27.75	20	
<i>PI 17</i>	47	-27.78	13.5	
<i>PI 18</i>	51	-26.59	30	
<i>PI 19</i>	55	-23.89	59	0.06
<i>PI 20</i>	60	-23.68	51	0.05
<i>PI 21</i>	64	-23.98	36	0.01
<i>PI 22</i>	68	-23.95	33	0.01
<i>PI 23</i>	72	-23.51	64	
<i>PI 24</i>	76	-23.94	67	
<i>PI 25</i>	81	-26.40	47	
<i>PI 26</i>	85	-26.85	37.5	
<i>PI 27</i>	89	-27.00	36	
<i>PI 28</i>	94	-27.31	204	
<i>PI 29</i>	99		100	
<i>PI 30</i>	103	-24.95	49	
<i>PI 31</i>	107	-24.42	5.4	
<i>PI 32</i>	111	-24.73	2.2	
<i>PI 33</i>	115	-24.01	5.3	

Data tables A: TJ data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Partridge Island**

All data are new for Chapter 3. Italicised samples were collected on a different day to non-italicised.

Sample	Depth (cm)	d13Corg (‰)	Hg (ppb)	TOC (%wt)
<i>PI 34</i>	119	-23.56	6.9	
<i>PI 35</i>	120	-23.98	61	
<i>PI 36</i>	122	-26.29	7.6	
<i>PI 37</i>	126	-25.53	10	
<i>PI 38</i>	134	-24.55	44.5	
<i>PI 39</i>	135	-25.46	19	
<i>PI 40</i>	149	-24.09	10	
<i>PI 41</i>	164	-26.62	8.4	
<i>PI 42</i>	174	-23.68	10	
<i>PI 43</i>	184	-27.32	15	

Data tables A: TJ data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Igounane***All data are new for Chapter 3.*

Sample #	Height (cm)	Hg (ppb)
40	0	13.5
39	70	1.9
13	87	4.1
14	97	5.3
15	99	7.2
16	117	2.4
17	121	2.7
18	133	2.6
19	148	1.8
20	168	0.9
21	180	2.5
22	192	4.2
23	210	3.2
24	223	2.1
25	234	2.3
26	255	1.1
27	270	1.9
28	277	4
29	287	2.7
29A	290	7.4
30	291	32
31	303	12
32	320	4.3
33	325	28.5
34	329	5.4
35	359	0.4
36A	359	4.9
36	363	35
37	366	8.1
38	376	2

APPENDIX 3

Data table B: T-OAE data: Age corrected Rhenium-Osmium analyses by N-TIMS

Mochras

All data are new for Chapter 4, age assumed to be 183 Ma

							Indication of uncertainties				
Sample	Depth (m)	Re conc (ppt)	Os conc (ppt)	¹⁸⁷ Re/ ¹⁸⁸ Os	¹⁸⁷ Os/ ¹⁸⁸ Os	¹⁸⁷ Os/ ¹⁸⁸ Os(i)	Re conc (ppt)	Os conc (ppt)	¹⁸⁷ Re/ ¹⁸⁸ Os	¹⁸⁷ Os/ ¹⁸⁸ Os	¹⁸⁷ Os/ ¹⁸⁸ Os(i)
2494-1	760.2	3281	55	329.6820	1.319818	0.313156	58	1.59	11.1063	0.001923	0.001923
2525-2	769.7	4382	62	406.8807	1.604696	0.362314	77	1.77	13.7070	0.002338	0.002338
2559-5	780.1	4263	59	416.8321	1.685530	0.412762	75	1.70	14.0422	0.002456	0.002456
2591-9	790	2111	57	200.0704	1.073221	0.462320	37	1.64	6.7400	0.001564	0.001564
2624-7	800	1330	44	166.2177	1.160025	0.652490	23	1.25	5.5995	0.001690	0.001690
2641-8	805.2	933	33	153.6493	1.114034	0.644876	16	0.95	5.1761	0.001623	0.001623
2657-3	809.9	745	44	87.8490	0.803262	0.535021	13	1.27	2.9595	0.001170	0.001170
2665-10	812.5	790	51	83.4372	1.052678	0.797908	14	1.46	2.8108	0.001534	0.001534
2679-3	816.6	1626	63	139.7647	1.137873	0.711111	29	1.82	4.7084	0.001658	0.001658
2693-11	821.1	730	50	77.2209	0.922188	0.686400	13	1.44	2.6014	0.001344	0.001344
2719-11	829	547	51	56.2872	0.862927	0.691058	10	1.47	1.8962	0.001257	0.001257
2723-9	830.2	894	60	78.7504	0.884888	0.644429	16	1.72	2.6529	0.001289	0.001289
2731-0	832.4	739	57	68.2457	0.766734	0.558350	13	1.62	2.2991	0.001117	0.001117
2740-5	835.3	1248	64	101.6235	0.737214	0.426914	22	1.83	3.4235	0.001074	0.001074
2769-4	844.1	1165	65	93.2704	0.704594	0.419799	21	1.85	3.1421	0.001027	0.001027
2793-2	851.4	780	54	75.9316	0.790830	0.558978	14	1.54	2.5580	0.001152	0.001152
2806-10	855.5	862	60	74.2376	0.739943	0.513263	15	1.73	2.5009	0.001078	0.001078
2818-4	859	820	70	60.4929	0.706510	0.521799	14	2.01	2.0379	0.001029	0.001029
2831-7	863.1	853	65	67.6752	0.670902	0.464260	15	1.86	2.2798	0.000978	0.000978
2839-1	865.4	2541	185	69.1374	0.496435	0.285329	45	5.31	2.3291	0.000723	0.000723
2854-0	869.9	2888	65	242.1997	1.149937	0.410397	51	1.86	8.1592	0.001675	0.001675
2881-2	878.3	2620	89	155.2922	0.821457	0.347282	46	2.54	5.2315	0.001197	0.001197
2897-0	883	3964	67	333.8279	1.452139	0.432818	70	1.92	11.2460	0.002116	0.002116
2925-0	891.5	2601	57	253.9199	1.320552	0.545225	46	1.63	8.5541	0.001924	0.001924
2942-8	896.9	3474	38	555.8834	2.092603	0.395250	61	1.08	18.7266	0.003049	0.003049

Blanks and Standards

	Standards	Re conc (ppt)	Os conc (ppt)	¹⁸⁷ Re/ ¹⁸⁸ Os	¹⁸⁷ Os/ ¹⁸⁸ Os	¹⁸⁷ Os/ ¹⁸⁸ Os(i)
	SDO-1	75837	583	1266.4885	7.956614	0.125614
	SDO-1	76354	581	1278.3435	7.942469	0.038167
	SDO-1	77459	600	1256.2795	7.948661	0.180786
Average blank values (n=3)		1.483	0.732		0.186884	
DTM 100pg Os average values (n=6)		187Os/188Os :	0.174			
Re resolution standard (125ppt) average values (n=6)		187Re/188Os :	1.672			

Indication of uncertainties: based on analyses of SDO-1

		% Error (2 standard deviations)
Re (ppt)		1.7671
Os (ppt)		2.8645
¹⁸⁷ Re/ ¹⁸⁸ Os		3.3688
¹⁸⁷ Os/ ¹⁸⁸ Os		0.1457
Absolute SDO values and error (2 standard deviations) assuming Toarcian age (183Ma)		
¹⁸⁷ Os/ ¹⁸⁸ Os(i)		4.080147±0.03091

APPENDIX 3

Data table C: T-OAE data: Molybdenum and Uranium enrichment

Mochras

All data are new for Chapter 4, Archean shale standards: $Mo/Al = 0.0000135$; $U/Al = 0.0000331$

Sample	Depth (m)	Mo (ppm)	U (ppm)	Al (%wt)	Al (ppm)	Mo/Al	U/Al	MoEF(Al)	UEF(Al)
2428 – 7	740.23	1.021	2.813	3.666	36660.389	2.79E-05	7.67E-05	2.06	2.32
2494 – 1	760.20	0.829	1.554	2.671	26712.223	3.10E-05	5.82E-05	2.30	1.76
2525 – 5	769.75	0.566	3.017	6.209	62085.667	9.12E-06	4.86E-05	0.68	1.47
2559 – 5	780.11	0.464	2.535	4.929	49287.310	9.41E-06	5.14E-05	0.70	1.55
2591 – 9	789.97	0.9	2.498	4.924	49244.047	1.83E-05	5.07E-05	1.35	1.53
2624 – 7	799.97	0.423	2.95	5.951	59513.235	7.11E-06	4.96E-05	0.53	1.50
2641 – 8	805.18	0.462	2.778	6.186	61861.720	7.47E-06	4.49E-05	0.55	1.36
2657 – 3	809.93	0.4	2.498	9.387	93874.823	4.26E-06	2.66E-05	0.32	0.80
2679 – 3	816.64	0.424	2.966	10.273	102733.490	4.13E-06	2.89E-05	0.31	0.87
2693 – 11	821.11	0.412	2.6	9.334	93337.168	4.41E-06	2.79E-05	0.33	0.84
2719 – 11	829.03	0.546	3.28	8.334	83335.549	6.55E-06	3.94E-05	0.49	1.19
2731 – 0	832.41	0.524	3.416	9.000	89998.787	5.82E-06	3.80E-05	0.43	1.15
2740 – 5	835.28	0.63	3.574	7.744	77442.886	8.14E-06	4.62E-05	0.60	1.39
2754 – 8	839.62	0.651	2.928	6.064	60642.886	1.07E-05	4.83E-05	0.80	1.46
2769 – 4	844.09	0.645	3.356	7.467	74671.474	8.64E-06	4.49E-05	0.64	1.36
2777 – 2	846.48	0.448	3.168	7.914	79135.600	5.66E-06	4.00E-05	0.42	1.21
2793 – 2	851.36	0.675	3.398	7.231	72307.410	9.34E-06	4.70E-05	0.69	1.42
2806 – 10	855.52	0.681	3.643	8.291	82913.094	8.21E-06	4.39E-05	0.61	1.33
2831 – 7	863.07	1.102	3.354	7.999	79994.914	1.38E-05	4.19E-05	1.02	1.27
2854 – 0	869.90	1.476	2.902	4.860	48595.877	3.04E-05	5.97E-05	2.25	1.80
2881 – 2	878.18	0.878	2.11	3.399	33993.803	2.58E-05	6.21E-05	1.91	1.88
2897 – 0	883.01	1.633	2.897	4.023	40227.731	4.06E-05	7.20E-05	3.01	2.18
2917 – 2	889.15	1.488	1.899	3.055	30551.243	4.87E-05	6.22E-05	3.61	1.88
2942 – 8	896.92	2.692	1.559	1.470	14695.192	1.83E-04	1.06E-04	13.57	3.21
2967 – 0	904.34	1.869	2.873	3.722	37221.059	5.02E-05	7.72E-05	3.72	2.33
2999 – 10	914.35	1.287	2.184	1.863	18629.564	6.91E-05	1.17E-04	5.12	3.54

Data tables D: T-OAE data: $\delta^{13}\text{C}$, Hg, TOC, Hg/TOC**Mochras**

Hg, TOC, and Hg/TOC data from below 815m are from Percival et al. (2015)

Sample	Depth (m)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	Hg (ppb)	TOC (%wt)	Hg/TOC
2507 – 1	764.16		40.5	0.72	56.250
2511 – 1	765.38		37	0.68	54.412
2515 – 5	766.70		30	0.87	34.483
2520 – 3	768.17		46.5	0.79	58.861
2524 – 4	769.42		38.5	0.7	55.000
2528 – 6	770.69		48.5	0.82	59.146
2532 – 10	772.01		48	0.94	51.064
2536 – 10	773.23		76	0.84	90.476
2540 – 11	774.47		34	0.67	50.746
2546 – 3	776.10		53.667	0.71	75.587
2550 – 7	777.42		47.5	0.57	83.333
2554 – 4	778.56		71.5	0.73	97.945
2558 – 4	779.78		40.5	0.68	59.559
2562 – 5	781.03		34.5	0.45	76.667
2566 – 5	782.24		49.5	0.64	77.344
2570 – 9	783.57		44.5	0.85	52.353
2574 – 8	784.76		51.5	0.71	72.535
2578 – 7	785.95		49	0.76	64.474
2582 – 8	787.20		63	0.84	75.000
2586 – 9	788.44		83	1.1	75.455
2590 – 7	789.61		48	0.68	70.588
2594 – 6	790.80		57	0.71	80.282
2598 – 7	792.05		53.5	1.01	52.970
2604 – 0	793.70		40.5	0.65	62.308
2607 – 8	794.82		44.5	0.84	52.976
2611 – 9	796.06		40.5	0.92	44.022
2615 – 1	797.08		35	0.62	56.452
2619 – 4	798.37		29.5	0.5	59.000
2623 – 11	799.77		58.5	0.72	81.250
2626 – 3	800.48		50.5	0.96	52.604
2629 – 7	801.50		30	0.71	42.254
2634 – 3	802.92		71.5	1.44	49.653
2638 – 10	804.32		39	0.92	42.391
2642 – 8	805.49		39	0.77	50.649
2646 – 9	806.73		46	0.68	67.647
2651 – 7	808.20		42	1.03	40.777

Data tables D: T-OAE data: $\delta^{13}\text{C}$, Hg, TOC, Hg/TOC**Mochras**

Hg, TOC, and Hg/TOC data from below 815m are from Percival et al. (2015)

Sample	Depth (m)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	Hg (ppb)	TOC (%wt)	Hg/TOC
2655 – 3	809.32		48	0.95	50.526
2659 – 2	810.51		41.5	0.81	51.235
2679 – 10	816.81		118	1.69	69.822
2694 – 6	821.28		191.5	1.76	108.807
2698 – 8	822.55		81	1.61	50.311
2709 – 0	825.70		100.5	1.07	93.925
2716 – 7	828.01		63.5	0.9	70.556
2723 – 2.5	830.03		48	0.42	114.286
2730 – 4	832.21		45.5	0.46	98.913
2737 – 5	834.36		84.5	0.53	159.434
2740 – 10	835.41		63.5	0.77	82.468
2750 – 7	838.38		35	0.78	44.872
2761 – 1	841.58		47	0.87	54.023
2770 – 0	844.30		22	1	22.000
2781 – 11	847.93		27.5	0.85	32.353
2794 – 6	851.76		42.7	0.92	46.413
2805 – 11	855.24		58.5	0.8	73.125
2813 – 10	857.66		60	1.21	49.587
2817 – 8	858.82	-25.3			
2820 – 0	859.54	-25.2	67	1.3	51.538
2822 – 2	860.20	-25.1			
2824 – 7	860.93	-26.7			
2826 – 5	861.49	-26.4	65.5	1.01	64.851
2828 – 3	862.05	-26.6			
2830 – 7	862.76	-26.6			
2832 – 4	863.30	-26.8	168	1.19	141.176
2833 – 6	863.65	-25.9			
2835 – 5	864.24	-26.3			
2837 – 8	864.92	-25.6			
2839 – 1	865.35	-25.6	43	1.3	33.077
2841 – 3	866.01	-25.6			
2843 – 8	866.75	-25.7			
2845 – 6	867.31	-25.4			
2854 – 0	869.90		25.5	0.87	29.310
2881 – 2	878.18		25.5	0.71	35.915
2897 – 0	883.01		26.5	1.02	25.980

Data tables D: T-OAE data: $\delta^{13}\text{C}$, Hg, TOC, Hg/TOC**Mochras**

Hg, TOC, and Hg/TOC data from below 815m are from Percival et al. (2015)

Sample	Depth (m)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	Hg (ppb)	TOC (%wt)	Hg/TOC
2906 – 10.5	886.02		22	0.97	22.680
2925 – 9	891.77		22.5	0.68	33.088
2939 – 9	896.04		24.5	0.78	31.410
2955 – 4	900.79		26.5	0.81	32.716
2967 – 0	904.34		34	1.1	30.909
2984 – 2	909.57		33	0.91	36.264
2999 – 10	914.35		28.5	0.85	33.529
3009 – 4	917.24		10.8	0.35	30.857
3024 – 11	921.99		15	0.38	39.474
3035 – 9	925.30		8.7	0.32	27.188
3054 – 1	930.88		20	0.88	22.727
3067 – 0	934.82		32	1.2	26.667

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**IODP 1260B (Demerara Rise)***All data are new for chapter 5*

mbsf (of top)	Hg (ppb)	TOC (%)	Hg/TOC
415.31	163.5	4.6	35.543
416	135.5	10.7	12.664
416.41	111.5	9.2	12.120
417.995	103	9.3	11.075
418.25	46.5	3.8	12.237
418.74	79.5	11.7	6.795
419	101.5	11	9.227
419.065	115.5	9	12.833
419.105	54	9.4	5.745
419.27	93.5	8.7	10.747
419.295	103	8.4	12.262
419.39	27.5	4.2	6.548
419.43	11.9	3	3.967
419.625	10		
419.65	17		
419.78	92	7.4	12.432
419.82	39.5	7.5	5.267
419.855	30.5	2.9	10.517
419.91	109	9.5	11.474
419.96	160.5	11.1	14.459
420.05	172	12.8	13.438
420.11	153	11.8	12.966
420.15	122	11.5	10.609
420.21	131	12.2	10.738
420.25	143.5		
420.31	182.5	9.4	19.415
420.36	170	12	14.167
420.41	121	10.2	11.863
420.46	144.5	9.7	14.897
420.5	52.5	9.3	5.645
420.575	51.5	2.5	20.600
420.59	49		
420.66	44	2.6	16.923
420.71	126	17	7.412
420.76	74	15	4.933
420.81	55	13.4	4.104

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**IODP 1260B (Demerara Rise)***All data are new for chapter 5*

mbsf (of top)	Hg (ppb)	TOC (%)	Hg/TOC
420.87	113	15.9	7.107
420.91	66	16.2	4.074
420.955	68.5	14.5	4.724
420.99	59.5	13	4.577
421.05	48.5	11.6	4.181
421.095	38.5	10.1	3.812
421.23	4.7	0.5	9.400
421.38	88	11.6	7.586
421.41	109.5	6.1	17.951
421.445	146.5	16	9.156
421.505	181	13.3	13.609
421.53	169.5	17.2	9.855
421.57	94.5	20.5	4.610
421.61	120.5	10.1	11.931
421.645	117.5	11.1	10.586
421.715	17.5	5.9	2.966
421.735	30.5	3.8	8.026
421.77	94.5	7.4	12.770
421.825	148	13.9	10.647
421.94	84	12.7	6.614
422	65	8.8	7.386
422.02	74.5	8.8	8.466
422.055	81.5	9	9.056
422.17	80	7.7	10.390
422.19	80	7.9	10.127
422.31	73	9	8.111
422.47	67.5	8.2	8.232
422.55	76	9	8.444
422.805	40	5	8.000
422.855	97.5	6.6	14.773
422.905	68	7.4	9.189
422.96	65	7.6	8.553
422.98	70	7.3	9.589
423.01	60.5	7.2	8.403
423.11	10.8	1.4	7.714
423.31	40.5	4.4	9.205

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**IODP 1260B (Demerara Rise)***All data are new for chapter 5*

mbsf (of top)	Hg (ppb)	TOC (%)	Hg/TOC
423.36	47.5	5.4	8.796
423.41	61.5	6.5	9.462
423.46	49.5	7.3	6.781
423.51	62.5	6.1	10.246
423.535	54	7.3	7.397
423.56	95	8.2	11.585

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Tarfaya***TOC data from Tsikos et al. (2004)*

Sample	mbs (top)	Hg (ppb)	TOC (%wt)	Hg/TOC
S57-120	-23.41	381	12.240	31.127
S57-119	-23.79	264	8.850	29.831
S57-118	-24.16	291	8.720	33.372
S57-117	-24.51	152	10.060	15.109
S57-116	-24.9	232	8.280	28.019
S57-115	-25.29	214.5	8.736	24.554
S57-114	-25.69	235	7.909	29.713
S57-113	-26.09	197	12.850	15.331
S57-112	-26.48	55.5	2.730	20.330
S57-111	-26.87	86.5	4.024	21.496
S57-110	-27.27	110.5	4.796	23.040
S57-109	-27.65	84.5	4.368	19.345
S57-108	-28.07	184.5	6.320	29.193
S57-107	-28.49	333.5	15.640	21.324
S57-106	-28.89	85.5	3.408	25.088
S57-105	-29.24	268.5	11.600	23.147
S57-104	-29.62	114.5	5.061	22.624
S57-103	-30	156.5	6.818	22.954
S57-102	-30.47	44.5	1.540	28.896
S57-101	-30.87	188.5	9.635	19.564
S57-100	-31.27	279	9.772	28.551
S57-99	-31.67	195.5	8.666	22.559
S57-98	-32.07	240.5	7.500	32.067
S57-97	-32.41	91.5	4.351	21.030
S57-96	-32.77	217.5	13.010	16.718
S57-95	-33.16	262.5	9.961	26.353
S57-94	-33.57	156	6.171	25.280
S57-93	-33.92	54.5	1.692	32.210
S57-92	-34.31	51.5	1.975	26.076
S57-91	-34.61	83	3.082	26.931
S57-90	-35	132	4.835	27.301
S57-89	-35.41	223.5	10.890	20.523
S57-88	-35.8	296	14.440	20.499
S57-87	-36.26	328.5	9.643	34.066
S57-86	-36.78	282.5	12.300	22.967
S57-85	-37.52	71.5	4.393	16.276

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Tarfaya***TOC data from Tsikos et al. (2004)*

Sample	mbs (top)	Hg (ppb)	TOC (%wt)	Hg/TOC
S57-84	-37.94	17	0.671	25.335
S57-83	-38.34	67	0.755	88.742
S57-82	-38.75	160.5	7.090	22.638
S57-81	-39.17	303.5	7.708	39.375
S57-80	-40.07	161.5	4.200	38.452
S57-79	-40.44	246	14.240	17.275
S57-78	-40.8	210	13.310	15.778
S57-77	-41.22	112	3.818	29.335
S57-76	-41.63	179.5	9.562	18.772
S57-75	-42	153	7.661	19.971
S57-74	-44.61	115.5	12.160	9.498
S57-73	-44.81	126.5	7.625	16.590
S57-72	-45.15	153.5	6.913	22.205
S57-71	-45.32	177	7.592	23.314
S57-70	-45.54	120.5	10.840	11.116
S57-69	-45.74	79	2.335	33.833
S57-68	-45.94	60.5	2.071	29.213
S57-67	-46.13	87	3.709	23.456
S57-66	-46.32	148.5	4.485	33.110
S57-65	-47	367	12.280	29.886
S57-64	-47.19	310.5	8.415	36.898
S57-63	-47.46	253.5	9.906	25.591
S57-62	-47.61	274.5	17.350	15.821
S57-61	-47.84	314	14.700	21.361
S57-60	-48.08	241	14.360	16.783
S57-59	-48.31	140	5.236	26.738
S57-58	-48.5	145.5	12.040	12.085
S57-57	-48.69	110	8.351	13.172
S57-56	-48.92	161.5	12.140	13.303
S57-55	-49.13	248.5	21.580	11.515
S57-54	-49.36	192	11.340	16.931
S57-53	-49.57	303	15.050	20.133
S57-52	-49.8	227.5	15.550	14.630
S57-51	-49.51	340	25.930	13.112
S57-50	-50.16	301	16.610	18.122
S57-49	-50.35	91.5	7.511	12.182

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Tarfaya***TOC data from Tsikos et al. (2004)*

Sample	mbs (top)	Hg (ppb)	TOC (%wt)	Hg/TOC
S57-48	-50.56	67.5	2.696	25.037
S57-47	-50.76	91	3.881	23.448
S57-46	-51	104.5	4.373	23.897
S57-45	-51.13	156	5.875	26.553
S57-44	-51.36	167	13.820	12.084
S57-43	-51.55	146	9.306	15.689
S57-42	-51.75	218.5	15.960	13.690
S57-41	-51.92	171	10.510	16.270
S57-40	-52.11	192	9.031	21.260
S57-39	-52.3	161.5	10.840	14.899
S57-38	-52.51	157	7.367	21.311
S57-37	-52.7	121	5.283	22.904
S57-36	-52.92	84.5	4.566	18.506
S57-35	-53.12	63	2.308	27.296
S57-34	-53.33	80	2.455	32.587
S57-33	-53.52	75	2.613	28.703
S57-32	-53.73	127	7.879	16.119
S57-31	-54	253	10.910	23.190
S57-30	-54.16	270.5	10.960	24.681
S57-29	-54.35	247	10.310	23.957
S57-28	-54.53	202	8.093	24.960
S57-27	-54.76	231	12.080	19.123
S57-26	-54.95	209.5	5.534	37.857
S57-25	-55.13	205	6.561	31.245
S57-24	-55.34	127.5	4.560	27.961
S57-23	-55.51	164.5	5.938	27.703
S57-22	-55.71	153.5	6.277	24.454
S57-21	-55.89	122	6.387	19.101
S57-20	-56.08	146	8.040	18.159
S57-19	-56.29	25	1.018	24.558
S57-18	-56.49	162	6.841	23.681
S57-17	-56.72	200	5.868	34.083
S57-16	-56.87	75	2.982	25.151
S57-15	-57.07	162	6.611	24.505
S57-14	-57.25	118.5	6.621	17.898
S57-13	-57.42	87	3.888	22.377

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Tarfaya***TOC data from Tsikos et al. (2004)*

Sample	mbs (top)	Hg (ppb)	TOC (%wt)	Hg/TOC
S57-12	-57.59	91	1.931	47.126
S57-11	-57.77	83	4.001	20.745
S57-10	-58	119	6.100	19.508
S57-9	-58.16	124.5	5.243	23.746
S57-8	-58.36	96.5	6.647	14.518
S57-7	-58.57	164.5	8.326	19.757
S57-6	-58.69	177.5	9.903	17.924
S57-5	-58.91	178	6.166	28.868
S57-4	-59.12	145.5	3.828	38.009
S57-3	-59.35	132	8.493	15.542
S57-2	-59.52	188	5.209	36.091
S57-1	-59.68	117.5	9.309	12.622

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Utah composite***All data are new for Chapter 5*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
RSB0766	84.5	170.50	1.70	100.29
RSB0765	84.2	61.00	4.00	15.25
RSB0742	79.5	15.50	0.48	32.29
RSB0552-CDR2-58.68A	58.68	23.50	1.25	18.80
RSB0552-CDR2-41.6A	41.6	86.50	0.64	135.16
RSB0552-CDR2-38.43A	38.43	93.50	4.00	23.38
RSB0552-CDR2-36.8A	36.8	29.50	0.21	140.48
RSB0552-CDR2-36.0A	36	94.50	1.58	59.81
RSB0552-CDR2-35.55A	35.55	34.50		
RSB0556-KMT1-35.08	35.08	108.50	6.33	17.14
RSB0552-CDR2-24.25A	24.25	19.00	0.59	32.20
RSB0552-CDR2-22.8A	22.8	43.50	0.24	181.25
RSB0527-CDR4-17.62B	17.62	82.00	7.62	10.76
RSB0527-CDR4-17.0A	17	73.50	1.90	38.68
RSB0527-CDR4-16.9A	16.9	68.00	0.78	87.18
RSB0527-CDR4-13.2A	13.2	42.00	1.31	32.06
RSB0527-CDR4-12.4A	12.4	23.00	0.64	35.94
RSB0527-CDR4-12.0A	12	41.00	1.20	34.17
RSB0527-CDR4-11.6A	11.6	37.00	0.84	44.05
RSB0527-CDR4-11.2A	11.2	36.50	1.66	21.99
RSB0527-CDR4-10.2A	10.2	77.50	6.76	11.46
RSB0527-CDR4-08.0A	8	60.00	5.81	10.33
RSB0527-CDR4-05.2A	5.2	74.00	8.06	9.18
RSB0527-CDR4-03.7A	3.7	77.50	8.46	9.16
RSB0749-10.75	0.92	60.00	2.95	20.34
RSB0749-10.35	0.52	72.00	3.36	21.43
RSB0749-09.80	-0.23	24.00	1.12	21.43
RSB0749-08.63	-1.2	13.00	1.20	10.83
RSB0749-08.33	-1.5	29.00	1.12	25.89
RSB0749-08.03	-1.8	62.50	1.99	31.41
RSB0749-07.73	-2.1	20.00	1.52	13.16
RSB0543-CWC1-m2.1A	-2.1	103.00	2.72	37.87
RSB0749-07.43	-2.4	29.00	2.20	13.18
RSB0749-05.60	-4.23	66.00	1.42	46.48
RSB0749-01.43	-8.4	70.00	0.92	76.09
RSB0749-01.38	-8.45	35.50	3.43	10.35

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Utah composite***All data are new for Chapter 5*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
RSB0749-01.28	-8.55	34.50	3.64	9.48
RSB0749-01.18	-8.65	36.50	2.65	13.77
CWC2-m19.5A	-19.5	90.00	0.30	300.00
RSB0731	-30.7	163.00	1.93	84.46
RSB0730	-31.6	205.50	7.33	28.04
BKM1-07.4A	-62.6	215.00	12.72	16.90
RSB0534-BKM1-05.6A	-64.4	207.00	2.18	94.95
BKM1-03.8A	-66.2	53.50	3.23	16.56

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**IODP 1138A (Kerguelen Plateau)***TOC data from Dickson et al. (2017)*

Depth (mbsf)	Hg (ppb)	TOC (%wt)	Hg/TOC
654.31	39	0.783	49.817
654.36	61	0.590	103.350
654.41	50.5	0.958	52.741
654.465	119	5.909	20.139
654.51	50	4.997	10.006
654.56	43	0.986	43.621
654.62	101	1.450	69.632
654.665	97.5	4.168	23.391
654.725	65	3.214	20.224
654.76	73.5	3.724	19.736
654.82	65	0.477	136.188
654.86	69.5	0.677	102.708
654.905	65	0.974	66.760
655.01	70.5	2.561	27.532
655.06	58.5	1.557	37.568
655.115	73.5	1.407	52.251
655.16	108.5	3.610	30.055
655.21	87.5	5.998	14.588
655.265	76	1.140	66.648
655.32	82.5	1.530	53.910
655.36	99.5	5.186	19.188
655.41	78	6.049	12.894
655.465	76.5	0.734	104.273
655.51	80	0.996	80.307
655.56	148	6.512	22.728
655.595	80.5	1.134	70.987
655.595	140.5	1.326	105.971
655.6	80.5	1.672	48.144
655.63	80	2.767	28.913
655.65	96.5	1.920	50.263
655.685	82	1.417	57.879
655.71	98	1.168	83.869
655.75	70.5	1.318	53.495
655.78	128	4.362	29.347
655.81	92	4.620	19.915
655.84	120	5.319	22.559

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**IODP 1138A (Kerguelen Plateau)***TOC data from Dickson et al. (2017)*

Depth (mbsf)	Hg (ppb)	TOC (%wt)	Hg/TOC
655.89	137	9.775	14.016
655.94	152.5	12.353	12.346
655.99	118	4.481	26.333
656.04	174.5	9.962	17.517
656.08	115.5	5.458	21.161
656.14	136	9.074	14.988
656.19	149.5	12.340	12.115
656.24	179.5	14.916	12.034
656.285	175	12.166	14.384
656.34	170	10.700	15.888
656.39	188.5	16.987	11.097
656.44	136	3.670	37.054
656.49	72.5	1.308	55.446
656.54	93	2.416	38.488
656.59	69	0.910	75.788
656.64	93.5	1.176	79.485
656.69	73	0.900	81.095
656.74	59	0.514	114.784
656.79	59	0.414	142.525
656.84	61.5	0.655	93.925
656.89	32.5		
656.95	28	0.255	109.605
657	23.5		
657.05	17.5	0.517	33.837
657.08	9.5	0.498	19.083
657.1	10.1	0.416	24.251
657.14	10.9	0.424	25.682
657.19	9.4	0.428	21.938
657.24	31.5	0.272	115.852
657.29	14	0.430	32.544
657.34	20	0.440	45.448
657.39	15.5	0.625	24.812
657.44	10.3	0.361	28.548
657.49	21.5	0.781	27.543
657.54	10.5	0.616	17.057
657.59	13	0.562	23.137

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**IODP 1138A (Kerguelen Plateau)***TOC data from Dickson et al. (2017)*

Depth (mbsf)	Hg (ppb)	TOC (%wt)	Hg/TOC
657.64	7.4	0.597	12.405
657.69	14	0.624	22.445
657.74	7.9	0.476	16.592
657.79	4.4	0.258	17.050
657.84	10.8	0.340	31.732
657.89	11.9	0.322	36.900
657.95	10.3	0.153	67.202
657.99	1.5	0.270	5.553
658.04	3	0.112	26.707
658.09	12	0.289	41.537
658.15	16.5	0.326	50.575
658.2	7	0.249	28.159
658.24	3.1	0.268	11.548

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Eastbourne***All data are new for Chapter 5*

Sample	Height (m)	Hg (ppb)
WC 6.0	19.9	24
WC 5.8	19.7	17
WC 5.6	19.5	7
WC 5.4	19.3	15
WC 5.2	19.1	8
WC 5.0	18.9	8.6
WC 4.8	18.7	7.9
WC 4.6	18.5	23
WC 4.4	18.3	18
WC 4.2	18.1	14
WC 4.0	17.9	12
WC 3.8	17.7	10.6
WC 3.6	17.5	9
WC 3.4	17.3	12.5
WC 3.2	17.1	5.7
WC 3.0	16.9	9.5
WC 2.8	16.7	14
WC 2.6	16.5	9.2
WC 2.4	16.3	9.1
WC 2.2	16.1	6.6
WC 2.0	15.9	8.8
WC 1.8	15.7	13.5
WC 1.6	15.5	13
WC 1.4	15.3	5.4
WC 1.2	15.1	14.5
WC 1.0	14.9	8.2
WC 0.8	14.7	52.5
WC 0.6	14.5	18.5
WC++40	14.4	
WC 0.4	14.3	14.5
WC 0.2	14.1	4.4
PM 800	14	8.6
WC 0.0	13.9	
PM 780	13.8	2.5
PM 760	13.6	0
PM 740	13.4	16.5

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Eastbourne***All data are new for Chapter 5*

Sample	Height (m)	Hg (ppb)
PM 720	13.2	1.6
PM 700	13	2.1
PM 680	12.8	44.5
PM 660	12.6	7.8
PM 640	12.4	11.3
PM 620	12.2	9.6
PM 600	12	19.5
PM 580	11.8	13.5
PM 560	11.6	19.5
PM 540	11.4	27.5
PM 520	11.2	14
PM 500	11	18.5
PM 480	10.8	6.9
PM 460	10.6	
PM 440	10.4	3.6
PM 420	10.2	3.5
PM 400	10	2.4
PM 380	9.8	8.3
PM 360	9.6	6.6
PM 340	9.4	6.4
PM 320	9.2	2.8
PM 300	9	
PM 280	8.8	13.5
PM 260	8.6	9
PM 240	8.4	7.9
PM 220	8.2	8.1
PM 200	8	13.5
PM 180	7.8	21
PM 160	7.6	16.5
PM 140	7.4	17
PM 120	7.2	12.2
PM 100	7	19
PM 80	6.8	11.1
PM 60	6.6	13.5
PM 40	6.4	13
PM 20	6.2	14

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Eastbourne***All data are new for Chapter 5*

Sample	Height (m)	Hg (ppb)
GC 0	6	11
GC 20	5.8	7.7
GC 40	5.6	
GC 60	5.4	8.9
GC 80	5.2	12
GC 100	5	7.3
GC 120	4.8	7.5
GC 140	4.6	2.6
GC 160	4.4	9.8
GC 180	4.2	6.5
GC 200	4	14
GC 220	3.8	10.5
GC 240	3.6	11
GC 260	3.4	15.5
GC 280	3.2	11
GC 300	3	21
GC 320	2.8	5
GC 340	2.6	13
GC 360	2.4	7.1
GC 380	2.2	9.3
GC 400	2	9
GC 420	1.8	
GC 440	1.6	6.3
GC 460	1.4	10
GC 480	1.2	0
GC 500	1	9.4
GC 520	0.8	11.7
GC 540	0.6	7.4
GC 560	0.4	25.5
GC 580	0.2	11
GC 600	0	5.9

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Pont d'Issole and Vergons***TOC data from Jarvis et al. (2011) and personal communication from Ian Jarvis*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
isl51b	23.50	69	1.49	46.309
isl51a	23.30	41.5	0.19	218.421
isl51	23.00	24.5	0.07	350.000
isl50	22.50	177.5	0.26	682.692
isl49a	21.80	50	0.11	454.545
isl49	21.00	35.5	0.07	507.143
isl48	20.55	78.5	0.67	117.164
isl47	20.05	35.5	0.13	273.077
isl46	19.75	92.5	0.21	440.476
isl44	19.20	114.5	0.12	954.167
isl43	19.00	170	0.34	500.000
isl41	18.40	174	0.41	424.390
isl40	17.90	41.5	0.26	159.615
isl39	17.45	95	0.39	243.590
isl37	17.10	74	1.23	60.163
isl36	16.70	67	0.4	167.500
isl35	16.25	28.5	0.3	95.000
isl34	15.90	158.5	1.73	91.618
isl33	15.60	29.5	0.23	128.261
isl32	15.15	191	3.54	53.955
isl31n	15.00	94	0.9	104.444
isl30n	14.50	105	2.11	49.763
isl29n	14.00	148.5	0.31	479.032
isl27n	13.00	94	0.29	324.138
isl26n	12.50	71	0.5	142.000
isl25n	12.00	94.5	1.23	76.829
isl23	11.30	98	1.47	66.667
isl21	10.30	65	0.29	224.138
isl20	9.95	69.5	0.07	992.857
isl19	9.75	28.5	0.25	114.000
isl18	9.55	77.5	0.12	645.833
isl17	9.40	50	0.2	250.000
isl16a	9.05	52.5	0.32	164.063
isl15a	8.75	58.5	0.24	243.750
isl15	8.45	44.5	0.33	134.848
isl14b	8.05	14	0.13	107.692

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Pont d'Issole and Vergons**

TOC data from Jarvis et al. (2011) and personal communication from Ian Jarvis

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
isl14a	7.60	31.5	0.21	150.000
isl14	7.20	62.5	0.17	367.647
isl13	6.75	101	1.34	75.373
isl12	6.05	123	0.63	195.238
isl11	5.40	75.5	0.74	102.027
isl10a	4.80	118	1.69	69.822
isl10	4.20	56	0.4	140.000
isl9	3.50	90	1.44	62.500
isl8	2.80	138.5	2.19	63.242
isl7	2.25	105	0.64	164.063
isl6	1.80	44.5	0.12	370.833
vgn436.5n	1.50	11.9	0.11	108.182
vgn436	1.00	11.5		
isl4	0.80	27.5	0.1	275.000
isl2	0.00	22.5	0.11	204.545
vgn435	0.00	14	0.23	60.870
vgn433	-2.00	15.5	0.22	70.455
vgn432	-3.00	36.5	0.17	214.706
vgn431	-4.00	29.5	0.12	245.833
vgn430	-5.00	48.5	0.34	142.647
vgn429	-6.00	58	0.29	200.000
vgn428	-7.00	71.5	0.18	397.222
vgn427	-8.00	16.5	0.13	126.923
vgn423	-12.00	72.50	0.21	344.180
vgn421	-14.00	31.00	0.13	232.108
vgn419	-16.00	89.00	0.30	294.269
vgn417	-18.00	24.50	0.17	142.232
vgn415	-20.00	166.50	0.34	482.966
vgn413	-22.00	125.50	0.22	567.042
vgn411	-24.00	36.50	0.26	137.854
vgn409	-26.00	44.50	0.16	274.088
vgn407	-28.00	113.00	0.22	508.841
vgn405	-30.00	66.00	0.22	305.250
vgn403	-32.00	13.00	0.11	115.239
vgn401	-34.00	82.50	0.21	395.646
vgn399	-36.00	44.50	0.15	288.517

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Pont d'Issole and Vergons***TOC data from Jarvis et al. (2011) and personal communication from Ian Jarvis*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
vgn397	-38.00	45.00	0.26	170.870
vgn395	-40.00	137.50	0.35	387.846
vgn393	-42.00	102.50	0.30	339.446
vgn391	-44.00	28.00	0.22	125.107
vgn389	-46.00	39.50	0.17	233.131
vgn387	-48.00	31.00	0.28	111.482
vgn385	-50.00	56.00	0.36	157.266
vgn383	-52.00	49.50	0.36	137.929
vgn381	-54.00	60.50	0.26	235.378
vgn379	-56.00	67.00	0.29	227.917
vgn377	-58.00	40.50	0.25	159.152
vgn375	-60.00	44.00	0.29	151.919
vgn373	-62.00	59.00	0.28	209.743
vgn371	-64.00	61.50	0.22	277.300
vgn369	-66.00	92.50	0.26	356.923
vgn367	-68.00	22.50	0.27	83.824
vgn365	-70.00	58.50	0.22	260.735
vgn363	-72.00	23.00	0.21	110.539
vgn361	-74.00	38.50	0.23	166.654
vgn359	-76.00	55.50	0.34	162.383
vgn357	-78.00	45.67	0.23	202.251
vgn355	-80.00	86.50	0.28	305.335
vgn353	-82.00	58.50	0.38	153.778
vgn351	-84.00	21.50	0.44	48.813
vgn349	-86.00	77.50	0.22	359.027
vgn347	-88.00	84.00	0.24	347.759
vgn345	-90.00	74	0.32	228.694
vgn343	-92.00	123.5	0.38	322.655
vgn341	-94.00	72	0.26	278.020
vgn339	-96.00	69	0.36	191.718
vgn337	-98.00	50.5	0.28	180.577
vgn335	-100.00	62	0.37	167.341
vgn333	-102.00	48.5	0.34	141.884
vgn331	-104.00	61	0.28	219.022
vgn329	-106.00	106.5	0.28	382.108
vgn327	-108.00	41	0.22	187.761

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Pont d'Issole and Vergons**

TOC data from Jarvis et al. (2011) and personal communication from Ian Jarvis

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
vgn325	-110.00	39.50	0.31	128.829

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Clot Chevalier***TOC data from personal communication from Andy Gale*

Height (cm)	Hg (ppb)	TOC (%wt)	Hg/TOC
3510	27.5	0.10	275.000
3480	46	0.12	383.333
3450	37	0.07	528.571
3420	35.5	0.13	273.077
3390	73	0.18	405.556
3360	21.5	0.08	268.750
3330	29	0.10	290.000
3300	60	0.07	857.143
3270	36	0.08	450.000
3240	27	0.12	225.000
3210	41	0.05	820.000
3180	25.5	0.05	510.000
3150	26.5	0.10	265.000
3120	25.5	0.14	182.143
3090	30.5	0.11	277.273
3060	27	0.08	337.500
3030	31	0.06	516.667
3000	32	0.14	228.571
2970	30	0.12	250.000
2940	24.5	0.13	188.462
2910	37	0.73	50.685
2880	68	0.11	618.182
2850	28.5	0.12	237.500
2820	46	0.10	460.000
2790	44	0.14	314.286
2760	72	0.12	600.000
2730	70.5	0.20	352.500
2700	56	0.16	350.000
2670	41	0.17	241.176
2640	55.5	0.13	426.923
2610	44.5	0.16	278.125
2580	36.5	0.10	365.000
2550	73.5	0.13	565.385
2520	66.5	0.28	237.500
2490	27.5	0.19	144.737
2460	35	0.27	129.630

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Clot Chevalier***TOC data from personal communication from Andy Gale*

Height (cm)	Hg (ppb)	TOC (%wt)	Hg/TOC
2430	116	0.40	290.000
2400	68.5	0.22	311.364
2370	52	0.23	226.087
2340	38	0.35	108.571
2310	34	0.47	72.340
2280	19	0.21	90.476
2250	21.5	0.24	89.583
2220	44.5	1.11	40.090
2190	37	0.53	69.811
2160	20	0.22	90.909
2130	31	0.25	124.000
2100	32.5	0.29	112.069
2070	29	0.40	72.500
2040	18	0.28	64.286
2010	43.5	0.60	72.500
1980	39.5	1.13	34.956
1950	19.5	0.10	195.000
1920	36	0.47	76.596
1890	30	0.94	31.915
1860	74.5	1.34	55.597
1830	38.5	1.16	33.190
1800	39.5	1.45	27.241
1770	23.5	0.31	75.806
1740	40.5	1.38	29.348
1710	31	1.07	28.972
1680	43	0.60	71.667
1650	34	1.38	24.638
1620	24.5	0.83	29.518
1590	26	1.07	24.299
1560	52.5	1.36	38.603
1530	39.5	0.78	50.641
1500	41	0.10	410.000
1470	46.5	0.22	211.364
1440	46.5	0.20	232.500
1410	30.5	0.34	89.706
1380	38.5	0.36	106.944

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Clot Chevalier***TOC data from personal communication from Andy Gale*

Height (cm)	Hg (ppb)	TOC (%wt)	Hg/TOC
1350	39.5	0.70	56.429
1320	42.5	1.06	40.094
1290	27	1.03	26.214
1260	35	1.35	25.926
1230	35.5	1.67	21.257
1200	60.5	1.18	51.271
1170	25.5	0.40	63.750
1140	23	0.23	100.000
1110	32.5	1.10	29.545
1080	25	1.20	20.833
1050	27.5	1.07	25.701
1020	25.5	1.39	18.345
990	28	0.29	96.552
960	36	0.42	85.714
930	27.5	1.05	26.190
900	25	1.36	18.382
870	31	1.05	29.524
840	18	0.60	30.000
810	21.5	1.03	20.874
780	18	1.36	13.235
750	23	1.50	15.333
720	19.5	1.46	13.356
690	21.5	1.53	14.052
660	18.5	1.15	16.087
630	12.5	0.24	52.083
600	16.5	0.35	47.143
570	22.5	0.23	97.826
540	8	0.11	72.727
510	38.5	1.07	35.981
480	18	0.30	60.000
450	9.6	0.20	48.000
420	13	0.17	76.471
390	15	0.22	68.182
360	9.5	0.12	79.167
330	6.8	0.09	75.556
300	27	1.63	16.564

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Clot Chevalier***TOC data from personal communication from Andy Gale*

Height (cm)	Hg (ppb)	TOC (%wt)	Hg/TOC
270	61	0.41	148.780
240	58.5	1.03	56.796
210	6.7	0.11	60.909
180	8	0.18	44.444
150	7	0.12	58.333
120	9.2	0.15	61.333
90	11	0.17	64.706
60	7.5	0.11	68.182
30	6.6	0.06	110.000
0	9.3	0.28	33.214

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Furlo***All data are new for Chapter 5*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
BF 48	1.295	88		
BF 47	1.285	62	0.14	442.857
BF 46	1.27	146		
BF 44	1.215	451.5		
BF 43	1.195	135.5	0.16	846.875
BF 42	1.18	253		
BF 41	1.16	212		
BF 40	1.14	260	3.31	78.550
BF 39	1.11	95.5		
BF 36	1.035	276.5	3.37	82.047
BF 34	0.995	652.5	11.09	58.837
BF 33	0.955	570		
BF 32	0.93	479		
BF 30	0.905	264	6.18	42.718
BF 29	0.885	129.5		
BF 28	0.85	36		
BF 26	0.8	220.5	9.77	22.569
BF 25	0.775	84		
BF 24	0.74	106		
BF 23	0.705	890	7.5	118.667
BF 22	0.67	550.5		
BF 21	0.63	203.5		
BF 20	0.56	311	5.1	60.980
BF 19	0.49	317		
BF 18	0.445	80		
BF 17	0.415	255.5		
BF 15	0.35	1215	9.42	128.981
BF 14	0.325	254		
BF 13	0.315	29.5		
BF 12	0.3	14		
BF 11	0.275	182	6.1	29.836
BF 9	0.21	25.5		
BF 7	0.145	171.5	4.04	42.450
BF 6	0.105	298	3.45	86.377
BF 5	0.085	65		
BF 4	0.075	338	4.9	68.980

Data tables E: OAE 2 data: Hg, TOC, Hg/TOC**Furlo***All data are new for Chapter 5*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
BF 2	0.035	115.5		
BF 1	0.015	190.5	1.97	96.701
F. Bon -168	-1.68	18.5		
F. Bon -301	-3.01	1885	8.6	219.186
F. Bon - 322	-3.22	468		
F. Bon -392	-3.92	398	8.09	49.197
F. Bon -414	-4.14	171	3.21	53.271
F. Bon -435	-4.35	550		
F. Bon -455	-4.55	786	9.22	85.249
F. Bon -712	-7.12	41	1.19	34.454
F. Bon -799	-7.99	1120	11.25	99.556
F. Bon -824	-8.24	455.5		
F. Bon -850	-8.5	53	0.37	143.243
F. Bon -978	-9.78	5.4		
F. Bon -1082	-10.82	780	3.07	254.072
F. Bon -1173	-11.73	74	2.15	34.419
F. Bon -1199	-11.99	53.5		
F. Bon -1286	-12.86	332.5	4.16	79.928
F. Bon -1464	-14.64	82	0.83	98.795
F. Bon -1564	-15.64	1420	6.26	226.837
F. Bon -1565.5	-15.655	34.5		
F. Bon -1646	-16.46	60.5	0.27	224.074
F. Bon -1803	-18.03	26	0.08	325.000
F. Bon -1829	-18.29	30.5		

Data tables F: K–Pg data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Seymour Island***All data are new for Chapter 5*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
D6.004.44	14.8	32.5	0.390	83.272
D6.004.43	14.3	29.5	0.394	74.886
D6.004.42	13.8	30.5	0.338	90.254
D6.004.41	13.3	36.5	0.286	127.563
D6.004.40	12.8	31.5	0.275	114.383
D6.004.39	12.3	18	0.235	76.626
D6.004.38	11.8	26	0.353	73.682
D6.004.37	11.3	29	0.296	98.110
D6.004.36	10.8	20	0.276	72.353
D6.004.35	10.3	24	0.320	74.897
D6.004.34	9.8	27.5	0.296	93.052
D6.004.33	9.3	33	0.279	118.478
D6.004.32	8.8	28	0.301	93.148
D6.004.31	8.3	26	0.335	77.578
D6.004.30	7.8	23.5	0.289	81.290
D9.035.1	7.65	14	0.32	43.750
D6.004.29	7.3	24	0.345	69.583
D6.004.28	6.8	24	0.309	77.667
D6.004.27	6.3	17	0.359	47.415
D6.004.26	5.8	15.5	0.263	59.017
D6.004.25	5.3	16.5	0.252	65.356
D6.004.24	4.8	25.5	0.305	83.544
D6.004.23	4.3	39.5	0.230	171.517
D6.004.22	3.8	38.5	0.400	96.213
D6.004.21	3.3	25	0.323	77.285
D6.004.20	2.8	45	0.295	152.646
D9.032.1	2.65	16.5	0.17	97.059
D6.004.19	2.3	19	0.310	61.255
D6.004.18	1.8	16	0.310	51.630
D6.004.17	1.3	27	0.299	90.290
D6.004.16	0.8	20	0.360	55.583
D6.004.15	0.3	30	0.300	99.904
D9.029.1	-0.15	20.5	0.37	55.405
D6.004.14	-0.3	16	0.232	68.922
D5.1292.1	-0.5	13.5	0.390	34.615
D6.004.13	-0.8	46.5	0.518	89.754

Data tables F: K–Pg data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Seymour Island***All data are new for Chapter 5*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
D9.009.1	-1.05	19	0.38	50.000
D6.004.12	-1.3	43	0.477	90.141
D9.028.1	-1.35	19.5	0.36	54.167
D6.004.11	-1.8	39.5	0.372	106.231
D6.004.10	-2.3	37.5	0.440	85.249
D6.004.9	-2.8	48.5	0.350	138.683
D9.026.1	-2.85	31	0.30	103.333
D9.008.1	-2.85	18	0.36	50.000
D6.004.8	-3.3	31	0.404	76.746
D5.1289.1	-3.5	23	0.430	53.488
D6.004.7	-3.8	30	0.357	84.068
D6.004.6	-4.3	46	0.343	133.975
D6.004.5	-4.8	35.5	0.310	114.572
D6.004.4	-5.3	31	0.315	98.398
D6.004.3	-5.8	24.5	0.377	65.032
D9.007.1	-5.85	27	0.42	64.286
D6.004.2	-6.3	34	0.379	89.793
D6.004.1	-6.8	31.5	0.359	87.770
D5.1279.1	-13.5	18	0.430	41.860
D9.006.1	-14.85	25.5	0.49	52.041
D5.1253.1	-19.5	22	0.500	44.000
D5.1268.1	-23.5	17.5	0.540	32.407
D5.1248.1	-29.5	20	0.29	68.966
D5.1258.1	-33.5	17	0.32	53.125
D5.1242.1	-39.5	17.5	0.35	50.000
D5.1237.1	-49.5	16	0.37	43.243
D5.1230.1	-59.5	17.5	0.26	67.308
D5.1225.1	-67.5	19.5	0.22	88.636
D5.1120.1	-77.5	15	0.2	75.000
D5.1215.1	-87.5	17.5	0.27	64.815
D5.1210.1	-97.5	21.5	0.31	69.355
D5.1205.1	-107.5	14	0.24	58.333
D5.1198.1	-117.5	22.5	0.27	83.333
D5.1192.1	-127.5	19.5	0.19	102.632
D5.1187.1	-137.5	19.5	0.31	62.903
D5.1184.1	-141.5	24	0.29	82.759

Data tables F: K–Pg data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Seymour Island***All data are new for Chapter 5*

Sample	Height (m)	Hg (ppb)	TOC (%wt)	Hg/TOC
D5.1179.1	-151.5	20	0.3	66.667
D5.1174.1	-161.5	19	0.28	67.857
D5.1168.1	-171.5	13	0.12	108.333
D5.1165.1	-174.5	12	0.51	23.529
D5.1162.1	-177.5	15.5	0.35	44.286
D5.1160.1	-181.5	17.5	0.26	67.308
D5.1155.1	-191.5	13	0.23	56.522
D5.1151.1	-199.5	10.6	0.15	70.667
D5.1147.1	-211.5	26.5	0.44	60.227
D5.1142.1	-221.5	14	0.18	77.778
D5.1137.1	-231.5	15	0.33	45.455
D5.1132.1	-241.5	18	0.31	58.065
D5.1128.1	-251.5	23.5	0.4	58.750
D5.1121.1	-261.5	27.5	0.49	56.122
D5.1116.1	-271.5	24.5	0.63	38.889
D5.1106.1	-281.5	18.5	0.43	43.023
D5.1096.1	-291.5	20.5	0.33	62.121
D5.1086.1	-301.5	13.5	0.34	39.706
D5.1077.1	-311.5	21	0.33	63.636
D5.1061.1	-326.5	24.5	0.44	55.682
D5.1051.1	-336.5	18	0.4	45.000
D5.1040.1	-346.5	19.5	0.37	52.703
D5.1032.1	-356.5	18.5	0.39	47.436
D5.1021.1	-366.5	17	0.37	45.946
D5.1011.1	-376.5	21.5	0.51	42.157
D5.1001.1	-386.5	21	0.43	48.837

Data tables F: K–Pg data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Bass River (IODP 174AX)***All data are new for Chapter 5*

Depth (mcd)	Hg (ppb)	TOC (%wt)	Hg/TOC
383.499	17	0.2	85.000
383.667	14.5	0.19	76.316
383.850	23.5	0.74	31.757
384.292	15	1.14	13.158
384.429	30	1.14	26.316
384.475	44	1.29	34.109
384.536	42	1.04	40.385
384.597	36.5	1.09	33.486
384.673	30.5	1.22	25.000
384.734	27	1.19	22.689
384.810	21	1.16	18.103
384.932	37	0.95	38.947
385.084	40	0.77	51.948
385.176	29.5	1.01	29.208
385.298	17	1.26	13.492
385.404	22.5	0.85	26.471
385.465	23.5	1.31	17.939
385.587	23.5	0.94	25.000
385.892	28	0.55	50.909
385.938	34.5	1.02	33.824
385.999	29	0.66	43.939
386.044	28.5	0.89	32.022
386.090	22.5	0.9	25.000
386.151	26	1.15	22.609
386.197	30.5	1.13	26.991
386.243	26.5	1.18	22.458
386.304	35	1.07	32.710
386.349	29.5	1.1	26.818
386.410	30.5	1.06	28.774
386.456	32.5	1.1	29.545
386.502	30	0.85	35.294
386.563	26.5	0.88	30.114
386.608	28.5	1.04	27.404
386.654	38	1.06	35.849
386.715	19	0.66	28.788
386.761	50	0.94	53.191

Data tables F: K–Pg data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Bass River (IODP 174AX)***All data are new for Chapter 5*

Depth (mcd)	Hg (ppb)	TOC (%wt)	Hg/TOC
386.806	84	0.78	107.692
386.852	29.5	0.47	62.766
386.913	43	0.61	70.492
386.959	36	0.91	39.560
387.020	47.5	0.86	55.233
387.066	41	0.8	51.250
387.111	51	0.9	56.667
387.172	40.5	0.64	63.281
387.218	38	0.93	40.860
387.279	42.5	0.89	47.753
387.325	32.5	0.99	32.828
387.370	40	0.86	46.512
387.431	35	0.49	71.429
387.477	28	0.7	40.000
387.523	32.5	1.02	31.863
387.584	40.5	0.75	54.000
387.629	33.5	0.87	38.506
387.660	37	0.49	75.510
387.736	47.5	0.77	61.688
387.782	51.5	0.66	78.030
387.828	38	0.56	67.857
387.858	30.5	0.29	105.172
387.904	17	0.29	58.621
387.980	28.5	0.36	79.167

Data tables F: K–Pg data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Zumaia***Al₂O₃ data from Batenburg et al. (2012)*

Sample	Depth (cm)	Hg (ppb)	TOC (%wt)	Al ₂ O ₃ (%wt)
ZK 1	-4.9	13	0.22	7.96
ZK 2	-14.6	6.9		4.64
ZK 3	-24.4	6.8		6.48
ZK 4	-34.1	10		7.79
ZK 5	-44.8	5.7	0.13	7.35
ZK 6	-56.3	10		7.98
ZK 7	-70.5	9.9		8.51
ZK 8	-83.3	18	0.09	9.45
ZK 9	-92.0	6.9	0.09	8.14
ZK 10	-100.7	4.3		8.13
ZK 11	-111.3	3.8		7.63
ZK 12	-123.8	11.5	0.17	9.58
ZK 13	-136.3	20	0.17	7.87
ZK 14	-149.0	7.5		10.12
ZK 15	-161.7	9.3	0.15	11.04
ZK 16	-175.3	4.4		10.14
ZK 17	-189.3	4.1		6.63
ZK 18	-198.3	8.2		8.31
ZK 19	-204.8	4.4	0.31	9.52
ZK 20	-219.0	4.7		8.99
ZK 21	-236.2	18.5		10.58
ZK 22	-248.5	15		11.98
ZK 23	-260.8	29	0.15	12.14
ZR 30	-281.0	47	0.07	12.63
ZR 29	-291.6	19.5	0.13	11.16
ZR 28	-302.3	11	0.15	10.18
ZR 27	-312.9	12.5	0.02	10.59
ZR 26	-323.5	13.5	0.12	11.53
ZR 25	-334.1	8.8	0.24	11.00
ZR 24	-344.8	4.6	0.19	11.24
ZR 23	-355.4	8.4	0.07	11.54
ZR 22	-366.0	23	0.1	12.16
ZR 21	-376.6	9.5	0.09	11.92
ZR 20	-387.3	3	0.08	11.43
ZR 19	-397.9	9.7		11.24
ZR 18	-408.5	7.1	0.03	10.88

Data tables F: K–Pg data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Zumaia***Al₂O₃ data from Batenburg et al. (2012)*

Sample	Depth (cm)	Hg (ppb)	TOC (%wt)	Al ₂ O ₃ (%wt)
ZR 17	-419.1	2.6		9.81
ZR 16	-429.8	4.3		10.32
ZR 15	-440.4	4.5		10.47
ZR 14	-451.0	7.9		11.20
ZR 13	-461.7	22	0	11.99
ZR 12	-472.3	26	0.06	11.73
ZR 11	-482.9	7.1		10.68
ZR 10	-493.5	10		10.35
ZR 9	-504.2	9.2		10.08
ZR 8	-514.8	11.5	0.12	9.65
ZR 7	-525.4	7.3		10.52
ZR 6	-536.0	6.4	0.1	11.57
ZR 5	-546.7	5.5		11.77
ZR 4	-557.3	13		12.27
ZR 3	-567.9	10		12.08
ZR 2	-578.5	6	0.03	9.37
ZR 1	-589.2	6.6		12.11
ZU 100	-1558.0	7.3		7.29
ZU 99	-1568.0	6.2		7.58
ZU 98	-1578.0	5.9		8.20
ZU 97	-1587.1	3.7		6.27
ZU 96	-1595.4	5.5		6.87
ZU 95	-1603.7	4.1		8.27
ZU 94	-1612.0	23.5		8.41
ZU 93	-1620.3	18		7.88
ZU 92	-1628.6	4.6		7.73
ZU 91	-1636.9	3		7.84
ZU 90	-1646.5	3.56667		6.76
ZU 89	-1657.5	3.5		5.84
ZU 88	-1668.5	3.5		6.80
ZU 87	-1679.5	4.8		8.63
ZU 86	-1690.5	8.5		8.78
ZU 85	-1701.5	21.5		10.38
ZU 84	-1712.5	8.7		9.60
ZU 83	-1723.5	4.4		8.05
ZU 82	-1734.3	3.7		5.61

Data tables F: K–Pg data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Zumaia***Al₂O₃ data from Batenburg et al. (2012)*

Sample	Depth (cm)	Hg (ppb)	TOC (%wt)	Al ₂ O ₃ (%wt)
ZU 81	-1744.9	3.2		6.97
ZU 80	-1755.6	3.2		6.67
ZU 79	-1766.2	4.8		6.72
ZU 78	-1776.8	15		9.62
ZU 77	-1787.4	12		10.46
ZU 76	-1798.1	7.4		10.31
ZU 75	-1808.7	15.5		9.93
ZU 74	-1820.6	3.7		7.75
ZU 73	-1833.7	2.3		5.76
ZU 72	-1846.8	3		6.68
ZU 71	-1859.9	3.03333		7.35
ZU 70	-1873.1	2.3		6.96
ZU 69	-1886.2	17.5		11.51
ZU 68	-1899.3	21		11.40
ZU 67	-1912.4	32.5		12.28
ZU 66	-1923.0	4.5		7.40
ZU 65	-1931.0	4.5		7.36
ZU 64	-1939.0	9.2		7.65
ZU 63	-1947.0	15		7.91
ZU 62	-1955.0	38		9.79
ZU 61	-1969.6	46		11.88
ZU 60	-1980.9	39		11.59
ZU 59	-1992.1	15		10.71
ZU 58	-2003.4	3.8		8.60
ZU 57	-2014.3	3.4		7.59
ZU 56	-2024.8	3.3		6.92
ZU 55	-2035.4	1.9		7.40
ZU 54	-2045.9	4.2		8.21
ZU 53	-2056.5	5.1		8.41
ZU 52	-2067.1	5.5		8.93
ZU 51	-2077.6	14.5		10.18
ZU 50	-2088.2	8.4		9.94
ZU 49	-2098.7	12.5		9.47
ZU 48	-2109.4	7		9.02
ZU 47	-2120.1	5.3		8.61
ZU 46	-2130.8	2.9		8.91

Data tables F: K–Pg data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Zumaia***Al₂O₃ data from Batenburg et al. (2012)*

Sample	Depth (cm)	Hg (ppb)	TOC (%wt)	Al ₂ O ₃ (%wt)
ZU 45	-2141.5	4.4		8.25
ZU 44	-2152.2	3.86667		9.07
ZU 43	-2162.9	4.23333		9.51
ZU 42	-2173.6	5.6		9.59
ZU 41	-2184.3	8.9		11.24
ZU 40	-2195.0	19		11.06
ZU 39	-2205.7	9.7		10.67
ZU 38	-2216.8	6.1		9.07
ZU 37	-2228.5	3.5		8.82
ZU 36	-2240.2	2.9		9.14
ZU 35	-2251.8	4.9		8.86
ZU 34	-2263.5	7.6		10.82
ZU 33	-2275.2	12		12.08
ZU 32	-2286.8	22		11.73
ZU 31	-2298.5	22.5		12.53
ZU 30	-2310.2	19.5		11.53
ZU 29	-2320.1	3.8		8.63
ZU 28	-2328.4	4.3		8.58
ZU 27	-2336.6	15.5		9.72
ZU 26	-2344.9	4.9		9.03
ZU 25	-2353.1	6.5		10.55
ZU 24	-2361.4	17.5		11.83
ZU 23	-2369.6	14		11.98
ZU 22	-2377.9	9.1		11.56
ZU 21	-2386.4	5.1		8.48
ZU 20	-2395.2	4.2		8.24
ZU 19	-2403.9	5.4		8.31
ZU 18	-2412.7	9.4		9.64
ZU 17	-2421.5	23		11.12
ZU 16	-2430.3	13.5		11.05
ZU 15	-2439.1	14		10.90
ZU 14	-2447.8	6.9		9.59
ZU 13	-2456.6	6.8		10.19
ZU 12	-2466.4	5.9		9.34
ZU 11	-2477.1	5.5		8.02
ZU 10	-2487.9	4.7		7.45

Data tables F: K–Pg data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**Zumaia***Al₂O₃ data from Batenburg et al. (2012)*

Sample	Depth (cm)	Hg (ppb)	TOC (%wt)	Al ₂ O ₃ (%wt)
ZU 9	-2498.6	7.3		7.66
ZU 8	-2509.4	6.1		9.36
ZU 7	-2520.1	7		9.92
ZU 6	-2530.9	26.5		10.67
ZU 5	-2541.6	6.3		9.98
ZU 4	-2550.1	6.4		7.42
ZU 3	-2556.4	4.4		7.44
ZU 2	-2562.6	5.1		6.93
ZU 1	-2568.9	3.3		7.71

Data tables F: K–Pg data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**East Gilbert Creek (Montana)***All data are new for Chapter 5*

Height (cm)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	Hg (ppb)	TOC (%wt)	Hg/TOC
3000	-26.40933	48.5	0.4	121.250
2970		72	0.3	240.000
2940	-26.07510	32	0.3	106.667
2910		71.5	1.6	44.688
2880	-26.06865	8	50.2	0.159
2820	-26.37501	34	30.8	1.104
2760	-25.97617	267.5	39	6.859
2730	-26.44382	50.5	0.4	126.250
2700	-25.75736	366.5	48.6	7.541
2670	-25.93067	23	0.2	115.000
2650	-25.66965	51	0.2	255.000
2640	-26.23129	42	0.2	210.000
2630	-25.90701	116.5	20.3	5.739
2620	-26.34247	99.5	0.5	199.000
2610	-26.02391	340	0.7	485.714
2580	-27.03830	36.5	0.2	182.500
2550	-26.94587	28.5	0.1	285.000
2520	-26.58713	24.5	0.1	245.000
2490	-26.35599	20	0.1	200.000
2460	-26.45871	53.5	0.2	267.500
2430		34.5	0.2	172.500
2400	-25.73689	92	1.6	57.500
2370	-26.36869	67	0.2	335.000
2340	-26.11045	38.5	0.2	192.500
2310	-25.83674	59.5	0.2	297.500
2280	-26.51390	43.5	0.3	145.000
2070		147.5	0.2	737.500
2040		34	0.2	170.000
2010		31	0.2	155.000
1980		23	0.3	76.667
1950		126.5	0.2	632.500
1920		124	0.3	413.333
1890		53.5	0.8	66.875
1860		79.5	0.9	88.333
1830		92.5	0.5	185.000
1800		138.5	0.2	692.500

Data tables F: K–Pg data: $\delta^{13}\text{C}$, Hg, TOC, and Hg/TOC**East Gilbert Creek (Montana)***All data are new for Chapter 5*

Height (cm)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	Hg (ppb)	TOC (%wt)	Hg/TOC
1770		83.5	0.6	139.167
1740		65.5	1.1	59.545
1710		116.5	1.2	97.083
1680		145	1.4	103.571
1650		67	0.6	111.667
1620		77.5	0.3	258.333
1590		66.5	0.3	221.667
1560		74.5	0.6	124.167
1530		63.5	1	63.500
1500		277.5	0.6	462.500
1470		186.5	0.5	373.000
1440		92	1.2	76.667
1380		68.5	1.1	62.273
1320		115	0.3	383.333
1260		172.5	0.2	862.500
1200		102	0.3	340.000
1140		99.5	0.2	497.500
1080		52	0.1	520.000
960		34.5	0.6	57.500
900		22.5	0.3	75.000
870		46	0.5	92.000
690		79	1	79.000
-30		262.5	1.9	138.158
-60		165.5	0.2	827.500
-90		115	0.5	230.000
-120		30.5	0.5	61.000
-150		44	0.5	88.000
-180		31	0.34	91.176