

Krypton-81 dating of the deep Continental Intercalaire aquifer with implications for chlorine-36 dating

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Abstract

Deep groundwater samples from the Continental Intercalaire (CI) aquifer in the Northern Tunisian Sahara have been analyzed for noble gases ^3He , ^4He , Ne and ^{81}Kr , and for ^{14}C to better constrain the groundwater residence time of this large transboundary aquifer. Its significant radiogenic ^4He content and background-level ^{14}C both indicate water older than a few tens of thousands of years. Distinct helium concentrations and Ne/He ratios suggest different groundwater flow paths through the Tozeur and Kebili regions. ^{81}Kr is applied for the first time on the CI aquifer, providing more direct evidence for the presence of old groundwater with $^{81}\text{Kr}/\text{Kr}$ ratios at 63% – 15% of the atmospheric value, corresponding to residence times of 150 – 630 ka. These newly obtained ^{81}Kr ages enable a re-evaluation of the previously reported data from the Tozeur region in order to better constrain the input values of $^{36}\text{Cl}/\text{Cl}$ and Cl. The initial $^{36}\text{Cl}/\text{Cl}$ ratio is found to be 4 – 6 times larger than previously assumed, and the initial Cl concentration 6 – 15 times smaller. The results of ^{81}Kr dating and the recalibrated ^{36}Cl dating define an eastward age progression across > 500 km of flow path from the Algerian to Tunisian sections. This study exemplifies the utility of ^{81}Kr not only as an independent and conservative chronometer, but also as a supplemental measurement to better calibrate the parameters required for other age tracers, including cosmogenic ^{36}Cl and radiogenic ^4He .

1. Introduction

The North Western Sahara Aquifer System (NWSAS), the most important and intensively exploited system in northern Africa (Abid et al., 2009), contains a set of layers with changing facies and thickness moving from the area of the Chotts towards the Saharan platform (Fig.1). Numerous multidisciplinary studies including chemical,

isotopic and modelling techniques have been undertaken in the Continental Intercalaire (CI) aquifer within NWSAS to aid groundwater resource management (Edmunds et al., 2003); (Chkir and Zouari, 2007); (Abid et al., 2009); (Trabelsi et al., 2009); (Abid et al., 2010); (Abid et al., 2011); (Abid et al., 2012); (Moulla et al., 2012). This deep aquifer contains water older than the 30 ka limit of radiocarbon dating (e.g., Edmunds et al., 2003). ^{36}Cl analysis also suggested the presence of non-renewable water (Guendouz and Michelot, 2006). In this study, we applied the ^{81}Kr dating method to the deeper CI aquifer in southern Tunisia. The aquifer extends from the Saharan Atlas to the extreme south of the country along 700 km of eastward flow path, towards the Algerian section. The ^{36}Cl groundwater ages estimated in a previous investigation range from 16 ka to 1 Ma with considerable uncertainties due to complicated chloride dissolution and uncertainties in the initial $^{36}\text{Cl}/\text{Cl}$ ratios (Guendouz and Michelot, 2006).

The noble gas radionuclide ^{81}Kr ($T_{1/2} = 229 \pm 11$ kyr) has proven to be a reliable tracer for studying groundwater ages and dynamics in the age range of 40 – 1,300 ka, leading to the recognition that many deep aquifers in semi-arid and arid regions are much older than the ages determined earlier by radiocarbon dating (Collon et al., 2000; Sturchio et al., 2004; Aggarwal et al., 2014; Gerber et al., 2017; Matsumoto et al., 2018; Yokochi et al., 2019). The ultralow isotopic abundance of ^{81}Kr ($< 10^{-12}$) in gases dissolved in groundwater can be analyzed using the Atom Trap Trace Analysis (ATTA) method (e.g., Chen et al., 1999; Jiang et al., 2012; Lu et al., 2014). We applied this tracer for the first time to the Tunisian part of the CI aquifer in order to better understand the age structure of this important groundwater system.

2. Field Area

The CI is the largest confined aquifer of NWSAS covering an area of about one million km². Numerous studies have already been carried out to infer the hydrogeology of the basin (Mamou et al., 2006; Edmunds et al., 1997). The CI aquifer is constituted by middle Jurassic to lower Cretaceous continental formations with heterogeneous sandy units showing variable clay content. The geological sequence of the aquifer is differentiated into several units of detrital sediments separated by clay and gypsum rich strata. The aquifer units are confined by marl and clay layers of the Cenomanian age, reaching, in some areas, a thickness of more than 600 m.

The CI aquifer covers the regions of Tozeur (or Chott basin), Kebili (or Nefzaoua basin) (Fig. 1a). It is an essential natural resource for the water supply of the area. The most important production takes place in the geothermal regions of Kebili and Tozeur with 1,000 L/s and 600 L/s withdrawn, respectively. In the Kebili region, the water bearing bed of the CI aquifer is logged in the so-called “Kebeur El Haj” formations (K.H.F) composed of alternating detrital and clayey sequences (Neocomian). In the south-eastern part of the Nefzaoua in Ksar Ghilane region (CIK 1), the CI aquifer is logged in the Albian formations (Ab.F). The reservoir depth ranges between 700 and 2,300 m with strong artesian head (150 – 170 m). The water temperature increases from 37°C in the recharge area to above 60°C at depth. In Tozeur region, the CI aquifer is principally logged in the Sidi Aich (S.A.F) sand (Lower Aptian) and Boudinar (B.D.F) formations (Barremian) at depth ranging between 1,500 and 2,500 m. The aquifer is confined and the majority of boreholes are characterized by an artesian head of 60 – 200 m above the ground level and with discharge temperature of about 70°C. Figure 1(b) and 1(c) shows a simplified cross section of the Tozeur and Kebili regions, respectively, with sampled wells.

Groundwater flow in the CI occurs along defined flow paths, despite the presence of impeding geological structures (Fig. 1a). The main flow path in Kebili basin is directed from the Tunisian Dahar in south-eastern Tunisia to the north-west discharge zone (Chotts region). The SE-NW flow direction highlights the flow line coming from the Lower Cretaceous outcrops located on the Dahar upland. The hydrogeological settings show evidence of active recharge in these outcrops through water runoff, especially evident in the extreme south of Tunisia where the CI well depths in Dahar area vary from 21 m to 120 m, indicating shallow and highly confined conditions prevailing along the flow lines towards the Nefzaoua area (Dhaoui et al., 2016). In the Djerid basin, the principal W-E groundwater flow line comes from the Algerian frontier towards the discharge zone in the Gulf of Gabes. Tectonic activity has played a major role in the isolation of this aquifer section from the flow coming from the extreme south of the country toward Chott Djerid (Kamel et al., 2005). Only the west-east flow component coming across the Algerian-Tunisian border seems to ensure hydraulic continuity between the different compartments of the CI aquifer in the Djerid (Edumens et al, 2003; Abid et al., 2009).

3. Method

Nine groundwater samples were collected along two flow paths from the main CI hydrogeological units of the survey area in February 2015 (Fig. 1). The first SE-NW flow path begins in the aquifer outcrop area and ends at Chott in the confined parts of the aquifer. The second W-E flow path moves from the Algerian frontier towards the discharge zone in Chott region.

Borehole depths range from 700 to > 2000 m (Table 1 and Fig. 1(b, c)). Five boreholes were sampled in the Nefzaoua basin: four from the Neocomian levels (CIK

2, CIK3, CIK 4 and CIK 5) and one borehole from the Albian level (CIK 1). Four boreholes were sampled from the Barremian (CIT 2 and CIT 4) and the Lower Aptian (CIT1 and CIT 3) levels in the Djerid basin.

In order to ensure that water is representative of actual aquifer conditions, all samples were collected from currently exploited wells. Temperature, pH and electrical conductivity (EC) were measured *in situ*. All samples were analyzed for main chemical parameters using standard methods. Analyses of cations (Ca^{2+} , Mg^{2+} , Na^{+} and K^{+}) and anions (Cl^{-} , SO_4^{2-} , NO_3^{-}) were carried out in the Laboratory of Radio-Analyses and Environment (LRAE), University of Sfax. The overall detection limit for ions was 0.04 mg/l. The total alkalinity (as HCO_3^{-}) was determined by titration with 0.1 M HCl solution using methyl orange and bromocresol green indicators. The reliability of the chemical data was assessed by checking ion balance. Calculated charge balance errors are found to be less than $\pm 5\%$.

Stable isotope compositions of oxygen and hydrogen (^{18}O , ^2H) in the groundwater samples were measured by laser spectrometry (LGR DLT100) at the LRAE. The isotope contents are reported in the usual δ notations relative to the Vienna standard mean ocean water (VSMOW) standard. Typical analytical uncertainty of the reported values is about $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1.5\text{‰}$ for $\delta^2\text{H}$ (one-sigma level).

Samples for dissolved inorganic carbon (DIC) isotope analysis were collected in 500 ml stainless steel bottles to avoid any contact with the atmosphere (Peterson et al., 2014). The preparation prior to analysis was carried out at IDES laboratory in Orsay. The ^{14}C measurements were performed at the ARTEMIS AMS facility in Saclay according to published procedures (Delqué-Količ et al., 2013). The results, expressed in percent modern carbon (pMC), have been corrected for the blank level of 0.2 – 0.4 pMC depending on the batch. Stable DIC isotope ratios were measured at IDES laboratory in

Orsay (France) using Isotopic Ratio Mass Spectrometry (IRMS, typical precision of 0.15‰), and reported as $\delta^{13}\text{C}$ ‰ (i.e., per mille difference from Vienna Pee Dee Belemnite Standard [VPDB]).

For noble gas isotopes, groundwater samples were collected in copper tubes and isolated with pinch-off metal clamps to avoid gas exchange with the atmosphere. Dissolved gases were extracted and analyzed using magnetic sector (for helium) and quadrupole (for neon and argon) mass spectrometers at the Isotope Hydrology Laboratory of IAEA (Matsumoto et al., 2017).

For ^{81}Kr , dissolved gases (20 – 30 L STP) were extracted from groundwater in the field and stored in pressurized cylinders. Gas samples were purified by cryogenic distillation and gas chromatography at the Isotope Hydrology Laboratory at IAEA to produce ~ 10 μL (STP) sized, nearly pure krypton (Hillegonds; et al., 2015), for ATTA work at the Trace Radioisotope Analysis Center (TRACER), Argonne National Laboratory (Jiang et al., 2012).

4. Results and Discussion

4.1. Chemical Composition

Results for major anions, cations and *in situ* measurements are listed with borehole information in Table 1. Temperature ranges from 34°C to 72°C; the lowest value was measured at the CIK 1 borehole situated in the local recharge area of Daher mountains, whereas higher values were measured in the boreholes in the Tozeur basin. Groundwater pH values range between 6.6 and 7.6. The measured conductivity of the groundwater samples range from 2.6 to 9.9 ms/cm (i.e. TDS from ca. 2106 to 8498 mg/l). The ionic composition is dominated by Ca^{2+} (246–463 mg/l), Na^+ (261–2205 mg/l), Cl^- (268–4468 mg/l) and SO_4^{2-} (717–1410 mg/l) (Table 1). Concentrations of Mg^{2+} (43–224 mg/l) and

K⁺ (37-150 mg/l) are relatively lower. The dominant anions are chloride and sulphide. Consequently, the groundwater samples in both Kebili and Tozeur basins belong to the same water type: SO₄-Cl-Ca-Na. This chemical pattern corresponds to water interaction with the geological formations of the basin (carbonates and various evaporites) and cation exchange reactions.

4.2. Stable isotopes of oxygen and hydrogen ($\delta^{18}\text{O}$, $\delta^2\text{H}$)

Isotope ratios of oxygen and hydrogen in the samples range from -8.4 ‰ to -7.2‰ for $\delta^{18}\text{O}$ and from -61.5‰ to -50.3‰ for $\delta^2\text{H}$. The composition of water in the area closest to the outcrop (Ksar Ghilane borehole in Nefzaoua basin) is slightly more enriched in the heavy isotopes than deep groundwater of CI with a mean $\delta^{18}\text{O}$ value of -8‰. These results are in agreement with previous studies (Abid et al., 2009) (Edmunds et al., 2003).

The stable isotopes in the CI waters are compared to each other and to the overlying aquifers as well as to the modern rainfall (Fig. 2). The stable isotope data lie below the local meteoric water line (LMWL) and are all strongly depleted in both ^{18}O and ^2H , compared to modern Mediterranean rainfall and also to the shallowest groundwater. These observations reveal a scenario of the air mass evolution different from the present-day case. There is also a clear difference in stable isotope compositions between CIT and CIK samples (Fig. 2). The CIT samples' $\delta^{18}\text{O}$ and $\delta^2\text{H}$ cluster around -7.7 and -56 ‰, whereas the CIK samples have ratios slightly more depleted in heavy, with the exception of CIK1 which showed the most enriched $\delta^{18}\text{O}$ and $\delta^2\text{H}$. This is consistent with a view that the CIK and CIT samples originate from separate flow paths with different recharge areas.

4.3. Radiocarbon

Radiocarbon activities and $\delta^{13}\text{C}$ values of DIC are shown in Table 1 and are expressed as percent of Modern Carbon (pMC) and ‰ VPDB, respectively. CI groundwater shows ^{14}C activities and $\delta^{13}\text{C}$ values varying between 0.2 and 1.9 pMC, and between -10.9 ‰ and -7.9 ‰ respectively. The range of $\delta^{13}\text{C}$ values is typical for groundwater–rock interaction by the incongruent dissolution of carbonate (Sacks, 1996) in recharging meteoric water. Longer water residence times enhance equilibration with aquifer carbonate minerals resulting in lower ^{14}C activities and $\delta^{13}\text{C}$ composition closer to that of host rocks (Fontes and Garnier, 1979).

CI groundwater residence time is calculated using various models, taking into account different geochemical processes (carbonate dissolution, soil gas CO_2 dissolution, CO_2 gas-aqueous exchange, calcite, bicarbonate (HCO_3^-) exchange, gypsum dissolution or cation exchange, etc.). These models could be subdivided into: (i) purely chemical mixing (Tamers, 1975), (ii) isotopic mixing (Ingerson and Pearson Jr., 1964) and (iii) models of chemical mixing and isotopic exchange (Fontes and Garnier, 1979; Mook, 1976; Salem et al., 1980; Eichinger, 2016). In the present case, only the “Fontes and Garnier Eq.” model takes into account the two major processes occurring in the CI groundwater: gypsum dissolution and Ca/Na cation exchange reactions (Abid et al., 2009). The calculated ^{14}C ages according to this model (Table 1) show residence times of about 30 to 50 ka. Note that the hydrological significance of these ^{14}C ages is limited as these ages are clearly older than the applicable age range of the ^{14}C method (1 – 30 ka).

4.4. Helium and Neon

Groundwater residence times exceeding the ^{14}C dating limit are also qualitatively supported by the ^4He concentrations in the samples. As listed in Table 2, ^4He concentrations are at $10^{-6} \text{ cm}^3\text{STP/g}$, two orders of magnitude larger than that of ^4He dissolved in the air-equilibrated water at recharge. Very low $^3\text{He}/^4\text{He}$ ratios of $3 \sim 8 \times 10^{-8}$ suggest a long residence time to allow an accumulation of radiogenic ^4He (from U and Th decay) to dominate over air-derived ^4He (Fig. 3). The concentrations of U and Th in the aquifer matrix have not been measured. However, if we adopt the *in situ* ^4He accumulation rate of $3.3 \times 10^{-12} \text{ cm}^3\text{STP/g/yr}$ estimated by Patterson et al. (2005) for the Nubian Aquifer, lithology similar to that of the CI aquifers, accumulation times required to account the measured amount of ^4He are between 500 and 3,000 kyr (Table 2). Note that these accumulation times should be regarded as the upper limits for the groundwater residence times of respective samples, as additional ^4He flux from the underlying crust would significantly increase the ^4He accumulation rates (e.g., Aggarwal et al., 2014). In addition, $^3\text{He}/^4\text{He}$ and Ne/He ratios of the samples seem to define two distinct mixing lines (Fig. 3), suggesting that there may be a small but distinct difference in $^3\text{He}/^4\text{He}$ ratios of the radiogenic components between the samples from Kebili and Tozeur regions. This difference should reflect time-integrated Li/ (U+Th) ratios of the sources of radiogenic helium, and may be regarded as supporting evidence for that the groundwater from Kebili and Tozeur regions being hydrologically separated from each other.

4.5. Krypton-81

Concentration of ^{81}Kr in groundwater samples (Table 2) is expressed in terms of the air-normalized ratio, $R_{\text{sample}}/R_{\text{air}}$, where R_{sample} and R_{air} are the $^{81}\text{Kr}/\text{Kr}$ ratios of the

sample and of the atmosphere, respectively. R_{sample}/R_{air} ratios range from 0.15 to 0.63.

With the ^{81}Kr decay constant ($\lambda_{Kr} = 3.03 \times 10^{-6} \text{ yr}^{-1}$), the age (t_{Kr}) is calculated by

$$t_{Kr} = -\frac{1}{\lambda_{Kr}} \ln \left(\frac{R_{sample}}{R_{air}} \right)$$

The range of ages estimated for the samples is 420 ka to 605 ka for the Touzer region.

Except for a relatively younger age of 150 ka found in the sample from Ksar Ghilan (CIK1), the samples from Kebili region also defined a narrow ^{81}Kr age range, 550 to 630 ka.

Note that these ^{81}Kr ages are clearly much older than their ^{14}C ages, confirming the above-mentioned limitation of the ^{14}C method to provide reliable age information to the target aquifers. The results also reveal the presence of external ^4He flux from the continental crust, as the ^{81}Kr ages are younger than the ^4He accumulation times estimated without taking into account the ^4He flux.

The CIK1 sample with exceptionally younger ^{81}Kr age is from the borehole tapping the Albian sandstones in the Dahar uplift, where recharge from a local precipitation occurs. Recent isotopic investigation indicates current contribution of the Albian sandstones outcrops on the Dahar in the recharge of CI aquifer by direct rainwater infiltration (Dhaoui et al., 2016). This notion is also supported by the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data in which the CIK1 sample showed values intermediate between the local precipitation and the rest of the CIK samples (Fig. 2).

4.6. Chlorine-36 and Krypton-81

Figure 4 compares the present ^{81}Kr ages from the Tozeur area with the previously published ^{36}Cl ages from the Algerian part of the CI aquifer (Guendouz and Michelot, 2006). ^{36}Cl has a half-life of 301 kyr, thus it can also cover the age range older than the radiocarbon limit. However, its application is generally complicated by uncertainties in

the initial $^{36}\text{Cl}/\text{Cl}$ ratio and a complex subsurface production of nucleogenic ^{36}Cl as well as chloride dissolution within the aquifer (Bentley et al., 1986; Phillips et al., 1986; Michelot et al., 1989). As shown in Fig 4, the resulting ^{36}Cl ages show significant variabilities depending on assumptions made for the age calculation (Guendouz and Michelot, 2006).

As shown in Fig. 1, sampling points for the previous ^{36}Cl analyses (Guendouz and Michelot, 2006) and those for ^{81}Kr analyses from Tozeur area are considered to be from the same flow path from the recharge zone (the Saharan Atlas) to the discharge zone at the Tozeur area. The ^{81}Kr data define a narrow range of ages at the discharge, but the age progression from the Algerian section to the Tunisian section can only be crudely defined (Fig. 4). Some ^{36}Cl ages (> 1 Ma) in the Algerian section seem overestimated, suggesting that the assumptions in the ^{36}Cl age calculation do not adequately represent the actual conditions.

Among the samples analyzed for ^{81}Kr , there six wells where $^{36}\text{Cl}/\text{Cl}$ and Cl contents are also available (three sites from the Tozeur section from Petersen et al., 2014, and three sites from the Kebili section from Petersen et al., 2018). As shown in Fig. 5(a), the ^{81}Kr ages and $^{36}\text{Cl}/\text{Cl}$ ratios define a negative correlation as expected from similar decay constants of ^{81}Kr and ^{36}Cl . Age-dependent progression of Cl contents is also obvious in samples from Tozeur section, indicating an effect of chloride dissolution within aquifer (Fig. 5(b)). Chloride contents in samples from Kebili section are generally higher than those in samples from Tozeur area and showed no systematic variation. Boreholes in the Kebili section show a recent salinity increase (of 30% percent over the previous ten years) believed to be caused by intensive exploitation and consequent upward leakage from deep layers (probably the Jurassic). Thus, the Cl isotope system seems to be disturbed in the samples from Kebili section.

³⁶Cl ages can be calculated by using a general equation which takes into account (1) radioactive decay of ³⁶Cl derived from the meteoric-epigene input, (2) the *in situ* production of ³⁶Cl by thermal neutron capture (³⁵Cl(n,γ)³⁶Cl) within the aquifer and (3) chloride dissolution within the aquifer:

$${}^{36}R_{Meas}[Cl]_{Meas} = {}^{36}R_i[Cl]_i e^{-\lambda t} + {}^{36}R_e[Cl]_i (1 - e^{-\lambda t}) + {}^{36}R_e([Cl]_{Meas} - [Cl]_i)$$

where λ is the decay constant of ³⁶Cl ($2.303 \times 10^{-6} \text{ yr}^{-1}$), t is the time elapsed since the recharge, ³⁶R_{Meas} is the measured ³⁶Cl/Cl ratio, ³⁶R_i is the initial ³⁶Cl/Cl ratio (= the meteoric-epigene input), ³⁶R_e is the ³⁶Cl/Cl ratio of the thermal neutron capture which is considered to be under secular equilibrium when radioactive decay of meteoric ³⁶Cl and *in situ* production of ³⁶Cl are balanced, $[Cl]_{Meas}$ is the measured Cl content, $[Cl]_i$ is the initial chloride concentration. The simplest way for age calculation is to assume $[Cl]_{Meas} = [Cl]_i$ (no chloride dissolution within the aquifer), ³⁶R_e = 5×10^{-15} (adopted from a secular equilibrium value) (Fabryka-Martin et al., 1987) (Lehmann et al., 2003), and ³⁶R_i = 116×10^{-15} which is estimated by Guendouz and Michelot (2006) based on a theoretical value of the natural ³⁶Cl fallout rate at the Saharan Atlas (Lal and Peters, 1967; Parrat et al., 1996) and the average chloride content in precipitation. These simplifications yielded ³⁶Cl ages significantly older than the respective ⁸¹Kr ages (Table 3), suggesting that the assumptions are not applicable for these samples. Indeed, the chloride contents of the Tozeur samples are in the range of *ca.* 200 to 500 mg/L and generally high compared with chloride in young groundwater estimated to be about 85 mg/l in the Dahar recharge area in Tunisia (Dhaoui et al., 2016). The chloride concentrations have been reported to increase from the outcrops in the Atlas Mountains to the east along the transect, implying the progressive dissolution of non-marine evaporates along the flow lines (Edmunds et al., 2003). The calculated initial ³⁶Cl/Cl ratios are also based on a mean annual precipitation of the recharge area, an

evapotranspiration rate, and a chloride concentration in precipitation for the present-day arid conditions. It is highly likely that these conditions have changed with time, thus are not adaptable for age calculation (Trauth et al., 2009).

Instead of using those assumptions, we applied a pragmatic approach, using the ^{81}Kr data for the calibration of input parameters in the ^{36}Cl age calculation by finding the initial $^{36}\text{Cl}/\text{Cl}$ ratio and Cl concentration that yield a ^{36}Cl age matching the ^{81}Kr age. The balance between the initial and the measured Cl is reached by contribution along the flow path due to evaporite dissolution. We assume that the subsurface evaporites in question were formed more than 1.5 Myr ago; ^{36}Cl initially deposited has thus decayed to a level below the AMS detection limits. The results of our calculation are listed in Table 3. In order to force each groundwater sample to have a residence time determined by ^{81}Kr , it appears that (1) the initial $^{36}\text{Cl}/\text{Cl}$ ratio needs to be higher than the commonly assumed value by a factor of 3 to 6, and (2) initial chloride contents should be much lower than those observed (i.e., 50-80 mg/L in the calculation vs. 300-1200 mg/L determined experimentally). Considering the uncertainties associated with $^{36}\text{Cl}/\text{Cl}$, Cl and ^{81}Kr , these samples yielded rather consistent initial $^{36}\text{Cl}/\text{Cl}$ ratios and Cl contents with averaged values of $440 \pm 140 \times 10^{-15}$ and 67 ± 15 mg/L for the Torzeur section, and of $740 \pm 80 \times 10^{-15}$ and 50 ± 26 mg/L for the Kebili section. These values are close to those found by Dhaoui et al. (2016) in the recharge water in Dahar Mountains in south-eastern part of Tunisia.

The measurement of ^{36}Cl in the meteoric proxy archives of ice cores (Baumgartner et al., 1998; Wagner et al., 2001) and fossil rat urine (Plummer et al., 1997) showed that the cosmogenic production rate of ^{36}Cl can vary by a factor of two. In addition, the $^{36}\text{Cl}/\text{Cl}$ ratio of atmospheric deposition can vary as a result of change in the stable Cl deposition (Phillips, 2013), which can be produced by variation in the distance between

the aquifer recharge and the ocean, driven by sea-level changes. Davis et al (2003) reported that meteoric $^{36}\text{Cl}/\text{Cl}$ ratios vary from 50×10^{-15} in near ocean areas to $>1000 \times 10^{-15}$ in continental interior. Thus, the initial $^{36}\text{Cl}/\text{Cl}$ ratio in recharging water could differ from the theoretical ratio derived from the present-day environment by more than a factor of two, and the initial $^{36}\text{Cl}/\text{Cl}$ of about 400×10^{-15} is feasible. This is also consistent with the notion by Phillips (2013) that the ^{36}Cl deposition flux by Lal and Peters (1967) underestimates the actual deposition flux by a factor of approximately four.

Figure 4 also shows the recalculation of ^{36}Cl ages for the Algerian section of the aquifer with the initial $^{36}\text{Cl}/\text{Cl}$ and Cl values calibrated for the Tozeur section with the ^{81}Kr ages. Although these newly calculated ages generally agree with the previously determined age ranges by Guendouz and Michelot (2006), the assumptions used here are very different from the previous work. For example, the maximum ^{36}Cl ages were calculated based on the assumed initial $^{36}\text{Cl}/\text{Cl}$ ratio of 133×10^{-15} and the secular equilibrium $^{36}\text{Cl}/\text{Cl}$ ratio of 8×10^{-15} , presumably without taking into account the chloride dissolution within the aquifer. However, we note that the chloride dissolution is a very important process that needs to be assessed properly for reliable ^{36}Cl age estimation, as it is obvious from Fig. 5b that this sub-surface process largely controls total Cl content. The ages calculated without taking this process into account obviously overestimate the ages, yielding unrealistically old groundwater ages beyond 1 Ma in areas closer to the presumed recharge zone than the Tunisian section of the west to east flow line. With these ^{81}Kr -calibrated ^{36}Cl ages, we narrow the possible age ranges significantly, the age progression from the recharge to the east over > 500 km of transect much clearer. Accordingly, we suggest that the west-to-east flow velocity is closer to 1 m/yr, much higher than the previously calculated velocity of 0.5 m/yr.

5. Conclusion and Outlook

The obtained ^{81}Kr ages constitute robust and reliable data needed for the calibration of numerical flow models of the CI aquifer, which in turn allow the assessment of potential sustainability of this major water supply in the medium- and long-terms. CI groundwater should be regarded as non-renewable, “fossil” water. The absence of any current recharges presents a major issue for the effective management, sustainable conservation and protection of this transboundary groundwater resource.

Besides these direct implications, the ^{81}Kr ages permit us to calibrate the initial $^{36}\text{Cl}/\text{Cl}$ and Cl contents (thus the effect of chloride dissolution) in individual samples, revealing the groundwater age structure of the CI aquifer. The procedure presented in this work still ignores the possible addition of ^{36}Cl from precipitation within the last ~ 1 Ma, which would result in underestimated ^{36}Cl ages. In addition, provided that our estimate of the initial $^{36}\text{Cl}/\text{Cl}$ is about twice as large as $^{36}\text{Cl}/\text{Cl}$ in the present-day soil samples from the near recharge area (Guendouz and Michelot, 2006), it is probable that $^{36}\text{Cl}/\text{Cl}$ ratios can vary through the entire recharge history of the CI aquifer. Indeed, there are several processes that complicate the application of ^{36}Cl chronometer in groundwater dating (e.g., Phillips, 2013). This study demonstrates the utility of ^{81}Kr , not only to provide independent and conservative age information, but also to enhance use of ^{36}Cl data. Accumulation of data on Cl isotopes and concentrations from different aquifers, supported by firm chronological constraints from ^{81}Kr , should lead understanding of temporal and geographical variation in $^{36}\text{Cl}/\text{Cl}$ ratios as well as additional (subsurface) processes that influence the ^{36}Cl chronometer.

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Table 1. List of groundwater samples collected for the present study with chemical and isotope analyses results

Sample ID	Site	Aquifer Formation	Formation	Altitude (m)	Screen Interval (m)	CE (ms/cm)	T (°C)	pH	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	HCO_3^-	Cl^- (#)	NO_3^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	TDS (mg/l)	$\delta^{13}\text{C}$ ‰ (‰)	^{14}C (pmc) (‰)	^{14}C age (kyr)
<u><i>CI Tozeur (CIT) Region</i></u>																						
CIT1	Nefta	Sidi Aich Sand	Lower Aptian	100	2125-2260	2.8	73	7.0	-7.8	-55.2	146	296	1	1062	271	82	340	48	2212	-10.1	0.23	39
CIT2	Jhim	Boudinar Sand	Barremian	21	2404-2470	3.0	70	7.1	-7.7	-56.8	134	530	4	1049	348	56	363	52	2536	-9.18	1.9	27
CIT3	Tozeur	Sidi Aich Sand	Lower Aptian	87	1885-1997	3.0	65	7.4	-7.6	-56.1	134	536	10	1172	322	84	366	43	2485	-9.05	1.5	30
CIT4	Tazarit	Boudinar Sand	Barremian	33	2050-2168	4.8	68	6.7	-7.5	-54.1	183	414	31	1077	784	87	423	57	4042	-7.9	0.35	39
<u><i>CI Kébili (CIK) Region</i></u>																						
Ksar																						
CIK1	Ghilane	Sand/sandstone	Albian	211	625-667	4.18	34	7.1	-7.2	-50.3	201	1037	0	1410	740	53	443	224	4306	-10.9	0.3	45
		Kbeur El Haj																				
CIK2	Douz	Sand/Sandstone	Neocomian	70	1926-1994	9.88	44	6.7	-8.4	-61.2	146	1188	39	876	2205	150	463	150	8498	-10.8	0.17	48
		Kbeur El Haj																				
CIK3	Kébili	Sand/Sandstone	Neocomian	58	2285-2556	2.66	65	6.6	-8.4	-61.1	134	542	0	717	371	37	246	62	2182	-10.7	0.25	45
		Kbeur El Haj																				
CIK4	Limagues	Sand/Sandstone	Neocomian	81	1567-1752	2.8	69	7.6	-8.3	-61.5	140	606	3	773	342	40	276	65	2245	-8	0.73	39
		Kbeur El Haj Sand/																				
CIK5	Souk Lahad	Sandstone	Neocomian	40	1986-2200	3.4	67	7.1	-8.3	-61	134	586	21	683	306	40	268	68	2106	-10.84	0.33	43

(#) Chloride data shown as *Italic* are adopted from Peterson et al. (2014 and 2018).

(\$) Carbon isotope data shown as *Italic* are from Petersen et al. (2018), Abid et al., (2009 and 2012).

Table 2. Results of noble gas isotope analysis.

Sample ID	Site	Mass Spectrometer			ATTA	
		He ($\times 10^6$ cm ³ STP/g)	³ He/ ⁴ He ($\times 10^{-8}$)	Ne ($\times 10^7$ cm ³ STP/g)	⁸¹ Kr/Kr ($R_{\text{sample}}/R_{\text{air}}$)(#)	⁸¹ Kr Age ($\times 10^5$ yr)
CIT1	Nefta	2.64 ± 0.04	3.72 ± 0.05	2.61 ± 0.03	0.28 ± 0.02	4.20 ± 0.31
CIT2	Jhim	1.93 ± 0.05	5.10 ± 0.10	2.60 ± 0.06	0.20 ± 0.01	5.31 ± 0.3
CIT3	Tozeur	3.71 ± 0.10	4.18 ± 0.22	3.78 ± 0.08	0.16 ± 0.01	6.05 ± 0.35
CIT4	Tazarit	4.97 ± 0.13	3.03 ± 0.07	2.56 ± 0.06	0.23 ± 0.02	4.85 ± 0.36
CIK1	Ksar Ghilan	2.19 ± 0.06	5.63 ± 0.09	2.55 ± 0.06	0.63 ± 0.02	1.52 ± 0.13
CIK2	Douz	9.29 ± 0.24	3.69 ± 0.11	4.32 ± 0.09	0.15 ± 0.01	6.26 ± 0.36
CIK3	Kébili	2.01 ± 0.05	6.43 ± 0.15	2.56 ± 0.06	0.17 ± 0.01	5.85 ± 0.33
CIK4	Limagues	1.60 ± 0.03	7.03 ± 0.11	2.51 ± 0.02	0.19 ± 0.01	5.48 ± 0.31
CIK5	Souk Lahad	2.01 ± 0.03	7.79 ± 0.10	4.01 ± 0.04	0.17 ± 0.02	5.84 ± 0.47

Table 3. Re-evaluation of ^{36}Cl ages with ^{81}Kr ages.

Sample ID	Site	Measured Values (§)		^{36}Cl Age (ka) #	^{81}Kr Age (ka)	Calibrated Parameters by ^{81}Kr ages		
		Cl (mg/L)	$^{36}\text{Cl}/\text{Cl}$			Initial $^{36}\text{Cl}/\text{Cl}$	Initial Cl	^{36}Cl Age (ka)
CIT1	Nefta	296	2.54E-14	725	420 ±31	3.4E-13	50	420
CIT3	Tozeur	536	1.48E-14	1043	605 ±35	3.4E-13	90	605
CIT4	Tazarit	414	3.38E-14	575	485 ±36	6.0E-13	70	485
CIK1	Ksar Ghilan	1037	4.03E-14	498	152 ±13	7.4E-13	80	152
CIK2	Douz	1188	5.40E-15	2450	626 ±36	6.6E-13	40	626
CIK3	Kébili	542	1.20E-14	1200	585 ±33	8.2E-13	30	585

§) Cl isotope data are adopted from Guendouz and Michelot (2006) and Petersen et al. (2014; 2018)

#) Ages calculated with a generic initial $^{36}\text{Cl}/\text{Cl}$ and no chloride dissolution.

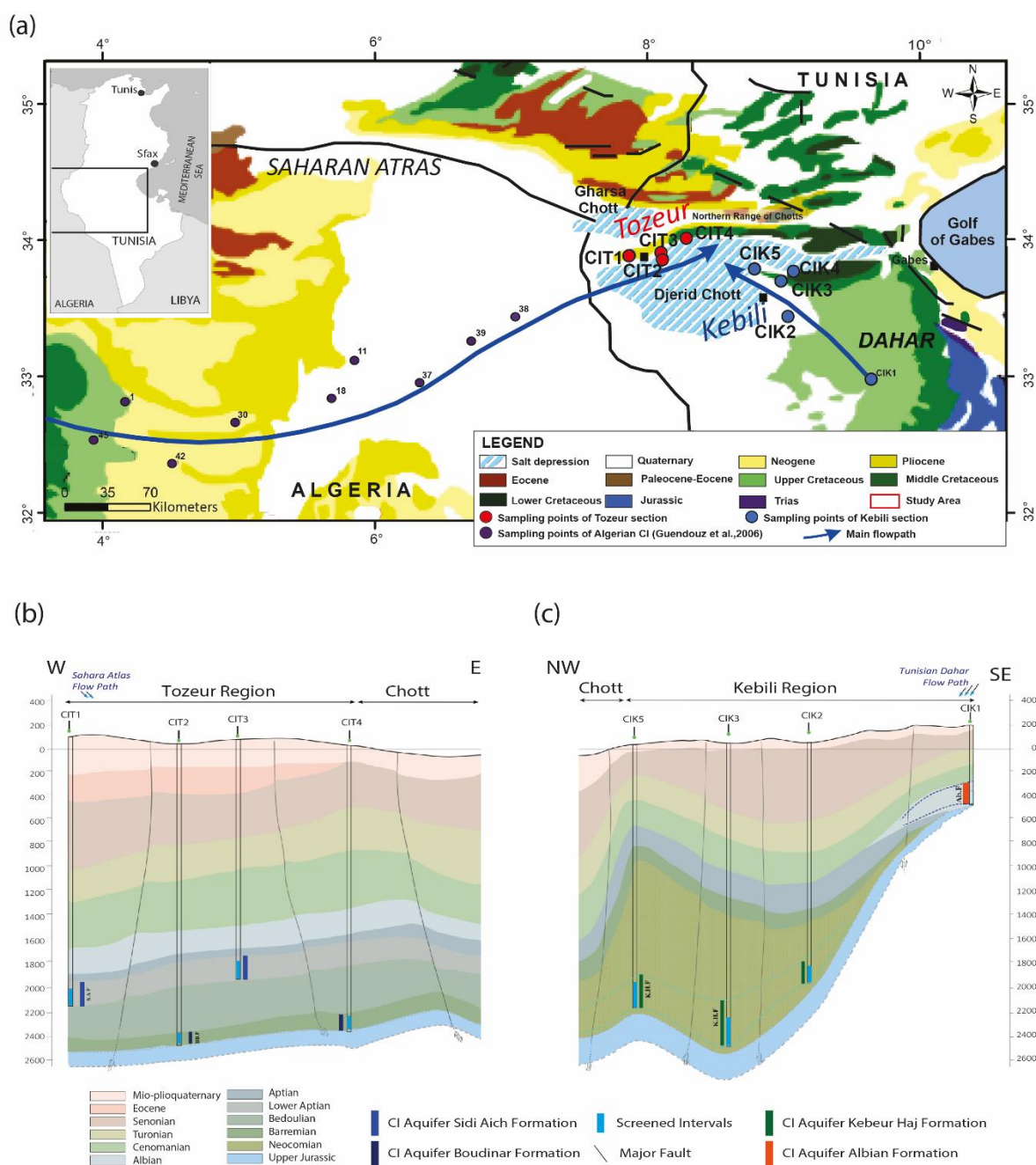


Fig.1. (a) Geological map of the sampling points in the CI aquifer (Tozeur and Kebili sections in Tunisia). Sampling points for the previous ^{36}Cl analysis (Guendouz and Michelot, 2006) are also shown on the Algerian side of the CI aquifer, and simplified cross sections of the CI aquifer in (b) Tozeur region and (c) Kebili region along the collected groundwater wells.

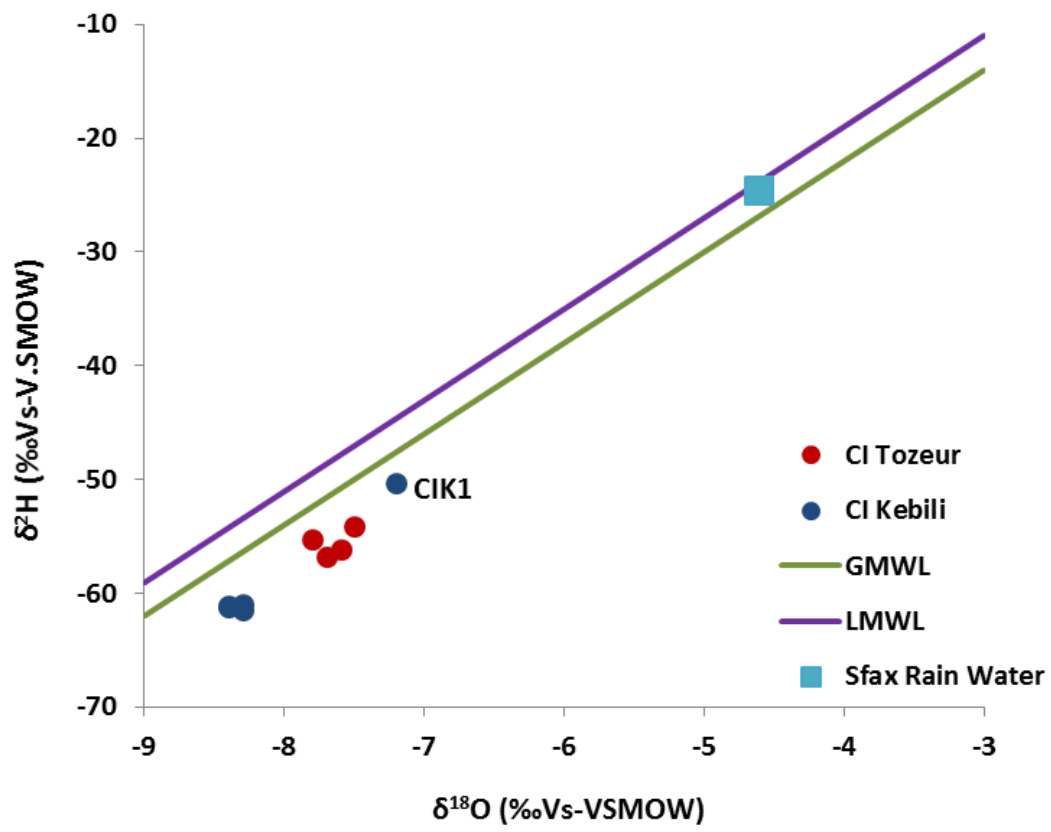


Fig. 2. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of CI groundwater in Kebili and Tozeur regions. GMWL: Global Meteoric Water Line; LMWL: Local Meteoric Water Line.

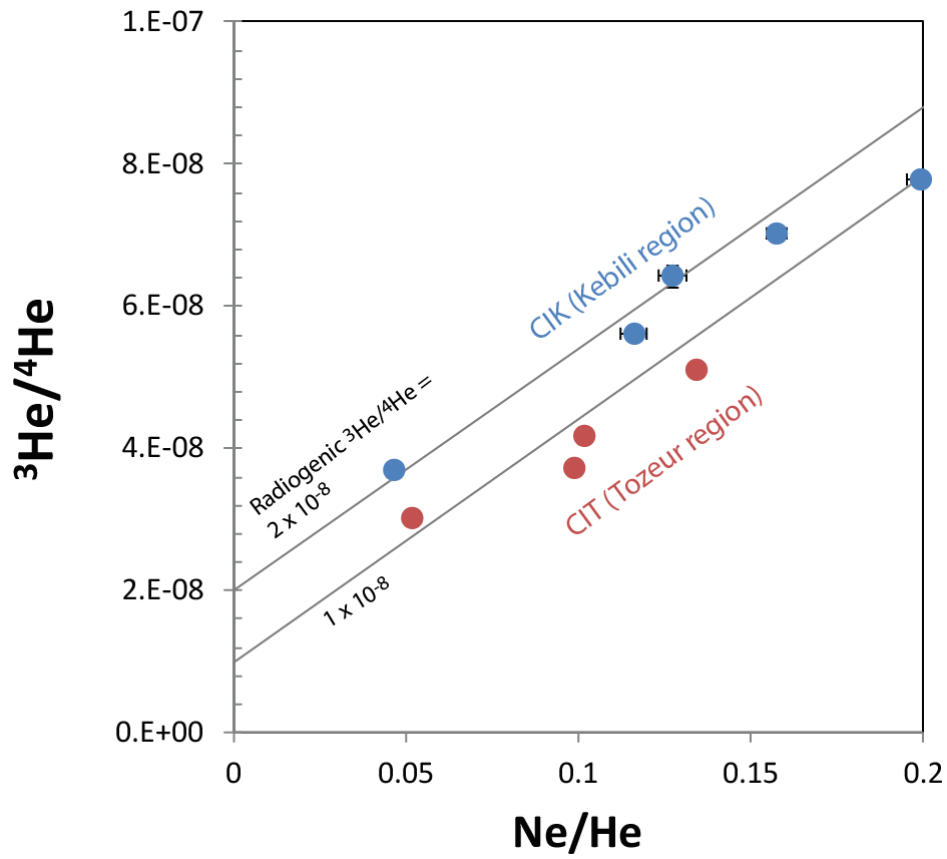


Fig. 3. Ne/He and $^3\text{He}/^4\text{He}$ ratios of the groundwater from CI aquifer in Tozeur and Kebili regions. Solid lines represent binary mixing lines between an atmospheric component and a crustal radiogenic component whose $^3\text{He}/^4\text{He}$ ratio is 1×10^{-8} or 2×10^{-8} .

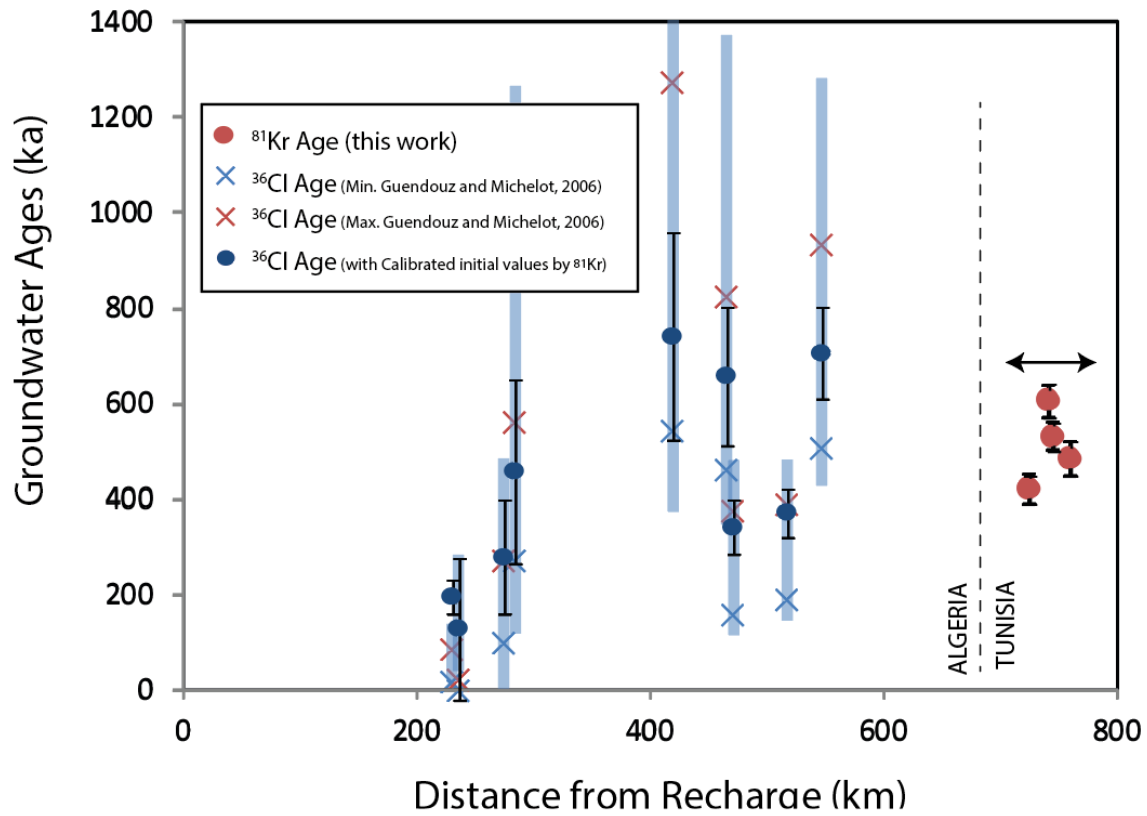


Fig. 4. ^{81}Kr ages (this study) and ^{36}Cl ages (Guendouz and Michelot, 2006; and this work) plotted against the distances from recharge. The minimum ^{36}Cl ages by Guendouz and Michelot (2006) were calculated by using $^{36}R_i = 116 \times 10^{-15}$ and $^{36}R_e = 0$, and their maximum ages were obtained with $^{36}R_i = 133 \times 10^{-15}$ and $^{36}R_e = 8 \times 10^{-15}$. The blue bands are to show the range that covered by the maximum and minimum ^{36}Cl ages of Guendouz and Michelot (2006) with quoted uncertainties. The ^{36}Cl ages re-evaluated based on the initial $^{36}\text{Cl}/\text{Cl}$ and Cl values calibrated with the ^{81}Kr ages are shown with blue dots (see text).

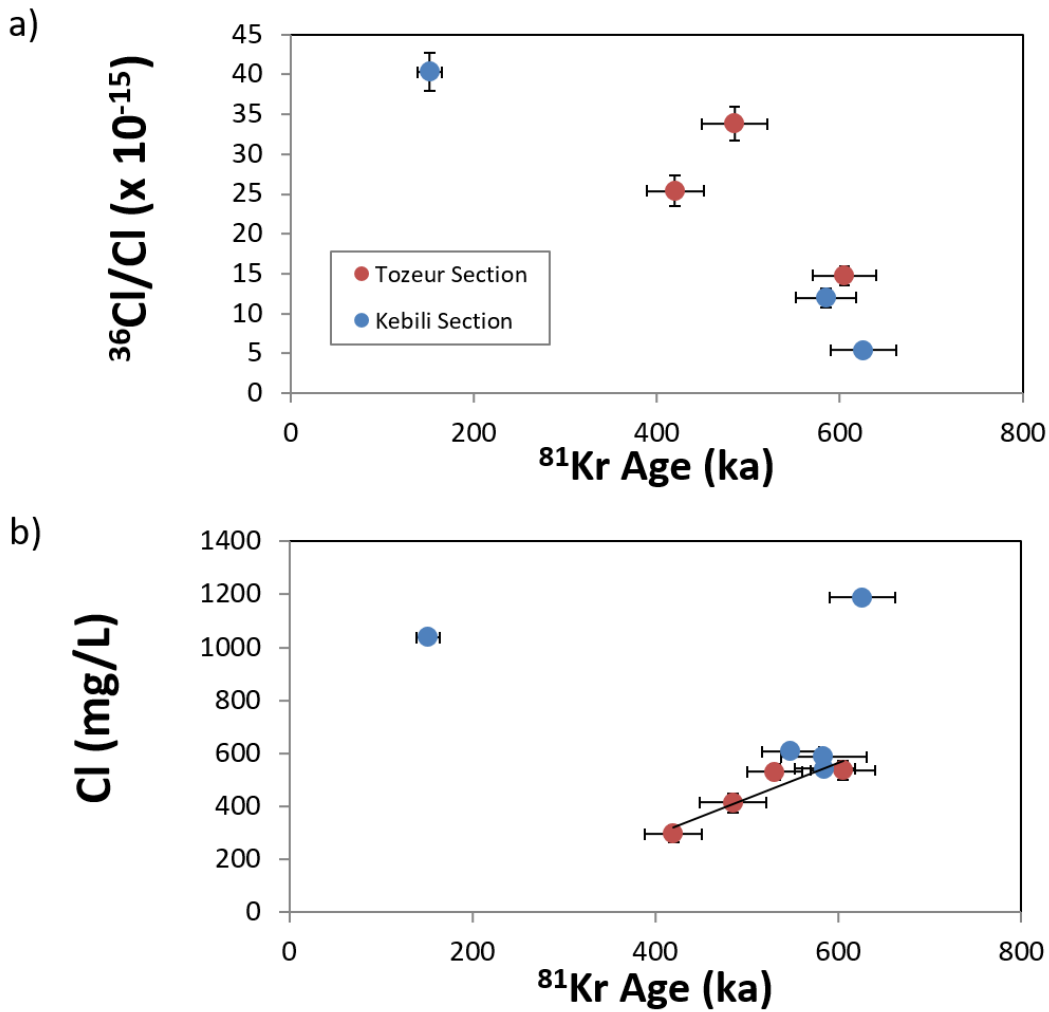


Figure 5 $^{36}\text{Cl}/\text{Cl}$ ratios and Cl contents versus ^{81}Kr ages.