

**Pairing U-Pb dating and clumped isotope palaeothermometry to
constrain the diagenetic history of dolomite from Resolution
Guyot**

Maria Gusarevich

MPhil

Imperial College London Department of Earth Science and Engineering

October 2020

Abstract

Constraining the temperature–time evolution of carbonate platforms is critical for understanding basin development, diagenetic pathways, and reservoir quality prediction. This study evaluates the integrated application of clumped isotope palaeothermometry ($\Delta 47$) and U–Pb carbonate geochronology to reconstruct the diagenetic history of Resolution Guyot (Pacific Ocean). By pairing independent temperature estimates with high-precision in situ age determinations, the research establishes a quantitative framework for resolving the timing and thermal conditions of dolomitisation and recrystallisation events.

U–Pb dating successfully constrained the age of dolomite precipitation, including single-analysis ages in samples characterised by low common Pb concentrations. Compared to Sr isotope stratigraphy, U–Pb geochronology provides greater reliability in systems influenced by multiple fluid sources and recrystallisation. Clumped isotope thermometry independently constrained cementation temperatures, enabling reconstruction of the platform's thermal evolution and fluid characteristics.

Petrographic and isotopic data indicate that white dolomite formed through recrystallisation of earlier brown dolomite. Recrystallisation resulted in near-complete loss of radiogenic Pb and uranium, while common Pb was preserved and isotopically reset. Application of both conventional Tera–Wasserburg (7–6TW) and 8–6T–W common-Pb correction approaches allowed dating of samples with high common Pb and low uranium contents. These findings provide new insight into U–Pb system behaviour during carbonate recrystallisation and demonstrate that common Pb signatures can retain geochronological significance.

Although extensive radiogenic loss can limit age resolution, integrating thermal and chronological proxies significantly enhances interpretation of diagenetic histories. This study demonstrates that coupling clumped isotope palaeothermometry with U–Pb geochronology provides a robust tool for basin analysis and carbonate reservoir characterisation.

Declaration of Originality

I declare that all work in this thesis is my own, unless otherwise stated or referenced. Maria Gusarevich, 2019

Declaration of Copyright

The copyright of this thesis rests with the author. Unless otherwise indicated, its contents are licensed under a Creative Commons Attribution-NonCommercial 4.0 International Licence (CC BY-NC).

Under this licence, you may copy and redistribute the material in any medium or format. You may also create and distribute modified versions of the work. This is on the condition that: you credit the author and do not use it, or any derivative works, for a commercial purpose.

When reusing or sharing this work, ensure you make the licence terms clear to others by naming the licence and linking to the licence text. Where a work has been adapted, you should indicate that the work has been changed and describe those changes.

Please seek permission from the copyright holder for uses of this work that are not included in this licence or permitted under UK Copyright Law.

Table of Contents

Abstract	2
Declaration of Originality	3
Declaration of Copyright	3
<i>The copyright of this thesis rests with the author. Unless otherwise indicated, its contents are licensed under a Creative Commons Attribution-NonCommercial 4.0 International Licence (CC BY-NC).</i>	3
<i>Under this licence, you may copy and redistribute the material in any medium or format. You may also create and distribute modified versions of the work. This is on the condition that: you credit the author and do not use it, or any derivative works, for a commercial purpose.</i>	3
<i>When reusing or sharing this work, ensure you make the licence terms clear to others by naming the licence and linking to the licence text. Where a work has been adapted, you should indicate that the work has been changed and describe those changes.</i>	3
<i>Please seek permission from the copyright holder for uses of this work that are not included in this licence or permitted under UK Copyright Law.</i>	3
Chapter 1: Introduction	6
1.1. General introduction.....	6
1.2. Thesis aims and objectives	8
1.3. Layout of the thesis	9
Chapter 2: Background and Methods	10
2.1. Theory of clumped isotope paleothermometry and U-Pb dating.....	10
The theory of multiply substituted isotopologues	10
Theory of carbonate paleothermometry	12
Theory of U-Pb geochronology	14
2.2. Laboratory measurements and analysis	15
Microscopic analysis.....	15
Subsampling for geochemistry.....	15
Mineral analysis: X-ray diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR)	16
Clumped isotope measurements and data processing	19
U-Pb isotope analysis: method and derivation of common lead corrected ages.....	30
Chapter 3: Reconstruction of environment and time of dolomitization using clumped isotope and U-Pb methods (Resolution Guyot, Pacific Ocean)	37
3.1. Introduction	37
3.2. Geological Background	39
3.3. Sample collection	43
3.4. Results.....	45
3.4.1. Dolomite core description and petrographic analysis.....	45
Mineralogy and grain size.....	58
Stable and clumped isotope measurements.....	58
U-Pb measurements	69

3.5. Discussion.....	79
3.5.1. Petrographic consideration and reconstruction of paragenetic dolomite types.....	79
3.5.2. Recrystallized versus pristine early dolomite: evidence from clumped isotope data.	83
3.5.3. Reconstruction of formation ages for $D_{RT1} - D_{RT3}$ dolomites using the LA-ICPMS U-Pb method..	89
3.5.4. Reconstruction of age of D4 dolomite and new approached to date recrystallized carbonate.....	90
3.5.5. Reconstruction of thermal history of Resolution Guyot dolomitization using clumped isotope and U-Pb methods.....	94
Chapter 4: Thesis Outcomes and Conclusions	100
4.1. Conclusions	100
4.2. Future work.....	102
References.....	105
Additional material.....	117
Chapter 2.....	117
APPENDIX 2.1. Stacey and Kramers' model and estimation of common Pb ratio values.....	117
APPENDIX 2.2. LA-ICP-MS operating conditions.....	119
APPENDIX 2.3. Additional Notes and Computational Formulas	121
Chapter 3.....	123
APPENDIX 3.1. Detailed results of clumped isotope and U-Pb measurements for dolomite samples, Resolution Guyot	123
APPENDIX 3.2. Results of U-Pb measurements of standards (WC-1, Mud Tank zircon, NIST 614) for dolomite and calcite samples from Resolution Guyot.....	135

Chapter 1: Introduction

1.1. General introduction

Constraining burial histories of sedimentary basins is essential not only to understand tectonic processes but also to understand the diagenesis of sediments. The temperature-time history significantly impacts porosity, permeability distribution within carbonate reservoirs, organic matter maturation, and migration of hydrocarbons from source rocks to a reservoir (Roehl and Choquette, 1985; Chilingarian et al. 1996; Moore and Wade, 2013).

Conditional palaeothermometry can be used to constrain temperature of cement precipitation. The most common methods are the vitrinite reflectance (VR) index (Sweeney and Burnham, 1990), the fluid inclusion technique (Goldstein and Reynolds, 1994), the conodont alteration index (Epstein et al. 1976), molecular indices, and standard oxygen isotope analysis (Kim and O'Neil, 1997). Although these techniques have been proved to be effective, they are limited by material availability, assumptions inherent to each proxy, and the usable temperature-time range. The vitrinite reflectance technique is limited by lithology (it is not suitable for carbonate rocks), as well as the presence of vitrine or other maceral groups (liptinite and inertinite) (Engel and Macko, 1993). The conodont alteration index gives a relatively broad temperature range. However, it can be applied only for narrow time intervals (Cambrian-early Triassic) (Epstein et al. 1976). Fluid inclusion analysis is limited by crystal size, resetting of trapped fluids (Goldstein and Reynolds, 1994), and the fact that the data acquisition process is very time-consuming. Finally, the conventional method of oxygen isotope palaeothermometry requires a priori knowledge of the isotopic composition of the fluid from which the carbonate precipitates, which is rarely available (Groot, 2009; Huntington et al. 2011; Moore and Wade, 2013, Sena et al. 2014; Cedric, 2015).

The method of carbonate clumped thermometry involves measuring the abundance of the double-substituted isotopologue of CO₂ that contains a ¹³C-¹⁸O bond (¹³C¹⁸O¹⁶O) relative to a stochastic distribution at high (>1000 °C) temperature (Ghosh et al. 2006; Schauble et al. 2006). The process of clumping is thermodynamically controlled (Wang et al. 2004). An increase in temperature causes an elevation of entropy and drives the system towards stochastic distribution (Schauble et al. 2006; Eiler et al. 2007). During the process of carbonate precipitation, the CO₂ isotopic system is in equilibrium with surrounding waters, so the number of heavy isotopologues reflects the temperature of the environment in which the mineral was precipitated. Thus, by measuring the quantity of “clumps” in the mineral lattice of a carbonate mineral, we can calculate the temperature at which the mineral was precipitated (Dennis et al. 2013).

At the same time, dating the age of geological material is critical for reconstructing the sequence of geological and diagenetic events, and by extension the thermal history of a basin. One of the main ways to determine rock age is micropalaeontology (Haq and Boersma, 1998). However, this approach depends on species abundance and their age range and cannot be applied to diagenetic material. An absolute age may be obtained using apatite fission-track analysis (Gallagher et al. 1998). This involves measuring the length of damage trails (fission tracks) created by nuclear particles emitted during the spontaneous decay of uranium (^{238}U), which anneal themselves at high temperatures (above $120\text{ }^{\circ}\text{C}$). Such behaviour permits the thermal history of sedimentary basins to be reconstructed. However, dependence on temperature makes it suitable only for dating low-temperature events (Gallagher et al. 1998). Another frequently used method is the U-series (^{234}U - ^{230}Th) dating of calcite. Even though this method is well known and proved to be reliable, it can only be used to date sediments of 500,000-year-old (Pike et al. 2012; Hoffmann et al. 2016).

U-Pb dating involves measuring the number of daughter isotopes (Pb, including initial common lead Pb_i) at present and comparing it to the number of parent isotopes (U), assuming that the system remains closed following the formation of the calcite. However, during the burial history, carbonate rocks (due to their biogenic origin and high chemical reactivity) are very unstable and pass through a series of diagenetic processes (dissolution, precipitation of secondary cement, and dolomitisation). These may produce dissolution and redistribution of the daughter/parent products (loss or uptake) within the texturally modified rock. Provided the rock remains at moderate to low temperatures ($<200\text{ }^{\circ}\text{C}$), the measured age of carbonate should correspond to the age of the carbonate producing the diagenetic event.

The advantage of the U-Pb method lies in two major factors. The decay of uranium passes through two independent decay schemes: ^{238}U - ^{206}Pb and ^{235}U - ^{207}Pb . Furthermore, the rate of decay allows us to apply the method to the entire geological time scale, from Archean Mushandike stromatolitic and Paleozoic limestone (DeWolf et al. 1991) to U-Pb dating of coral secondary calcite in Devonian limestones (Smith et al. 1991) and cement in Mesozoic ammonites (Li and Parrish, 2014), as well as Miocene corals (Denniston et al. 2008), paleosoils (Rasbury et al. 1998), and Quaternary speleotherms (Richards et al. 1998).

In this project, I propose to combine two isotope methods to constrain the temperature-time history of carbonate rocks: clumped isotope palaeothermometry and the radiogenic method of U-Pb. This approach is challenging, not only due to our lack of knowledge of the behaviour of the radiogenic system during the burial process (partial resetting of the radiogenic system) but also due to the usually low uranium content and high concentration of non-radiogenic Pb in most carbonate rocks (0.023 –

2.54 ppm) (Delaney and Boyle, 1982). However, the method of clumped isotope thermometry proves to be a powerful tool for paleoclimate reconstruction (Dennis et al. 2013), as well as burial diagenetic processes (Huntington et al. 2011; Dale et al. 2014; Vandeginste et al. 2014; MacDonald et al. 2017; Honlet et al. 2018). In addition, the development of a new technique for in-situ age determination using the laser ablation method (LA-MC-CP-MS) has proven to be more robust for the understanding of the chronology of diagenetic processes in carbonates, as well as providing more precise uranium content measurements (Li et al. 2010; Li and Parrish, 2014, Roberts and Walker, 2016; Parrish et al. 2017; Nuriel et al. 2017).

At the beginning of the current research in 2015, the number of works which combined both techniques was limited, and nothing has been yet published. However, interest in this topic grew in subsequent years. First, the pairing of clumped isotope palaeothermometry and U-Pb dating was used to study Eocene hypothermal events using carbonate soils from North America (Montana, USA), allowing insights into climate dynamics and temperature conditions during the Middle Eocene Climatic Optimum (Methner et al. 2016). Quade and colleagues' (2016) study also used clumped isotope palaeothermometry and U-Pd dating to reconstruct paleoenvironmental conditions on the example of spring carbonates (travertines) from Barrancas Blancas, Western Andes in the Atacama Desert, Chile. Lawson et al. (2017) used this combination of methods to reconstruct the thermal history of four generations of carbonate cement within the Hauterivian – Cenomanian interval of El Abra Formation, San Luis Potosi platform, north-eastern Mexico. Finally, one of the latest works studies the application of clumped isotope and U-Pb dating to reconstruct thermal and fluid flow history of the Middle Jurassic carbonate formation of the Paris basin (Mangenot et al. 2018). The approach was also used on more complex tectonic areas to determine timing and source of fluid circulation using samples from calcite breccias and veins, the Gondrecourt graben, eastern Paris Basin, France. Although all these studies demonstrated successful results, several limitations were also revealed. One of the first limitations is reordering of the clumped isotope system (Passey and Henkes, 2012) with increasing burial temperatures ($>100\text{ }^{\circ}\text{C}$). It creates difficulties reconstructing original temperatures of carbonate mineral cementation (Lawson et al. 2017). The recrystallisation process of carbonate minerals caused another difficulty during the burial process. The study by Mangenot et al. (2018) suggests the presence of a recrystallisation process in several of the studied samples; however, this was not elaborated on in the discussion.

1.2. Thesis aims and objectives

- 1) To apply recent methods of clumped isotope palaeothermometry and U-Pb dating to reconstruct the diagenetic history of carbonate rocks on an example of dolomite samples from carbonate platform of Resolution Guyot (Pacific Ocean);

- 2) To study the behaviour of the U-Pb radiogenic system during dolomite cementation and recrystallisation (incorporation of initial Pb, loss, and uptake of parent /daughter isotopes);
- 3) To study the temporal and spatial resolution at which diagenetic processes can be reconstructed using our combined proxy approach on calcite cement from vugs interiors;

1.3. Layout of the thesis

Chapter 1: General Introduction. This chapter presents the introduction, background and project aims.

Chapter 2: Background and Methods. This chapter provides the background to the clumped isotope and U-Pb dating theories with a detailed description of data acquisition procedures.

Chapter 3: Reconstruction of environment and time of dolomitisation using clumped isotope and U-Pb methods (Resolution Guyot, Pacific Ocean). This chapter discusses the environment and timing of dolomitisation (brown and white types of dolomite). Additionally, some insights are given into the behaviour of the radiogenic system during the recrystallisation process. This chapter is currently being prepared for publication.

Chapter 4: Thesis outcome and main conclusions. The final chapter of the thesis summarises the main outcomes of the project and highlights potential areas for future studies.

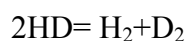
Chapter 2: Background and Methods

2.1. Theory of clumped isotope paleothermometry and U-Pb dating

The theory of multiply substituted isotopologues

Traditionally, stable isotope geochemistry is focused on studying isotopic species with only one rare isotope (i.e. concentration of species with such type of isotopes usually is very low: 10's of parts per million or less (Eiler, 2007)). Species containing two or more rare isotopes were neglected due to their low concentration and minor impact on bulk isotopic composition. The theory of clumped isotope geochemistry was first established in the 1940's with works of Urey (1947) and Bigeleisen and Mayer, (1947). However, it was realised that such multiply substituted isotopologues may provide a new tool for geochemical research due to their high diversity, different physical and chemical properties (different bond vibration frequencies, zero point energies, etc) only with a use of modern mass spectrometers which allowed to measure small isobaric differences (Zyakun, 2003; Eiler and Schauble, 2004; Eiler, 2007).

According to the theory of classical thermodynamics, bonds between two heavy isotopes (for instance, D-D in the D₂ system) vibrate more slowly and have less vibrational energy in comparison with bonds between a heavy and a light isotopes (HD) (Urey, 1947; Bigeleisen, 1955) (Fig.2.1). Therefore, the difference in energy between D₂ and H₂ is twice the difference between H₂ and HD. In this case, it can be expected that the total amount of energy in two systems, one containing only heavy-heavy bonds and one only light isotopes (D₂+H₂) is equal to the amount of energy in a single system containing isotopologues with heavy-light isotope bonds (2HD = H₂ + D₂). Thus, according to the rule of mean there should be no thermodynamic advantage for heavy isotopes to clump (Bigeleisen, 1955). In reality, the reduction in energy during the formation of double heavy – isotope (D₂) compared to the formation of heavy-light substitution (HD) is slightly higher than predicted by the rule of mean. This means that double heavy-isotope substitution will be more stable at low temperatures and statistically likely to be preserved. The temperature dependent nature of isotopic “clumping” may be explained in terms of the equilibrium constant for a homogeneous isotope exchange reaction or in other words isotopic disproportionation reaction” (Polyakov et al, 2005).



(Equation 2.1)

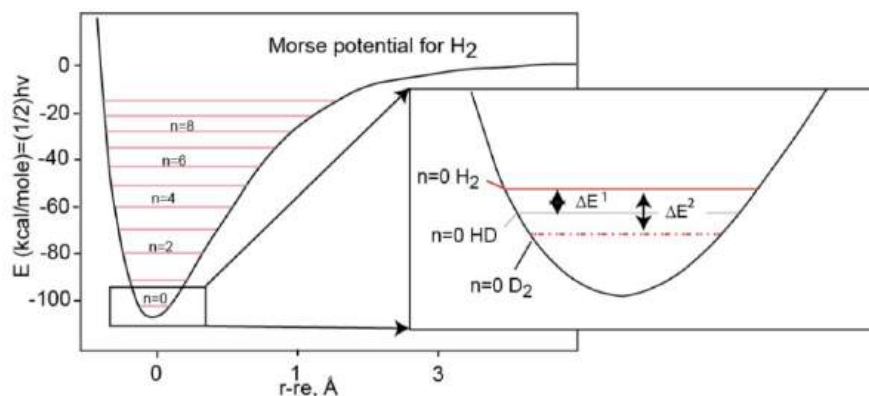


Figure 2.1. Energy of hydrogen bonds (y axis) against the bond distance (x axis). r_e is minimum energy-bond distance. Black bold line shows the Morse potential for H₂. Horizontal red colour lines represent the quantum states of energy. $N = 0$ and is the zero point energy (ZPE). The zoomed image shows the ZPE for isotopologues with hydrogen bond. The lowest ZPE represents the double-heavy substituted bond. ΔE^1 and ΔE^2 show difference in energy between H-D, H₂ and D₂ (Eiler, 2007).

Under stochastic distribution, the equilibrium constant $K = ([H_2][D_2])/[HD]^2 = ([H]_2[D]_2)/(2[H] \cdot [D])^2$ of this reaction will be equal to 0.25. In this case, all isotopes will be randomly distributed. However, the deviation from the rule of the mean and slightly higher stability of double heavy-isotope substitution (D₂) drives the isotope exchange reaction towards the right side causing an increase in the amount of double substituted heavy isotopologues in the system. At higher temperatures the vibration energy increases due to effect of entropy and this leads progressively to a stochastic distribution of isotopologues (Eiler, 2007) (Fig.2.2).

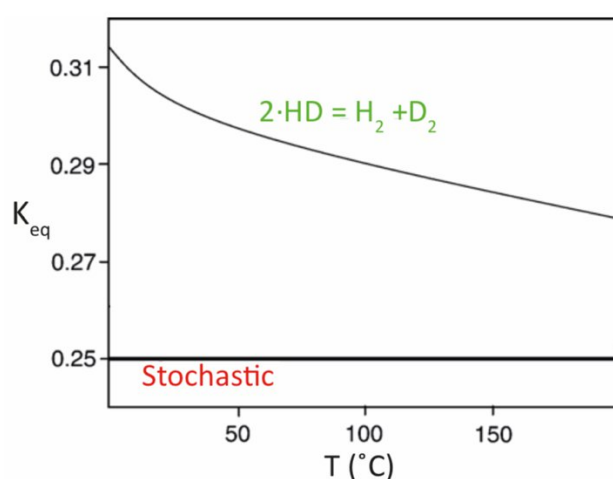


Figure 2.2. Temperature dependence of the equilibrium constants (K_{eq}) for the homogeneous isotope exchange reaction (Equation 2.1). The increase of temperature causes the gradual decrease of K_{eq} towards the stochastic distribution (Eiler, 2007)

Clumped –isotope analysis uses the notation Δ_i to express abundance of isotopologues compare to abundance of the same type of isotopologues under a stochastic distribution. The values of Δ_i is then expressed in the following way:

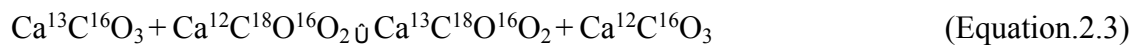
$$\Delta_i = \left(\frac{R_i}{R_i^*} - 1 \right) \times 1000 \quad (\text{Equation.2.2})$$

R_i expresses the distribution of isotopologues of interest relative to the isotopically normal isotopologues. R_i^* value indicates similar ratio but in case of stochastic distribution. The variable Δ_i is expressed in per mil (Eiler and Schauble, 2004). The system where all isotopes are distributed in the equal form between all isotopologues is defined as a reference frame.

Theory of carbonate paleothermometry

Applying to carbonate mineral, the process of clumping can be used as a paleothermometer to calculate temperature of carbonate mineral precipitation. The process of carbonate precipitation begins with dissolution of the atmospheric CO_2 gas in oceanic sea water though the isotope exchange reaction with CO_2 concentrated in water. Once CO_2 gets dissolved it reacts with water to form carbonate acid, H_2CO_3 . Carbonate acid transforms to bicarbonate HCO_3^- and H^+ ions and finally transforms to carbonate ion CO_3^{2-} . Isotopes of carbon and oxygen tend to rearrange in the dissolved inorganic carbon pool (the DIC) before carbonate mineral precipitation. This is possible due to the fact that the process of clumping is controlled by temperature of surrounded fluids from which mineral is precipitated. The temperature of surrounding waters causes re-equilibration of ^{13}C and ^{18}O in the CO_2 in DIC. As carbonate ions in CO_3 pool within the DIC is normally in equilibrium with the CO_2 pool, the precipitated carbonate mineral inherit the isotopic signal from the DIC via the CO_2 and CO_3 ions. Clumping process occurs within CO_3 group in dissolved state before carbonate mineral precipitation (Fig.2.3). The process of clumping is independent of the oxygen isotopic composition of parent fluid (Eiler, 2007).

The ^{13}C - ^{18}O clumping process via isotope exchange reaction may be expressed by the following equation 2.3:



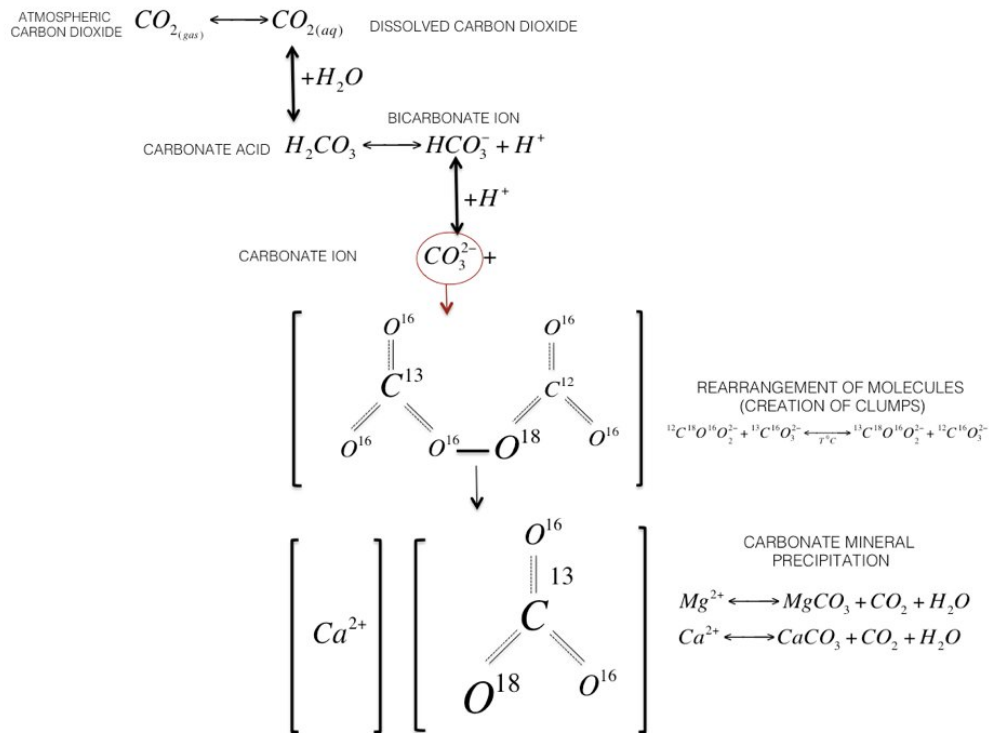


Figure 2.3. Schematic representation of carbonate precipitation and clumping process.

During sample measurements, the carbonate is reacted with anhydrous phosphoric acid to produce CO_2 gas. Out of 20 different isotopologues of the carbonate ion (CO_3^{2-}) 16 of them are multiply-substituted (Ghosh et al., 2006). The isotopologue of $^{13}C^{18}O^{16}O_2$ forms ~97% of all isotopologues measured on mass 47 of CO_2 gas (Huntington et al., 2011). The measured amount of the $C^{13}C^{18}O^{16}O_2$ isotopologue of mass 47 in CO_2 is proportional to the abundance of $^{13}C^{18}O^{16}O_2^{2-}$ within the carbonate lattice taking into account the acid fractionation factor (Ghosh et al., 2006 ; Guo et al., 2008). The excess abundance of isotopologues with mass 47 is measured against mass 44 ($^{12}C^{16}O^{16}O$), which is the most abundant isotopologue of CO_2 gas (Eiler, 2007). The abundance of $C^{13}C^{18}O^{16}O_2$ in analysed CO_2 gas is expressed using metric Δ_{47} and is defined as:

$$D_{47} = \frac{R^{47}}{R^{47*}} - 1 \div \frac{R^{46}}{R^{46*}} - 1 \div \frac{R^{45}}{R^{45*}} - 1 \div 1000 \quad (\text{Equation 2.4})$$

(Eiler and Shauble, 2004). $R^i = m_i/m_{44}$. R is abundance of isotopologues with mass i . R^* is the abundance of isotopologues with mass i under stochastic distribution (Affek and Eiler, 2006). The detailed calculation of Δ_{47} is presented in “Data processing and correction” paragraph below.

The process of clumping is thermodynamically controlled and the temperature of the fluid from which mineral was precipitated controls the abundance of isotopologues. The amount of

$^{13}\text{C} - ^{18}\text{O}$ bonds, or in other words the quantity of heavy isotopologues with mass 47, is inversely proportional to the temperature of the parent fluid. The advantage of clumped isotope paleothermometry is the ability to reconstruct the environment of mineral precipitation without prior assumption of the isotopic composition of parent fluids (Eiler, 2007; Schauble et al., 2006). Independently determined temperatures, coupled with the $\delta^{18}\text{O}_{\text{carbonate}}$, may then be used to reconstruct the $\delta^{18}\text{O}_{\text{fluid}}$. Using this methodology, a better understanding of the temperature of carbonate minerals (dolomite and calcite) precipitation, coupled with the origin of cementation fluids, should result in a better reconstruction of the environment of cement precipitation.

Theory of U-Pb geochronology

The method of U-Pb geochronology is based on radioactive decay of uranium (^{238}U and ^{235}U) (and ^{232}Th) into stable isotopes of lead (^{206}Pb , ^{207}Pb , and ^{208}Pb). In contrast to highly radiogenic minerals like zircon or monazite, carbonate minerals usually incorporate some common Pb upon formation from the precipitating fluid, and the proportion of radiogenic Pb is often highly variable.

In this study, I use the LA-ICP-MS method of analysis of U and Pb isotopes with in situ analysis of polished sections of sample, to allow multiple rapid analyses of $\sim 80\mu\text{m}$ areas within the petrographic context, similar to the general method for accessory minerals that is currently very widespread. The key developments that have made this feasible are (1) high sensitivity ICP-MS instruments (both quadrupole and multiple collector magnetic sector) and (2) the availability of a reliable radiogenic calcite reference material (Roberts et al., 2017).

These advances are illustrated in the studies of Li et al., 2014; Coogan et al., 2016 and Parrish et al. 2017 using a high sensitivity quadrupole instrument; they allow routine measurement of U-Pb isotopes in calcite at the sub-ppm U level. This method was successfully applied in structural geology for dating rift related fractures on the northern Atlantic margin (Roberts and Walker, 2016), the beginning of the Dead Sea transform (Nuriel et al., 2017), and age of folding in southern England (Parrish et al., 2017). LA-ICP-MS was also used to date the diagenesis in carbonate rocks, such as cementation in Mesozoic ammonites (Mangenot et al., 2018). These studies demonstrated that LA-ICP-MS is more robust for the age reconstruction in low-U carbonates as it allows measurement of small scale types of cements (small veins, calcite rims, single crystals) (Li et al., 2014; Coogan et al., 2016; Roberts and Walker, 2016)

with spots of 30-80 mm and a 2σ precision of $\pm 3-4\%$ of the age (Li et al., 2014). Although carbonates are often highly heterogeneous in terms of radiogenic Pb, the method allows rapid evaluation of the U-Pb ratio and thus, screening of samples for suitability.

2.2. Laboratory measurements and analysis

Microscopic analysis

Dolomite and calcite samples were personally selected for thin section analysis at IODP core repository and later cut in-house using saw. Thin sections were made and doubly polished in Mykina Lab, Poland. Thin sections were analysed under optical and cathodoluminescence (CL) microscopes. Transmitted light Zeiss Axioskop 40 with a Nikon DS-Filc camera was used to study thin sections. Cathodoluminescence (CL) microscopy was performed on a Nikon Eclipse 50i luminoscope equipped with a CITL cathodoluminescence MK5-2 stage. The CL microscope was operated at following conditions: current of 315 mA, an accelerating voltage of 15kV, vacuum at 0.003 mBar.

The goal of CL microscopy was to measure luminescence characteristics of carbonate cements (presence of zonation, brightness and pattern of luminescence effect) with an aim to understand better the diagenetic evolution of studies cements. For example, to trace different phases of cement precipitation (dolomitic or calcitic), episodes of dissolution, reconstruct environment of cementation (burial/meteoric or marine) (Boogs and Kinsley, 2006). The luminescence in carbonate minerals is a function of Mn/Fe ratio. The variation of Mn^{+2} and Fe^{2+} and their effect on luminescence is illustrated in Fig. 2.2. Thin sections were examined for the presence of a petrographic difference between two types of dolomites, evidence of a mineral mixing phase, or alteration of samples through diagenesis (Machel et al., 1991; Boggs and Kinsley, 2006).

Subsampling for geochemistry

Specific petrographic types of dolomite were sampled using a micro drill at low speed (1RPM) to avoid heating (and any potential resetting of clumped isotopes). The diameter of the drill was 0.3 mm and an area of $\sim 2 \text{ mm} \times 2 \text{ mm}$ constituted a typical sample to yield $\sim 40 \text{ mg}$ of carbonate powder. This significant volume and area clearly allow an analysis to potentially comprise more than one generation of carbonate, but care was taken to minimize heterogeneity of the sample by doing careful petrographic analysis prior to sampling. Collected powder was

stored in a desiccator and used for FTIR (~ 5 mg per sample) , XRD (~ 5 mg per sample) and clumped isotope (~ 30 mg per sample) analysis .

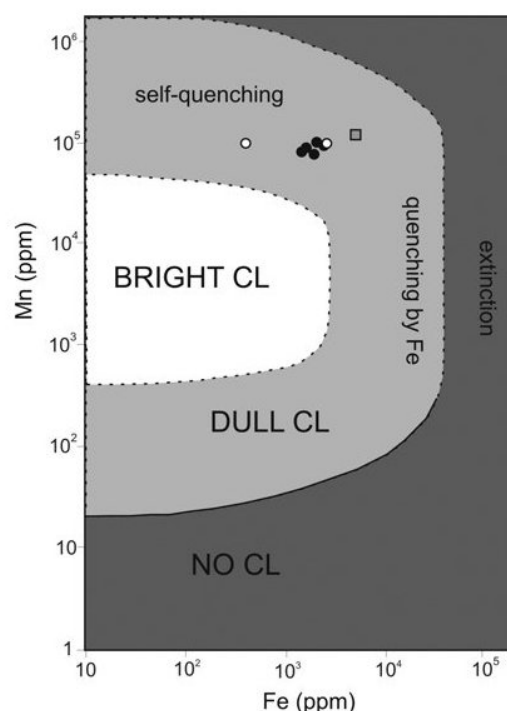


Figure 2.2. Variation of intensity the luminescence in carbonates as a function of Mn vs. Fe concentration (ppm on logarithmic scale) (modified after Machel et al., 1991, taken from Boggs and Kinsley, 2006).

Mineral analysis: X-ray diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR)

XRD measurements were performed at the Natural History Museum London for the purpose of mineralogical phase identification (calcite vs. dolomite). Prior to measurements, sample powder was mixed with acetone in an agate mortar. The received solution was then pipetted on a transmission foil and left to dry. The X-ray analysis was carried out on a XPERT-PRO diffractometer system over the 2θ range of 20-98 ($\text{CuK}\alpha$) with the step 0.017 [$^\circ 2\theta$] and integration time of 150 s. XRD scans were processed and analysed using XPert HighScore+ software. Minerals (mostly dolomite and calcite) were identified using XRD patterns using the PDF-2 database from ICDD.

FTIR method was used to ensure homogeneous mineral composition (dolomite or calcite) of studied samples. During FTIR measurements sample is fired with an infrared beam. This causes excitement of the molecular bonds within mineral structure of the sample, vibration

(either stretching or bending) and absorption of infrared light in the region between 400 to 4000 cm^{-1} . The absorption of infrared light is controlled by the chemical composition of studied mineral, its crystal structure and bonding of a mineral. The most useful region for mineral identification is between 1600 and 600 cm^{-1} (Thompson, 2000).

Every mineral has its own unique combination of different absorption peaks. The typical ATR-FTIR spectrum has the absorbance on the y-axis and wavenumbers (cm^{-1}) on the x-axis, increasing from left to right (Fig. 2.3). In carbonate minerals the vibration occurs within CO_3^{2-} group with absorption peaks situated within interval between 1600- 400 cm^{-1} . The position of the peaks change depending of the crystal structure and chemistry. Thus, different types of carbonate minerals (aragonite, calcite, dolomite) may be easily identified (Jones and Jackson, 1993). The elevated Mg concentration, which corresponds to dolomite mineralogy usually show the shift of the absorption curve towards higher **wavelength** (730 cm^{-1}) compare to calcite mineralogy with 710 cm^{-1} wavelength (Fig. 2.3).

Measurements were performed in the Organic Geochemistry Laboratory of Imperial College London. The Nicolet 5700 FTIR spectrometer is used in this study with a single bounce diamond ATR smart orbit accessory and a DTGS KBr detector. The sample powder is flattened with the clamp to ensure the direct contact of powder and the ATR diamond crystal. Samples are measured against internal standards of calcite and dolomite. The typical time for a single run is approximately 1 minute.

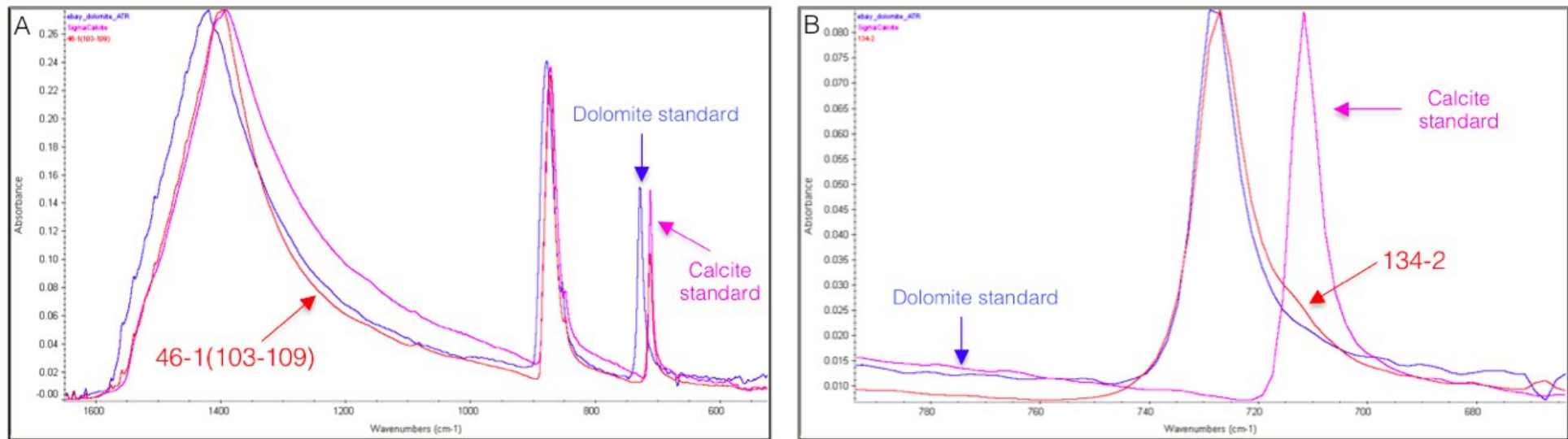


Fig.2. 3. FTIR spectra for one of the calcite samples (Sample 46-1/103-109cm) and dolomite sample (Sample 134-2-40-42). The dolomite sample (B) revealed high absorption characteristics compare to calcite mineral (A)

Clumped isotope measurements and data processing

Clumped isotope analysis was performed in the Qatar Stable isotope laboratory at Imperial College London.

• CO₂ extraction and purification

A measurement of single sample replicate requires between 5-6 mg of powder. Powder was then diluted in 100% phosphoric acid at 90 °C under vacuum for 10 minutes for calcite samples and for 20 minutes for dolomite samples to produce CO₂ gas (McCrea, 1950; Swart et al., 1991). The extraction of CO₂ gas from carbonate (calcite) mineral is described by equation 2.5. Evolved CO₂ gas was then purified manually in a vacuum line following the procedure of (Dennis and Schrag, 2010) (Fig. 2.4).

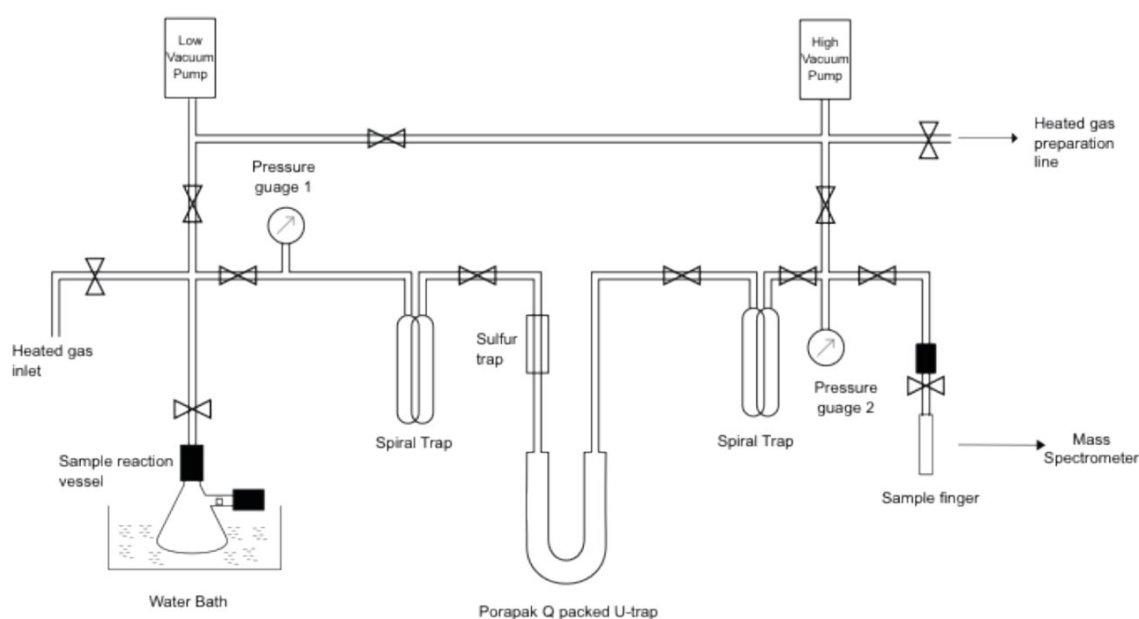


Figure 2.4. Illustration of acid digestion and manual cryogenic purification line. (Davies, 2018)

During acid digestion, the produced CO₂ gas was trapped in a spiral glass tube using liquid nitrogen (LN₂) allowing to remove non-condensable gases. Remained CO₂ gas was then released using ethanol slush at temperature of – 90 °C. CO₂ gas was then purified by migration through the Porapak Q (PPG) trap at temperature – 35 °C. CO₂ transfer is maintained until pressure on gauge 1 reaches 1.8×10^{-2} . The overall transfer time varied between 20-60 minutes

depending on the state of manual line. In between purification procedures the PPQ was heated to 140 °C under vacuum for 35 minutes to remove contamination. At the end, CO₂ gas was frozen at sample figure using nitrogen.

- **Mass Spectrometry**

Cleaned CO₂ gas was then analysed in the Thermo Fisher MAT 253 isotope ratio mass spectrometer equipped with a dual-inlet system and Faraday cups (m.z 44-49) (Fig.2.5). Measurements were done on two mass spectrometers ‘Pinta’ and ‘Nina’ in the Qatar Stable Isotope Laboratory at Imperial College London. Each measurement includes 8 acquisitions with 7 cycles per acquisition with 26 s integration time with initial source pressure of 15mbar to generate a m/z 44 ion beam signal of roughly 15kv. A typical time of single acquisition equals 20 min. The overall time of each measurement approximately 2-2.5 h. Sample gas was measured against Oztech reference gas (Dallas, TX, USA) with values of $\delta^{13}\text{C}_{\text{VPDB}} - 3.62\text{‰}$ and $\delta^{18}\text{O}_{\text{VSMOW}} 25.09 \text{‰}$ for Pinta and $\delta^{13}\text{C}_{\text{VPDB}} -3.63\text{‰}$, $\delta^{18}\text{O}_{\text{VSMOW}} 25.02\text{‰}$ for Nina. In November 2017, the reference gas was switched to a well- characterized high purity (HP) carbon dioxide with following isotope parameters: -36.97 for $\delta^{13}\text{C}_{\text{VPDB}}$, 8.6 for $\delta^{18}\text{O}_{\text{VSMOW}}$. Each of the samples was measured three to five times. The C¹³ and O¹⁸ values measured for the reference gases are in good agreement with the reference values.

Internal precision measures the reliability of the mass spectrometer in isolation based on repeated analysis of the same aliquot of gas. The internal precision of the mass spectrometer is defined as the level of reliability of the mass spectrometer and is measured using repeated analysis of sample gas. The low level of internal precision of mass spectrometer may be caused by the errors of a random origin (e.g.shot-noise), as well as not specified mass spectrometric fractionations (may be caused by exchanged of isotope of CO₂ molecules). The shot noise limit at 15kv signal is 0.009‰ (Merritt and Hayes, 1994). The average standard error of D₄₇ calculated for 20-heated gas equals 0.0109‰ ± 0.0008‰ (Davies, 2018).

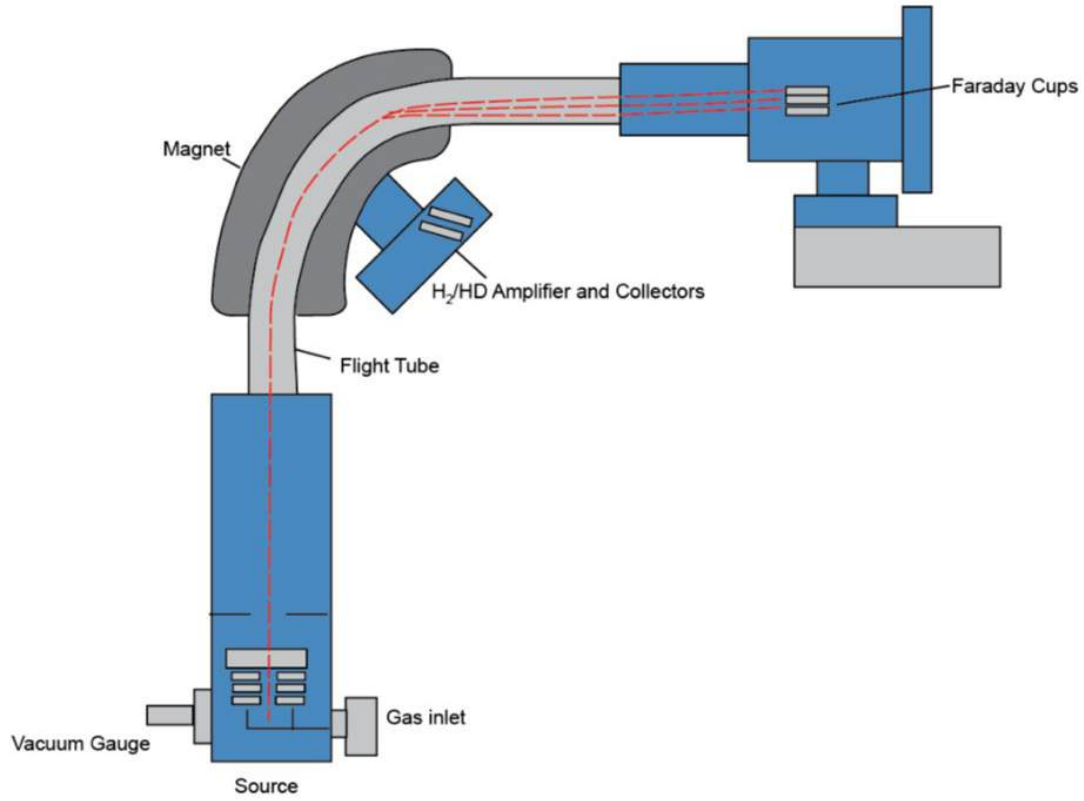


Figure 2.5. Diagram illustrating a gas-source sector of mass spectrometer. Modified from thermos MAT 253 guide (ThermoFinnigan, 2002)(modified image from Dale, 2014)

- **Data processing and correction**

Calculation of the bulk isotopic composition of $d^{13}\text{C}$, $d^{18}\text{O}$, d_{45-48} , and raw value of Δ_{47}

All calculations were done using Easotope software (John and Bowen, 2016).

The bulk isotopic composition of $d^{13}\text{C}$ and $d^{18}\text{O}$ can be calculated as:

$$d^{13}\text{C} = ((^{13}\text{C}/^{12}\text{C}_{\text{sample}}) / (^{13}\text{C}/^{12}\text{C}_{\text{standard}}) - 1) \times 1000 \quad (\text{Equation 2.6})$$

$$d^{18}\text{O} = ((^{18}\text{C}/^{16}\text{C}_{\text{sample}}) / (^{18}\text{C}/^{16}\text{C}_{\text{standard}}) - 1) \times 1000 \quad (\text{Equation 2.7})$$

Where ratios $^{13}\text{C}/^{12}\text{C}$ $^{18}\text{O}/^{16}\text{O}$ can be expressed as the relative abundance ratios $d R_{13}$ and R_{18} respectively:

$$d^{13}\text{C} = (R_{13\text{-sample}} / (R_{13\text{-standard}} - 1) \times 1000 \quad (\text{Equation 2.8})$$

$$d^{18}\text{O} = (R_{18\text{-sample}} / (R_{18\text{-standard}} - 1) \times 1000 \quad (\text{Equation 2.9})$$

The bulk isotopic composition for isotopologues with masses in the range between 45 and 48 can be then expressed using the following equation:

$$d_i = (R_{\text{sample}}^i / R_{\text{working gas}}^i - 1) \cdot 1000 \quad (\text{Equation 2.10})$$

i is mass number and $R^i = i/44$ of analysed CO_2

The relative abundance ratios R_{13} and R_{18} have to be first calculated for the working gas using international reference material (VSMOW and VPDB).

$$R_{13\text{WG}} = R_{13\text{VPDB}} \cdot \left(1 + \frac{^{13}\text{C}_{\text{WG}}}{1000}\right) \quad (\text{Equation 2.11})$$

$$R_{18\text{WG}} = R_{18\text{VSMOW}} \cdot \left(1 + \frac{^{18}\text{O}_{\text{WG}}}{1000}\right) \quad (\text{Equation 2.12})$$

These equations can be solved using Brandt parameters (used since 2016) (Brand et al., 2010) (Table 2.1).

Table 2.1. Santrock and Brandt Parameters

	Brandt Parameters (Brand et al., 2010)
$R_{13\text{VPDB}}$	0.01118
$R_{17\text{VSMOW}}$	0.00038475
$R_{17\text{VPDB CO}_2}$	0.00039310
$R_{18\text{VSMOW}}$	0.0020052
$R_{18\text{VPDB CO}_2}$	0.00208839
I	0.528

I is the terrestrial mass dependent fractionation factor between ^{17}O and ^{18}O .

Next step is calculation of the abundance ratio of the sample gas ($R_{44-49 \text{ sample}}$) are calculated using mass abundance ratios R_{44-49} and measured peaks of voltage intensity registered by Faraday caps of mass spectrometer for these particular masses:

$$R_{\text{mi sample}} = R_{\text{mi WG}} \frac{V_{\text{mi sample}}}{V_{\text{mi sample}}} \cdot \frac{R_{44 \text{ WG}}}{R_{\text{mi WG}}} \quad (\text{Equation 2.13})$$

=

R_{mi} is mass abundance ratio R_{44-49} . V_{mi} is measured voltage (mV).

The relative abundance ratios R_{13} , R_{17} and R_{18} of the sample gas are calculated by solving the following equation:

$$-3K^2 (R^{18})^k + 2K \cdot R^{45} \cdot (R^{18})^k + 2R^{18} - R^{46} = 0 \quad (\text{Equation 2.14})$$

Equation can be solved using a second-order Taylor polynomial where R_{sample}^{18} is $(^{18}\text{O}/^{16}\text{O})$, R^{45} and R^{46} are the sample gas ratios (45/44) and (46/44) and $K = R^{17}_{\text{VSMOW}} \times (R^{18}_{\text{VSMOW}})$. $R^{17}_{\text{sample}} = K \times (R^{18}_{\text{sample}})^{\lambda}$ and $R^{13}_{\text{sample}} = R^{45} - 2R_{17}$.

$R^{18} = ^{18}\text{O}/^{16}\text{O}$, R^{45} and R^{46} are the sample gas ratios. $K = R_{17\text{VSMOW}} \cdot (R_{18\text{VSMOW}})^{\lambda}$ (Daeron et al., 2016) (Table 2.1.)

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the sample are then calculated:

$$\delta^{18}\text{O}_{\text{VSMOW sample}} = \frac{R_{18 \text{ sample}} - R_{18\text{VSMOW}}}{R_{12\text{VSMOW}}} \cdot 1000 \quad (\text{Equation 2.15})$$

$$\delta^{13}\text{C}_{\text{VPDB sample}} = \frac{R_{13 \text{ sample}} - R_{13\text{VPDB}}}{R_{13\text{VBDP}}} \cdot 1000 \quad (\text{Equation 2.16})$$

Both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values are reported against Vienna PeeDee Belemnite (VPDB), and the $\delta^{18}\text{O}_{\text{fluid}}$ is reported against Vienna Standard Mean Ocean Water (VSMOW).

Parameter D_i expresses the excess of a multiply substituted isotopologues compared to a sample of the same bulk isotopic composition under stochastic distribution (Huntington et al., 2009) is calculated as:

$$D_i = (R^i_{\text{sample}}/R^i_{\text{stochastic}} - 1) \cdot 1000 \quad (\text{Equation 2.17})$$

Raw D_{47} for mass 47 equals:

$$D_{47\text{raw}} (\text{‰ WG}) = [(R^{47}/R^{47*} - 1) - (R^{46}/R^{46*} - 1) - (R^{45}/R^{45*} - 1)] \cdot 1000 \quad (\text{Equation 2.10})$$

R^{47*} , R^{46*} , R^{45*} are ratios of mass $i/44$ of the sample under stochastic distribution and are calculated as:

$$R^{45*} = R^{13} + 2 R^{17} \quad (\text{Equation 2.18})$$

$$R^{46*} = 2R^{18} + 2 R^{13} \cdot R^{17} + (R^{17})^2 \quad (\text{Equation 2.19})$$

$$R^{47*} = 2 R^{13} \cdot R^{18} + 2 R^{17} \cdot R^{18} + R^{13} \cdot (R^{17})^2 \quad (\text{Equation 2.20})$$

$R_{17} = {}^{17}\text{O}/{}^{18}\text{O}$ is calculated using the terrestrial mass-dependent fractionation ϵ between ${}^{18}\text{O}$ and ${}^{17}\text{O}$ (Table.2.1).

$$R_{17\text{WG}} = R_{17\text{VSMOW}} \cdot \left(1 + \frac{R_{18\text{WG}}}{R_{18\text{VSMOW}}}\right)^{\epsilon} \quad (\text{Equation 2.21})$$

Data Correction Procedures

Values for $\Delta_{47\text{raw}}$ have to be corrected in three steps. First, the correction for the non-linearity effect of the mass spectrometer (Huntington et al., 2009). Received values are then translated into the absolute reference frame of (Dennis et al., 2011) and adjusted using acid fractionation factor. Corrections are applied within a ‘correction time interval’ which is characterised by stable conditions of mass spectrometer.

Non-linearity effect of mass spectrometer and its correction

If two heated gases with different bulk isotopic composition δ_{47}' and δ_{47}'' are analysed, theoretically their state of reordering should be similar $\Delta_{47}' = \Delta_{47}''$ (we assume they reached stochastic distribution). Nevertheless, in practice, a linear trend is observed between two values of Δ_{47} .

It has been suggested that the observed relationship is probably caused by an imperfection in the mass-spectrometer (Eiler and Schauble, 2004; Huntington et al, 2009). Non-linearity may cause significant errors in final values of D_{47} especially if there is a large difference in isotopic composition between measured samples and standards (Ghosh et al., 2006; Huntington et al., 2010). The level of non-linearity may vary and depend on the state of mass spectrometer, time period of sample measurements, as well as specific conditions of mass spectrometer such as cleanliness, filament and turning (Bernasconi et al., 2013). Non-linearity correction was carried on using heated gases with different bulk isotopic composition (dolomite samples) and pressure baseline correction (calcite samples) (Bo He et al., 2012; Bernasconi et al., 2013).

- Heated gas correction

Heated gas correction was done by measuring the D_{47} for gasses with varying bulk isotopic composition (d_{47}) with values in the range between -47 ‰ and 10 ‰. Prior to measurements

studied gasses were heated up to 1000 °C in a quartz tube during approximately 2 hours and then quenched at room temperature following the procedure of Huntington et al., (2009).

Non-linearity effect of mass spectrometer causes the increase of Δ_{47} at heavier values of d_{47} . The received heated gas line can be defined in the form of the following mathematic equation $y = mx + c$ where $x = d_{47}$, $y = \Delta_{47}$, m is gradient of heated gas line and c = intercept value at y axis when $d_{47} = 0$. The received parameters for heated gas line is then used for non-linearity correction of a sample gas using following equation:

$$\Delta_{47 \text{ HG-corrected}} = m (d_{47 \text{ sample}}) + \Delta_{47 \text{ raw}} \quad (\text{Equation 2.22})$$

- Pressure Base (PBL) correction

The heated gas correction for non-linearity is time-consuming process as it requires the repeated measurement of heated gasses to monitor changes in slope. After understanding the primary cause of non-linearity effect, an alternative approach for correction has been proposed by Bo He et al., (2012) and Bernasconi et al., (2013).

The measurement of ion beam intensity involves comparison between the background voltage signal and the signal when the CO₂ gas is introduced to the source system. Background signal is a background noise measured when analyte gas is not introduced to the ion source and it was assumed to be stable during the whole process of sample measurement. However, the negative shifts in the background signal before and after main peak (Fig.2.6) was noticed (Bo He et al., 2012, Bernasconi et al., 2013). The magnitude of the background shift increases with increasing ion beam intensity. However, the PBL shift is more significant at highly sensitive collectors such as m/z 47, 48 and 49. In this case the difference may reach couple of hundreds mV and may cause significance offset (Bo He et al., 2012, Bernasconi et al., 2013).

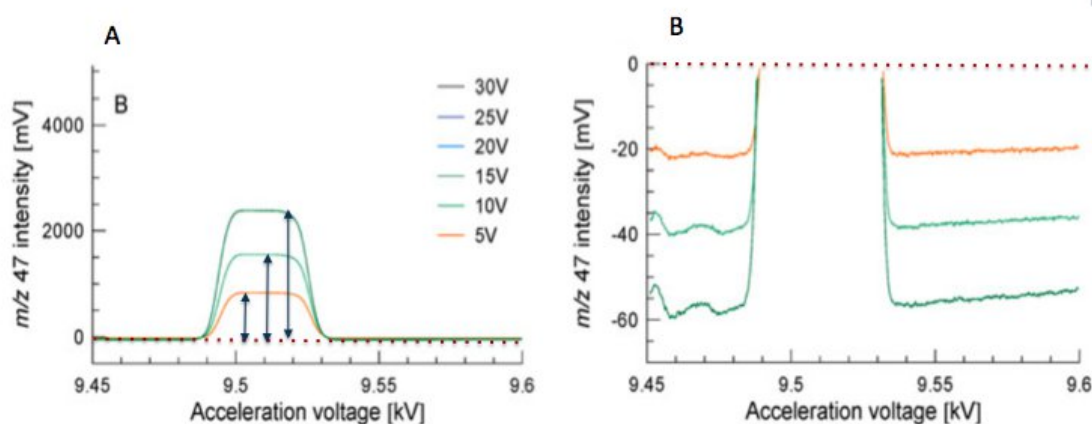


Fig. 2.6. A. The example of peak shape of m/z 47 obtained by scanning the high voltage and different intensities on the m/z 44. Dashed red line indicate the true background value (no gas is introduced to the system). The ion beam intensity corresponds to the distance from the peak value till background value (blue arrows)B. Expanded view of the lower part of the peak (section A). There is shift of baseline from expected true value. The amplitudes of background shift decreasing with increasing m/z 44 intensity. (modified from Bernasconi et al., 2013)

The shift in the baseline is thought to be due to secondary electrons entering the Faraday cups (He et al., 2012). It is assumed that the ion beam reaches the Faraday cup without deviation from the straight angle. However, the slight deviation of the ion beam trajectory from straight angle due to collision of the m/z 44 ion beam may cause the production of secondary electron flow. Another reason is repulsion of m/z 44 ions within Faraday cup itself (He et al., 2012).

The amount of secondary electron flow depends on the intensity of the m/z mass 44 beam (i.e., the pressure at which the sample gas is introduced into the ionization chamber and later to the flight tube) and its focus. The background effect decreases with increasing intensity of the ion beam (Fig.2.7).

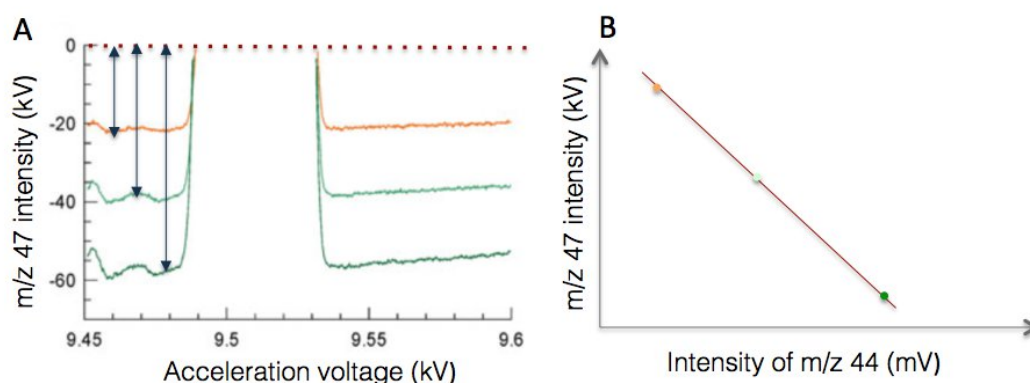


Fig. 2.7. Illustration of pressure base line effect. The increase of intensity leads to decrease of pressure base line shift. A) intensity of m/z 47 beam against acceleration voltage. B) Intensity of m/z 47 versus intensity of m/z 44.

PBL correction for calcite samples was done following the method of Bernasconi et al., (2013). The “pick shape” scans were run daily with variation of mass intensities between 12kv and 17

kv on the 44 beam (Fig.2.8). Scans were then loaded into Easotope program. The maximum peak height was manually selected on each scan. Peak heights were then plotted against minimum intensity for each mass in the selected background region. Program then fits the quadratic regression for the relationship on each mass 44-48 separately plotted versus intensity on m/z 44 (Fig.2.9). Regression fit is then used to correct for sample background.

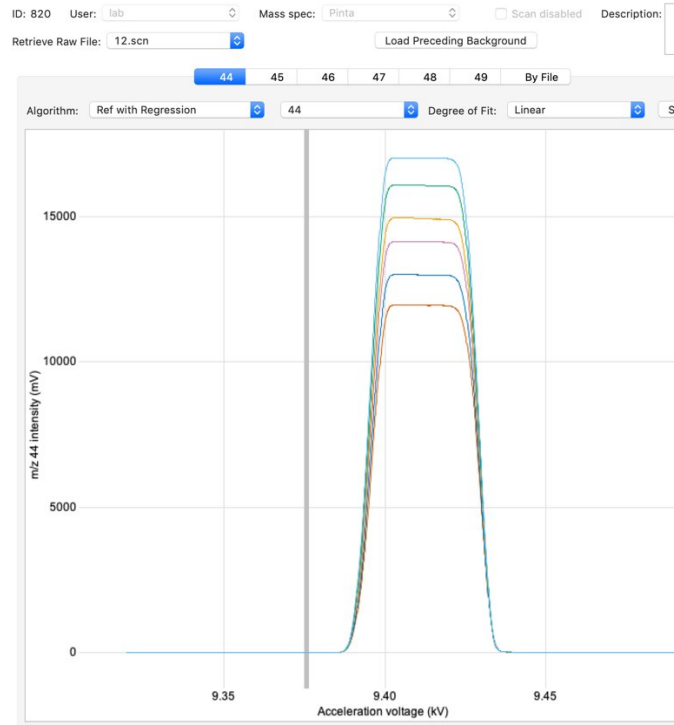


Fig. 2.8. Diagram illustrating example of measured “peak shape” scans on Pinta mass spectrometer with variation of mass intensities on the 44 beam between 12kv and 17kv. As an example, intensity for mass 44 is presented with acceleration voltages in the range between 9.3 and 9.45. (image is taken directly from Easoplot program)

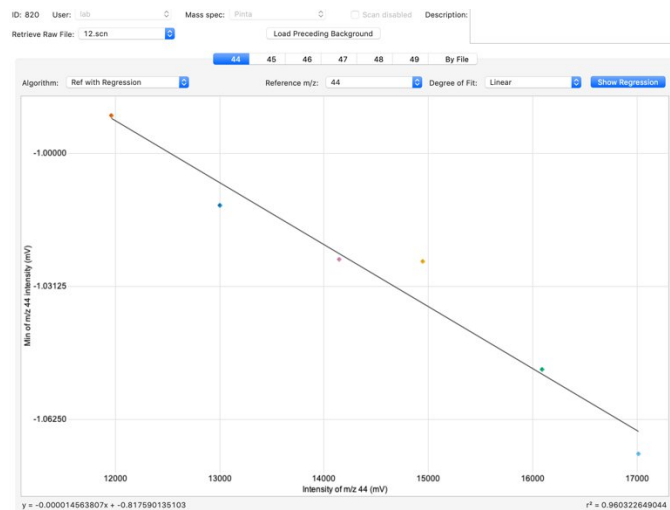


Fig. 2.9. Example of regression fit for background on mass 47 (y axis) versus intensity on m/z 44 (x axis) (image is taken directly from Easoplot program). Parameters of the slope are indicated at the bottom of the diagram.

Transformation results into the absolute reference frame

- Primary reference frame

After correction for non-linearity effect data have to be transformed into interlaboratory absolute reference frame using empirical transfer function (ETF). This enables to account for analytical effects of isotope scrambling (i.e fragmentation and recombination of molecules) in the ion source of the mass spectrometer, as well as it makes possible inter-comparison of results between laboratories (Dennis et al, 2011).

A primary reference frame involves equilibrating gases at different temperatures. Equilibrated gases are prepared by freezing 1 ml of water and an aliquot of tank CO₂ gas in a quartz tube. The tube is then sealed and placed into a water bath which is heated to 25°C, 50 °C or 80°C for three days. This allows the equilibration of the CO₂ gas and water in the tube to the conditions of water bath. After equilibration is reached, the tube is taken out and the water is frozen to prevent further equilibration. The water is then removed by using slush and liquid nitrogen traps. Remained gas is then run through the manual line for further purification and then measured on the mass spectrometer.

The measured values of Δ_{47} are then plotted against the theoretical or absolute Δ_{47} values for each temperature theoretically determined based on quantum mechanical and statistical thermodynamic theory of Wang et al., (2002). The received measured values of Δ_{47} after non-linearity correction for different temperatures plotted against «true» Δ_{47} values. The corresponding offsets defines the transfer function (Dennis et al, 2011). The values of Δ_{47} for sample can be then transferred to absolute value $\Delta_{47\text{ FR}}$ using the slope and the intercept of this transfer function.

- Secondary reference frame

However, the use of heated gases to reconstruct the reference frame results in small errors. The constrained equilibrated gas line based on measurement of heated gases has a tendency to evolve with time. Additionally, the preparation and analysis of heated gases is a very time-consuming process. For this reason, it was proposed to constrain secondary reference frame by comparing inter-laboratory carbonate standards with “accepted” values. Under “accepted” values it is understood the values for the same types of standards, which were officially accepted by clumped isotope community. Standards of ETH2 ($\Delta_{47} = 0.300\text{ ‰}$), ETH3 ($\Delta_{47} = 0.713\text{ ‰}$), Carrara Marble ($\Delta_{47} = 0.409\text{ ‰}$) and heated gases were used. Presented values for

Δ_{47} are own internal lab values. $\Delta_{47\text{-RF}}$ values were also recalculated to count for ^{17}O anomaly using Brand parameters (Brand et al., 2010).

Correction for acid fractionation

The process of acid digestion of carbonate samples was carried out at temperature of 90 °C. The acid digestion at this temperature allowed to speed up an analytical process, as the process of carbonate digestion at room temperature of 25 °C normally takes from 18 up to 24 hours (Ghosh et al., 2006). The decrease of time for sample digestion also allowed to increase the reproducibility of Δ_{47} (Wacker et al., 2013). However, the difference in digestion temperature effects relative abundance of ^{13}C - ^{18}O in CO_2 gas produced during acid digestion of carbonate samples with similar isotopic composition (Wacker et al., 2013). Fractionation factor of 0.082‰. (Deflise et al., 2015) was added to the final values of $\Delta_{47\text{-RF}}$ to correct for acid fractionation. The $\delta^{18}\text{O}$ values were also corrected for phosphoric acid digestion at 90°C using acid fractionation factors of 1.00813‰ for dolomite samples (Rosenbaum and Sheppard, 1986) and 1.00930 ‰ for calcite samples (Kim and O'Neil, 1997).

Metrics of contamination

Despite the fact that samples are passed through a series of purification procedures, it does not always allow to remove completely the contaminant molecules. Samples may be monitored for presence of any traces of contaminants (e.g. $^{32}\text{S}^{16}\text{O}$) by analysing the difference between signal of Δ_{48} of sample gas and Δ_{48} values for reference material (heated gas) (Huntington et al., 2009, Wacker et al., 2013). This parameter is called Δ_{48} offset. Samples with Δ_{48} offset values less than 1.5 ‰ may be considered as clean.

raw D_{48} can be calculated in similar way as raw D_{47} :

$$D_{48\text{raw}} (\text{‰ WG}) = [(R^{47}/R^{47*} - 1) - (R^{46}/R^{46*} - 1)] \cdot 1000 \quad (\text{Equation 2.23})$$

Although mass 49 is undetectable by mass-spectrometry, occasionally 49 parameter may be used to scan for contaminants (John and Bowen, 2016). As the masses 49 is almost undetectable its high value may indicate the presence of contaminants (e.g. sulphur). It is calculated based on difference in m/z 49 measured between the sample and reference gases

(Eiler and Schauble, 2004) and is computed using Easotope programme. Sample is considered contaminated if 49 parameter is above 0.2 value.

$$49_{\text{parameter}} = [R_{\text{sample}}^{49} - R_{\text{WG}}^{49}] \cdot 10^4 \quad (\text{Equation 2.24})$$

Where $R_{49} = 49(\text{mV})/44(\text{mV})$ and WG states for reference gas.

Converting Δ_{47} values to Temperature

Ghosh et al (2006) presented the temperature calibration equation for temperature range between 0 - 50 °C. Furthermore, different temperature relationships were obtained by inorganic calcite precipitated within slightly higher temperature range 7.5-90 °C (Dennis and Schrag, 2010). Multiple biogenic calibration were done for brachiopods and mollusks (Henkes et al, 2013), bivalves (Eagle et al, 2010) and deep sea corals (Thiagarajan et al, 2011). For this research, T °C were calculated using the latest calibration of Davies and John (2019) via the following equation:

$$\Delta_{47} = 0.04028 (\pm 0.00076) \cdot \frac{10^6}{T^2} + 0.23776 (\pm 0.00759) \quad (\text{Equation 2. 25})$$

Where T is expressed in K.

The oxygen isotopic composition of water was back-calculated using the equation 2.26 of Horita, (2014) for dolomite samples and equation 2.27 of Kim and O'Neil, (1997) for calcite samples.

$$10^3 \ln a_{\text{dolomite} - \text{water}} = 3.140 (\pm 0.022) \cdot \frac{10^6}{T^2} - 3.14 (\pm 0.11) \quad (\text{Equation.2.26})$$

$$10^3 \ln a_{\text{calcite} - \text{water}} = 18.03 \cdot \frac{10^3}{T} - 32.42 \quad (\text{Equation.2.27})$$

Where T is expressed in K.

U-Pb isotope analysis: method and derivation of common lead corrected ages.

U-Pb dates are obtained from carbonate minerals by doing six main steps, which are described below:

- **Sample collection, preparation, laser ablation ICP-MS analysis**

The main objectives for U-Pb sample selection were: (i) dolomitized part of the core (white and brown colour dolomite), (ii) calcite crystals filling vugs/vein interiors or replacing fossil fragments. The zones of interest were cut on small chips of several millimetres in size and were mounted in epoxy. The epoxy mounts were then polished and loaded into a multiple sample tray of an ASI RESolution 193nm laser connected to Jena Analytic PlasmaQuant Elite LA-ICP-MS instrument.

The method of LA-ICP-MS was adapted from LA-ICP-MS zircon geochronology and in detail follows that described by Parrish et al. (2017) and relevant to the Mass Spectrometry and Laser Ablation Laboratory of Portsmouth University where the work was done. In brief, the ablation procedure was performed with a laser power of 3-4 J/cm² using an 80-100 mm beam spot, with ablation time of 30s and 8 Hz repetition. Ablated material was carried into the ICP –MS system using Ar and He gases. Spatial resolution for laser and ICP-MS was $\pm 2\text{m}$ and sensitivity in the range between 30,000 - 40,000cps/ppm for ²³⁸U. This allowed to date samples with low concentration of uranium.

Overall, intensities of U, Th, Pb and Hg isotopes were measured, as well as background counts with the laser not firing. Detailed information regarding LA-ICP-MS operating conditions is presented in Table 1, Appendix 2.2 for Chapter 2. Samples were scanned for zones of interest with the highest concentration of radiogenic material by monitoring ²³⁸U/²⁰⁶Pb. Once these zones were identified, the automated analysis were performed on chosen locations.

- **Data correction procedure**

After ICP-MS measurements, the raw counts were exported to Iolite software (Paton et al., 2010) for initial stage of data processing (Fig.2.10). In Iolite programme measured U/Pb data were first corrected for base line (subtraction of counts arising from ionisation of the carrier gas from). Data were then corrected for down hole fractionation (correction for change in Pb/U as laser ablation pit deepens). Which is correction for change in Pb/U as laser ablation pit deepens. This results in linear trend with increasing depth of the ablated whole. The third step of data correction with Iolite software includes instrumental drift correction related to temporal variations of measurement of constant elemental or isotope ratios in SRM612

standard. Finally, data were corrected for Pb isotope mass bias effect (correction for the instrument's fundamental tendency to measure heavy isotopes preferentially). U/Pb data is then normalised to come into line with correct ratios of the SRM612 standard. The output of Iolite is a set of intensities of isotopes, ppm approximations, raw and corrected isotope ratios and their propagated uncertainties that are consistent with the correct U-Pb ratios of the SRM612 standard; this file is then able to be imported as data into Excel.

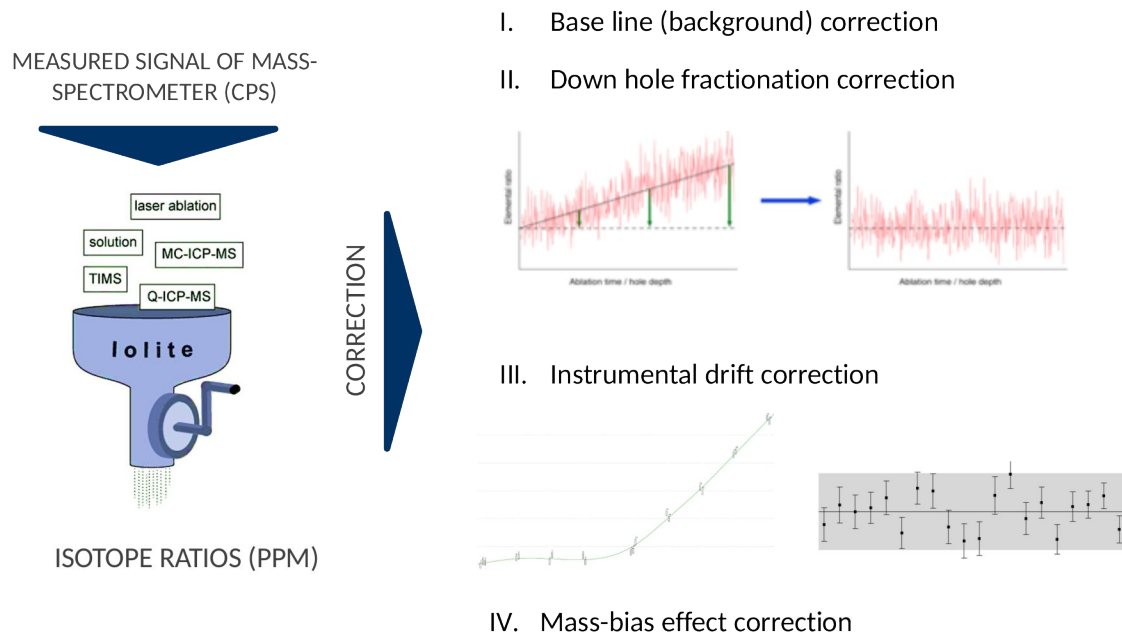


Figure 2.10. Diagram illustrating the Iolite correction procedure. (images are taken from iolite-software.com website)

Samples were measured against reference material using two standards: glass standard NIST 612 (38ppm U and Pb) and the 254.6 ± 6.4 Ma WC-1 calcite standard (5ppm U, > 85% radiogenic Roberts et al. 2017). Values for primary standard NIST 612 were used to correct for base line correction, down hole fractionation (using linear fit equation), Pb isotope mass bias effect, as well as initial normalisation procedure. Additional to NIST 612 and 254.6 ± 6.4 Ma WC-1 calcite standard, the 12ppm U Mud Tank zircon (Roberts et al., 2017) was measured and used as a secondary standard to monitor the potential biases due to composition matrix effects. Another glass standard NIST 614 was also included as “unknown”.

Results of U-Pb measurements of standards (WC-1, Mud Tank zircon, NIST 614) for dolomite and calcite samples from Resolution Guyot are tabulated in Table 1 of Appendix.3.2. Results

for WC-1 standards are also graphically presented in Figure 1, Appendix.3.2 dolomite samples from Resolution Guyot.

After data were processed in Iolite software (Paton et al., 2010), both standards and unknowns (studied samples) were imported into an Excel spreadsheet used at the University of Portsmouth for carbonate dating, written by R Parrish and used in Parrish et al. (2017).

The next step in data processing is secondary normalization using WC-1 calcite standard. The age and uncertainty was calculated for the 254 Ma WC-1 calcite standards measured along unknowns for analytical run of up to 3 hours. Calculated ages, corrected against the SRM612 glass ranged from 255 to 269 Ma and with uncertainties ranging from 1.86% to 3.14% (1 standard deviation). Calculated uncertainty for U-Pb of the WC-1 standard was then quadratically added to all individual analysis uncertainties. All data (including Mud Tank and zircon NIST 614) were then normalised using 254 Ma as the age for the WC-1 for each session.

Following this, the Mud Tank zircon, normalised relative to WC-1 calcite, indicates the bias between zircon and calcite samples. The level of bias was calculated as approximately 4.7% for 732 Ma zircon reference material. Any matrix-related bias within this study are mostly related to variable (Mg, Fe, Ca) compositions of carbonate matrix material. However, it may be also concluded that ~5% bias is likely to be far higher than any Fe-Mg-Ca variations within carbonate minerals. It also has to be mentioned that the dolomite samples were measured using WC-1 calcite standard as dolomite standard was not available.

- **Quantification of common Pb, common Pb correction, and regression strategy**

The Excel spreadsheet uses post-Iolite counts on all masses to calculate final concentration and isotope ratios, as well as correct for common lead. The most important of all of these final data reduction steps is dealing with common Pb correction.

When dating minerals by the U-Pb method, it is essential to differentiate between the Pb produced by radioactive decay (which is used to calculate ages) from that incorporated into the mineral initially (common Pb). The overall procedure used to deal with this is described below.

Common Pb is present in almost all analyses and must be subtracted to obtain ages. All four naturally occurring isotopes of Pb (204, 206, 207, 208) contribute to common Pb and their proportions have varied over the course of geological time due to decay of ^{232}Th , ^{235}U , and ^{238}U ; a commonly used model to approximate the isotope ratios of common Pb is that of Stacey and Kramers (1975), described in Appendix.2.1 for Chapter 2.

For carbonate minerals that have little or no Th incorporated during formation, the ^{208}Pb isotope is the best monitor of its quantity, first because it is the largest of the common Pb isotopes and most precisely measured, but also because ^{208}Pb has little if any radiogenic ^{208}Pb , unlike ^{206}Pb and ^{207}Pb .

The common ^{208}Pb is determined by the following expression:

$$^{208}\text{Pb}_{\text{com}} = [^{208}\text{Pb}_{\text{total}} - (^{232}\text{Th} \cdot \exp^{(\lambda^{232}\text{Th} \cdot T)} - 1)] \quad (\text{Equation.2.28})$$

Where λ^{232} is decay constant of ^{232}U and equals 4.94×10^{-11} , isotopes are expressed in counts per second, T is the proximate age of the mineral (Table 1.Appendix.2.1). The equations (2.1 and 2.2) for T is presented in Appendix.2.3 for chapter 2. In short, T is calculated using a mean value for Pb ratios predicted by Stacey and Kramer mode for age interval between 50-120 Ma. The use of an approximate age, T, is acceptable because in low Th minerals, the contribution is very small and not particularly sensitive to the choice of approximate age.

Common ^{206}Pb and ^{207}Pb are obtained by simply multiplying the $^{208}\text{Pb}_{\text{com}}$ by the appropriate S-K ratio, namely:

$$^{206}\text{Pb}_{\text{com}} = ^{208}\text{Pb}_{\text{com}} \times ^{206}\text{Pb}/^{208}\text{Pb}_{\text{S-K}} \text{ where } ^{206}\text{Pb}/^{208}\text{Pb}_{\text{S-K}} \text{ is } \sim 0.483$$

$$^{207}\text{Pb}_{\text{com}} = ^{208}\text{Pb}_{\text{com}} \times ^{207}\text{Pb}/^{208}\text{Pb}_{\text{S-K}} \text{ where } ^{207}\text{Pb}/^{208}\text{Pb}_{\text{S-K}} \text{ is } \sim 0.409$$

These counts of common Pb isotopes are then subtracted from total counts to obtain the radiogenic ^{207}Pb and ^{206}Pb , which are ratioed to ^{238}U (and ^{235}U) to obtain final ratios for age calculation. This approach is used in the calculation of single spot ages, particularly useful for analyses that are dominated by radiogenic ^{206}Pb .

The uncertainties for these final ages take into account the following:

- Uncertainty in count rates and ratios after Iolite processing, which includes normalisation, drift, down hole correction etc.
- Uncertainty assigned to the common Pb composition (weighted uncertainty reflecting its relative importance to the final counts of ^{206}Pb , ^{207}Pb , etc).
- Uncertainty in the secondary normalisation using the calcite standard WC-1 (via quadratic addition)

An expression that does this is given in Appendix 2.3, if readers are interested in detail. It has been adjusted slightly to conform to the errors obtained from the 2-point regression method within Isoplot, the latter of which uses an ellipsoidal rather than rectangular error ellipse for regressed points.

For situations where there are texturally related analyses that have quite large variations in the common Pb content, data forming a linear array can be regressed. There are two types of Tera-Wasserburg regressions to determine the ages. The first type is the conventional Tera-Wasserburg (Terra and Wasserburg, 1972) which plots the $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{238}\text{U}/^{206}\text{Pb}$. The age can be calculated using the T-W regression and intercept with Concordia using Isoplot (Ludwig, 2013). However, the application of this method to samples with low U content (and therefore low radiogenic ^{207}Pb counts) is likely to have more scatter and higher uncertainty than the method described below, as discussed by Parrish et al, (2017). This traditional T-W plot ignores ^{208}Pb and makes the common Pb correction using the measured ^{207}Pb and ^{206}Pb counts, both of which often contain substantial proportions of common Pb.

The Parrish et al. (2017) alternative derives the $^{208}\text{Pb}_{\text{com}}/^{206}\text{Pb}$ ratio, using procedures above using the measured signal of ^{232}Th and $^{208}\text{Pb}_{\text{total}}$. By subtracting the radiogenic ^{208}Pb ($^{208}\text{Pb}_{\text{rad}}$) from the $^{208}\text{Pb}_{\text{com}}$ (on the assumption of a plausible age range) and dividing by the ^{206}Pb signal, the ratio $^{208}\text{Pb}_{\text{com}}/^{206}\text{Pb}$ can be calculated. This ratio can then be plotted against $^{238}\text{U}/^{206}\text{Pb}$, and the data array intercept with the X-axis will define the radiogenic ratio, and therefore final age. This has been termed the ‘8-6 TW’ isochron (Fig.2.12). Linear regressions (with output of slope and uncertainty) produced in this thesis have relied upon the Isoplot software (Ludwig, 2013). All plots shown are produced by Isoplot and uncertainties are plotted as error ellipses.

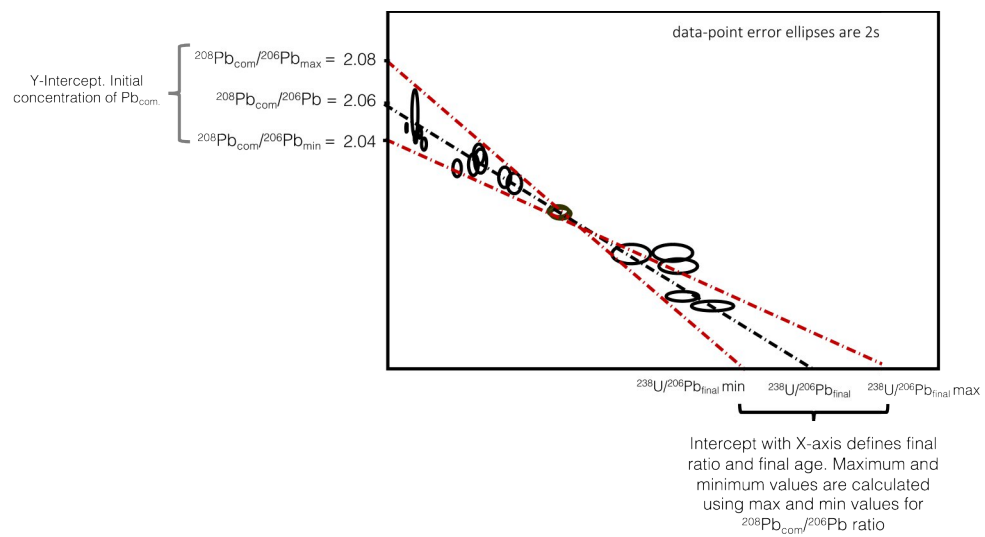


Figure 2.12. Graphical illustration of 8-6 TW diagram with illustration of age calculation procedure.

Chapter 3: Reconstruction of environment and time of dolomitization using clumped isotope and U-Pb methods (Resolution Guyot, Pacific Ocean)

3.1. Introduction

Carbonate rocks contain about half of the world's gas and oil resources due to its high porosity and permeability characteristics (Burchette, 2012). However, the petrographic characteristics of carbonate rock are highly variable due to chemical instability of carbonate minerals (Land, 1980, 1992; Machel et al., 1993; Machel, 1997; Kaczmarek and Sibley, 2014). Instability leads to early and complex diagenesis of the rock matrix, hence creating difficulties for reservoir properties predictions (Moore, 2013). The reconstruction of a temperature-time evolution for carbonate sedimentary basins is essential to understand the diagenetic evolution of carbonates. Common methods for paleothermometry (the vitrinite reflectance index (VR) (Sweeney and Burnham, 1990), the fluid inclusion technique (Goldstein and Reynolds, 1994), the conodont alteration index (Epstein et al., 1976), molecular indices, and standard oxygen isotope analysis (Kim and O'Neil, 1997)) are, however, mostly limited and are difficult to apply to carbonate rocks. For this reason, there remains a need for a more efficient method of paleotemperature reconstruction. The timing of diagenetic events is also difficult to reconstruct: fission track analysis (Gallagher et al., 1998), U-series (Pike et al., 2012; Hoffman et al., 2016), and Sr isotope ratio (Smalley et al., 1994; Hess et al., 1986) are not very precise dating methods.

Clumped isotope thermometry allows us to calculate the temperature of mineral precipitation without the need for assumptions about the isotopic composition of the diagenetic fluid, which can instead be back-calculated using the independently estimated clumped isotope temperatures (Eiler, 2007; MacDonald et al., 2017; Honlet et al., 2018). Recent studies demonstrate that this method of clumped isotope paleothermometry is a powerful tool to constrain the environment of carbonate rock diagenesis (Huntington et al., 2011; Dale et al., 2014; Vandeginste et al., 2014; MacDonald et al., 2017; Honlet et al., 2018).

Carbonate rocks have been also successfully analysed using U-Pb dating methods, with early studies more focussed on speleothems (Richards et al., 1998; Woodhead et al., 2006; Rasbury and Cole, 2009). Due to their meteoric origin speleothems are more enriched in uranium and

initially have high $^{238}\text{U}/^{204}\text{Pb}$ compared to carbonates of marine origin. The recent development of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) facilitates the dating of a wide variety of carbonate cement in situ, compared to previously used techniques such as Thermal Ionization Mass Spectrometry (ID-IRMS) TIMS, or ICP-MS. These methods require larger volume of samples and sample dissolution, though they benefit from higher precision analyses (Rasbury and Cole, 2009). Recent studies (Li et al., 2014; Coogan et al., 2016; Parrish et al., 2017., Roberts et al., 2017) have shown that carbonate cement and veins, even with initially low concentration of uranium can be successfully dated using the LA-ICP-MS technique. Although some studies were done to couple clumped isotope thermometry and U-Pb dating to reconstruct diagenetic history of carbonate rock matrix (Lawson et al., 2017; Pagel et al., 2018; Mangelot et al., 2018), these studies mostly focus on calcite and not dolomite.

Isolated carbonate platform of Resolution Guyot situated in the western part of Pacific Ocean (Sager et al., 1993). Limited source of common lead due to platform isolation from the continent, large amount of available geological information (Arnaud et al., 1995; Jenkyns, 1995, Paull et al., 1995; Winterer et al., 1995; Ogg, 1996; Jenkyns and Wilson, 1999; Röhl and Ogg, 2010), presence of dolomitization (Flood and Chivas, 1995; Flood et al., 1996) and previous age estimates based on Sr isotope method (Jenkyns et al., 1995) made Resolution Guyot an attractive test case for our approach. The core description revealed the presence of three types of dolomites: brown, light brown and white. The previous interpretations suggested precipitations of these dolomites as two separate dolomitization pulses at different temperature conditions (Flood et al., 1996; Flood and Chivas, 1995).

However, uncertainties remain in reconstructing the paleotemperatures and the environment of dolomite precipitation from Resolution Guyot. The previous studies suggested temperature range for brown color dolomite precipitation was 15- 30 °C (Flood and Chivas, 1995, Jenkyns et al., 1995, Flood et al., 1996). It may be considered quite ambiguous as it does not give clear understanding of environment of brown dolomite precipitation. Additionally, temperatures of dolomite precipitation were calculated using assumption regarding isotopic composition of dolomitized fluid. The paleotemperature of dolomite cementation was previously calculated using the Land (1985) equation for dolomite formation temperatures using an approximated isotopic composition of $\delta^{18}\text{O}_{\text{porewater}}$ of seawater for the Cretaceous period equals -2‰ (Lohman, 1988).

Timing of dolomitization was calculated using measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in dolomite sample by comparing received values with already known variation of Sr isotopes in sea water through time (Smalley et al., 1994; Hess et al., 1986). However, similar Sr ratio can occur at different geological time. Thus, the Sr age solution is not always unique. Additionally, Sr isotope method is based on assumption that sea waters is an only source of Sr in precipitated mineral. However, additional sources may exist. For example, volcanic basement of carbonate platform. In this case, the age estimate is no longer accurate.

For these reasons, there remains a need for more efficient methods of paleotemperature and age reconstruction, which would allow for a more accurate and detailed interpretation of the origin of dolomitizing fluids and a more robust interpretation of the environment of dolomitization.

In this chapter, we combine the clumped isotope paleothermometry and laser ablation U-Pb dating in early dolomites of Resolution Guyot with an aim to demonstrate that these two proxies may be successfully used to reconstruct the environment and age of dolomite precipitation with high accuracy. We also discuss the behaviour of radiogenic system during process of mineral recrystallization.

3.2. Geological Background

The samples used in this study were taken from core facilities of The International Ocean Discovery Program (IODP), obtained during a drilling campaign (ODP-Ocean Drilling Program, Leg 143, Site 866) of carbonate guyots in the Western Pacific Ocean. The aim of Leg 143 was to drill through the series of drowned shallow-water carbonate build-ups. The further description is based largely on Arnaud et al., 1995, and ODP Scientific Reports.

The selected for this study Site 866 was drilled at the periphery of Resolution Guyot. It represents a carbonate platform of 25 km long and is situated at a water depth of 1300-1400 mbsf (meters below sea floor) (Fig.3.1.a-c). The deposition of carbonate took place through Hauterivian-Albian (132.9 – 100.5 Ma) on the volcanic edifice of approximate age of 130 Ma and have originated as a result of the Pacific Plates movement over a hot spot (Winterer and Sager, 1995).

The Cretaceous carbonate units are covered by a thin (25-70m) pelagic cap of Cenozoic age. The overall thickness of carbonate succession reaches 1600 m.

Site 866 penetrates overall eight sedimentary units (Fig.3.2.). The oolitic facies and marine fauna of Unit VIII allowed to interpret this unit as a transgression over the volcanic edifice. The abrupt change from coarse-grained oolitic/peloidal grainstones of Unit VIII to finer-grained wackstone /packstone of units VII and VI (Fig.3.3. a-c), the presence of erosional surfaces, the high abundance of algae-laminities and organic-rich intervals were interpreted as the « keep-up» stage of the carbonate platform with gradual sea level rise and development of restricted lagoonal – peritidal conditions.

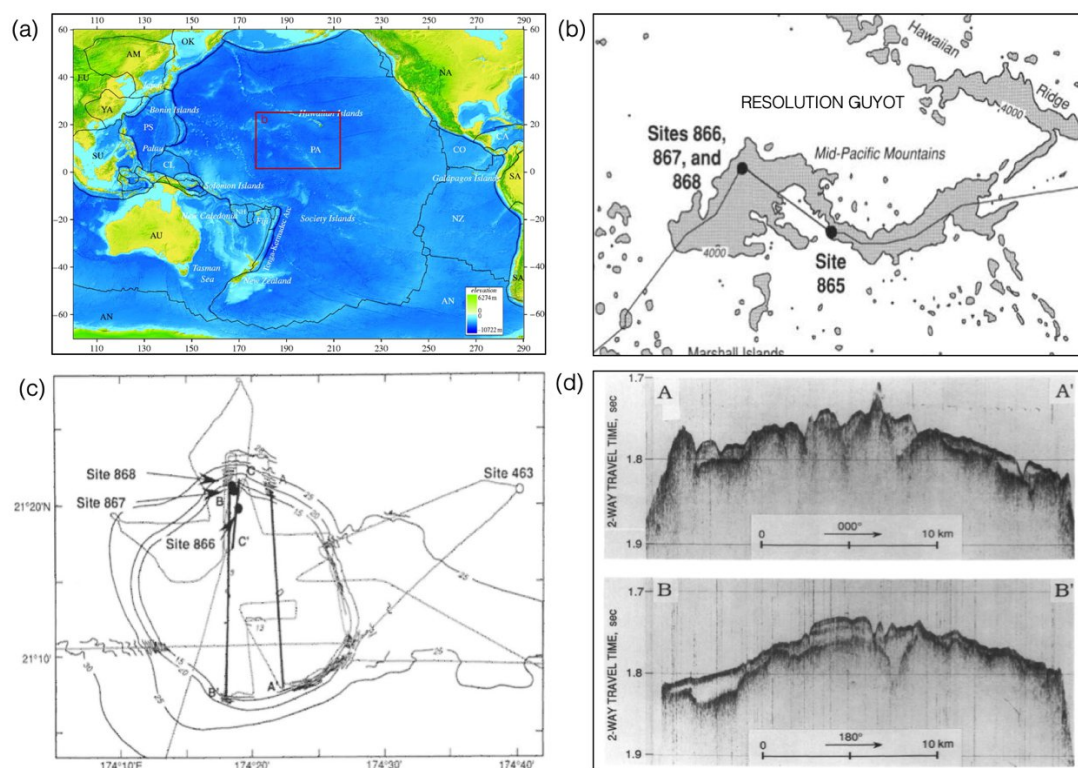


Figure 3.1. (a) Bathymetry map of Pacific ocean with illustration of elevation and main island chains. Red square indicates position of Resolution Guyot. (b) Map of Pacific ocean showing geographical position of Resolution Guyot. Position of Sites are indicated by filled circles (Winterer et al., 1995). (c) Contour map showing the topography on the surface of the Lower Cretaceous platform. Sites 866, 867, and 868 are indicated by filled circles. (d) Seismic profiles A-A' and B-B' across Resolution Guyot showing generalized bathymetry with Resolution Guyot dimensions. (Winterer et al., 1995)

The deposition of Unit V, comprising oolitic grainstones likely suggests a change in sedimentary environment. (Fig.3.3.d) The hydraulic sorting and fossil assemblage suggested deposition in a shallow, turbulent marine environment.

According to Arnaud and Flood (1995) sea level rise might have caused the deepening of environment and establishment of shallow marine conditions. The dominance of organic

material, the presence of lignitic and plant fragments in Unit IV indicates the change of shallow marine (Unit V) to a more restricted environment. The low faunal diversity of Unit III may be interpreted as restricted lagoonal conditions with some marine influence (Fig.3.3.f). The cessation of carbonate production took place at the end of the Albian with final episode of platform drawing when the deposition of the pelagic cap took place from Maastrichtian to Pliocene time (Arnaud and Flood., 1995). The samples of this chapter were mostly selected from Unit VII (white dolomite samples) and from Unit VIII light and dark brown dolomite). The exact position of selected samples is presented in Fig.3.2 and summarised in Table 3.1.

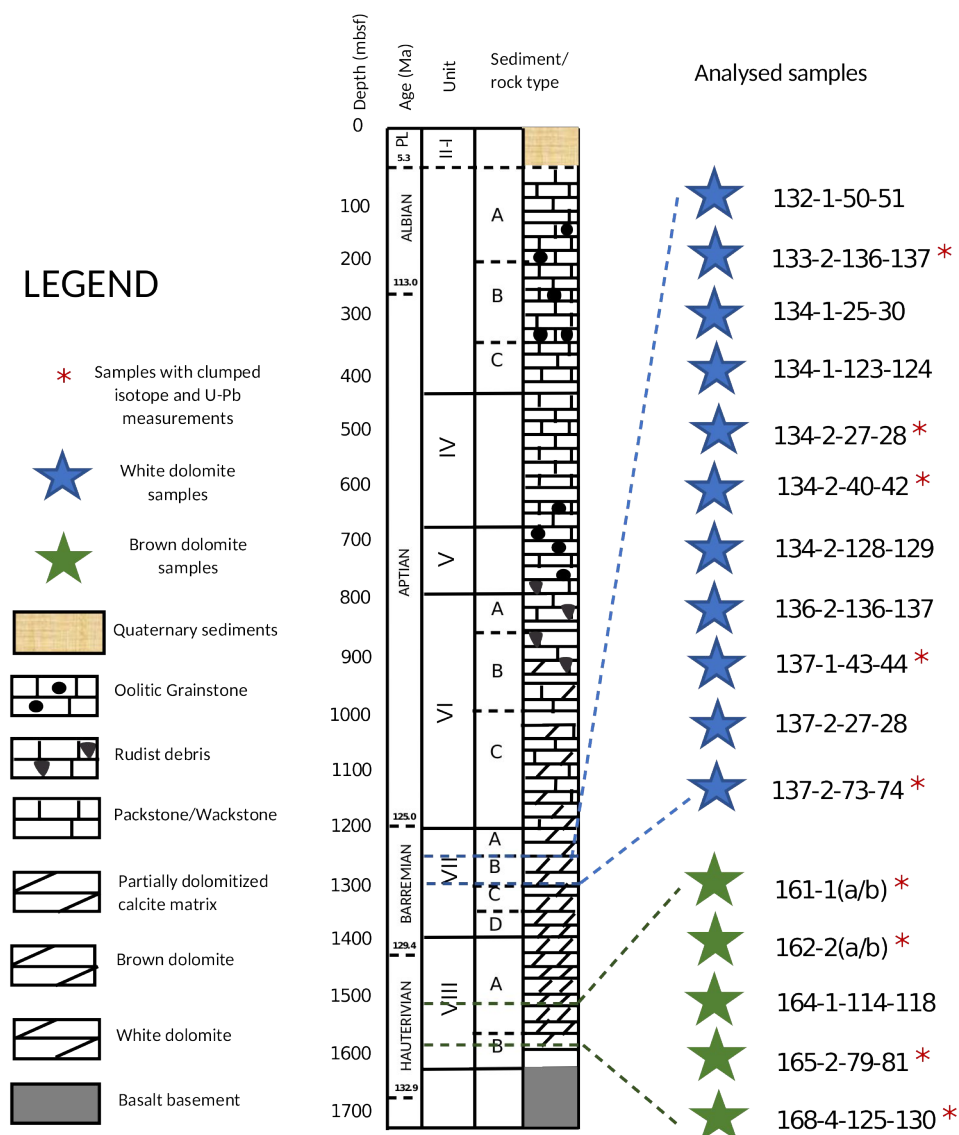


Figure 3.2. Chronostratigraphic chart of Site 866, Leg 143 of Resolution Guyot including age of the core matrix, lithological unit division and sedimentary rock types (modified from Winterer et al., 1995). Position of analysed samples of white and brown dolomite (blue and green star symbols) is indicated.

The studied sequence of limestone exhibits generally high levels of diagenesis. A dominant type is dissolution of aragonite fossils which has created moldic porosity (Fig.3.4.a-d). The fossil dissolution is present in all lithological units, especially in the oolitic Unit V and the upper portion of Unit VI (Arnaud, et al, 1995a; Röhl and Ogg, 2010). The carbonate sequence of Resolution Guyot was deposited mostly in shallow water. Thus, small eustatic changes might have caused subaerial exposure of the carbonates (Röhl and Ogg, 2010). A second diagenetic feature that has been observed in cores is dolomitization. The core description reveals three distinct types of dolomite, brown (dark and light) and white. The presence of brown dolomite is first recorded downcore at 500mbsf (section 143-866-56R-CC) and again at about 900mbsf (section 143-866-98R-1). The continuous presence of brown dolomite is recorded downhole below 1200 mbsf in Barremian age sediments (Units VII-VIII). The fine-grained dolomite of brown colour is completely replacing the carbonate matrix (Fig.3.4.a). There is evidence of secondary dolomite of more coarse-grained textures replacing the fossil fragments or filling the small scale vug interiors (Fig.3.4.a). It was noticed that colour of brown dolomite also varies from dark brown to light brown. The white dolomite (Fig.3.4.b) is mostly present within a interval at the depth from 1250-1300 mbsf (Fig.3.2).

The multiple stages of dolomitization of Resolution Guyot has already been the subject of discussion (Flood and Chivas, 1995, Jenkyns et al.,1995, Flood et al., 1996). These paleotemperatures were calculated by Flood et al (1996) using Land (1985) equation for dolomite formation temperatures using an approximated isotopic composition of $d^{18}O_{\text{porewater}}$ of seawater for Cretaceous period of -2‰ (Lohman, 1988). The strontium isotope data suggested that brown dolomitization occurred in a time interval between 102 - 120 Ma at water temperatures in the range between 30-15 °C. The reported temperature for white dolomite precipitation is 17 °C with an approximate age of 24 Ma. Endo-upwelling was proposed as a potential mechanism of the dolomitization process. The re-initiation of ocean seawater circulation, due to the shift from “greenhouse world” to “icehouse world”, was suggested as a potential reason for the second pulse of dolomitization. The use of both clumped isotope palaeothermometry and U-Pb in situ LA-ICP-MS dating should be able to more quantitatively resolve the history of diagenesis, dolomitization, and shed light on the environment during dolomite formation.

3.3. Sample collection

Rock samples were collected with an aim to study dolomite of two different colour: brown, and purely white. The aim was to study the thickest possible core interval. The position of collected samples, types of dolomite and corresponding stratigraphic unit, and corresponding analysis are presented in Fig. 3.2 and Table 3.1.

Overall, 11 samples of white dolomite and 6 samples of brown dolomite were collected. Brown dolomite was sampled from the zone which corresponds to Unit VIII of Hauterivian age (132.9-129.4 Ma) of core matrix. Samples with white dolomite were collected from a narrow interval at a depth of 1251mbsf to 1299.5mbsf, Unit VII. This interval corresponds to Barremian (129.4-125.0 Ma) age of core matrix.

Table 3.1. Table of all samples used in the current study with indication of acquired analyses.

Sample name ^a	Core details	Sample information ^b	Stratigraphic Depth (mbsf)	Type of analyses conducted.
132-1-50-51	132/1	WD	1245.50	U-Pb dating
133-2-136-137	133/2	WD	1251.13	U-Pb dating, Clumped isotope measurements, FTIR measurements
134-1-25-30	134/1	WD	1256.25	U-Pb dating, FTIR measurements
134-1-123-124	134/1	WD	1257.12	U-Pb dating, FTIR measurements
134-2-27-28	134/2	WD	1261.27	U-Pb dating, Clumped isotope measurements, FTIR measurements, Petrographic analysis
134-2-40-42	134/2	WD	1264.40	U-Pb dating, Clumped isotope measurements, FTIR measurements, Petrographic analysis
134-2-128-129	134/2	WD	1265.12	U-Pb dating, FTIR measurements
136-2-136-137	136/2	WD	1285.13	U-Pb dating, FTIR measurements
137-1-43-44	137/1	WD	1289.13	U-Pb dating, Clumped isotope measurements, FTIR measurements
137-2-27-28	137/2	WD	1289.27	U-Pb dating, FTIR measurements
137-2-73-74	137/2	WD	1290.73	U-Pb dating, Clumped isotope measurements, FTIR measurements
161-1 (a-b)	161/1	BD	1521.10	U-Pb dating, Clumped isotope measurements, FTIR measurements, Petrographic analysis
162-2(a-b)	161/2	BD	1533.10	U-Pb dating, Clumped isotope measurements, FTIR measurements, Petrographic analysis
164-1-114-118	164/1	BD	1550.10	Clumped isotope measurements, FTIR measurements, Petrographic analysis
165-2-79-81	165/2	BD	1561.79	U-Pb dating, Clumped isotope measurements, FTIR measurements, Petrographic analysis
167-2-114-118.	167/1	BD	1565.7	Petrographic analysis
168-4-125-130	168/4	BD	1595.12	U-Pb dating, Clumped isotope measurements, FTIR measurements, Petrographic analysis

^a All samples were picked up from Leg 143, Site 866.

^b WD-white dolomite. BD-brown dolomite

3.4. Results

3.4.1. Dolomite core description and petrographic analysis

Description of core samples of brown dolomite showed that it is fine-to-medium-grained (5-10 μm) with well-developed moldic porosity. Sample 161-1 (a-b) demonstrates the dissolved traces of fossil fragments (Fig.3.4.a, Fig.3.9.a-b). The formed moldic porosity has been then partly filled with coarse-grained dolomite. Also, in some samples the dolomitization process did not touch the void spaces left after dissolution of ooids and oncoids. (Sample 164-1-114-118) (Fig.3.4.c). A closer look at rock samples within the resin disks also revealed the presence of colour differences within the brown dolomite. For example, a visible gradation of colours from dark brown to light brown and finally to white is observed in samples 162-2 (a-b) and 161-1(a-b) (Fig.3.9 a-d).

Description of core samples of the white dolomite revealed that it is fine-grained with irregular contact with brown dolomite. Some samples exhibit presence of both types of dolomites: white and brown (Sample 133-2-136-137) (Fig.3.4.b; Fig.3.12.d). There are also single crystals of white dolomite present within the brown dolomite samples (example sample 161-1a,b; Fig.3.9.a-b).

Core samples were used to make thin sections, which were then analysed. Based on thin section description, five dolomite-rock textures have been recognized (Fig.3.5) and classified according to crystal-size and distribution (unimodal versus polymodal) of dolomite crystallites and crystal boundary shapes (planar-s, or non-planar-a) using the dolomite-rock classification scheme of Sibley and Gregg (1987). For crystal-size distributions the apparent maximum dimensions of the dolomite crystals were estimated and subdivided using Folk's (1962) size scale. Results are summarised in Figure 3.6 (a-k). Types of dolomite-rock textures and corresponding samples are summarised in Table.3.2 and Table.3.3.

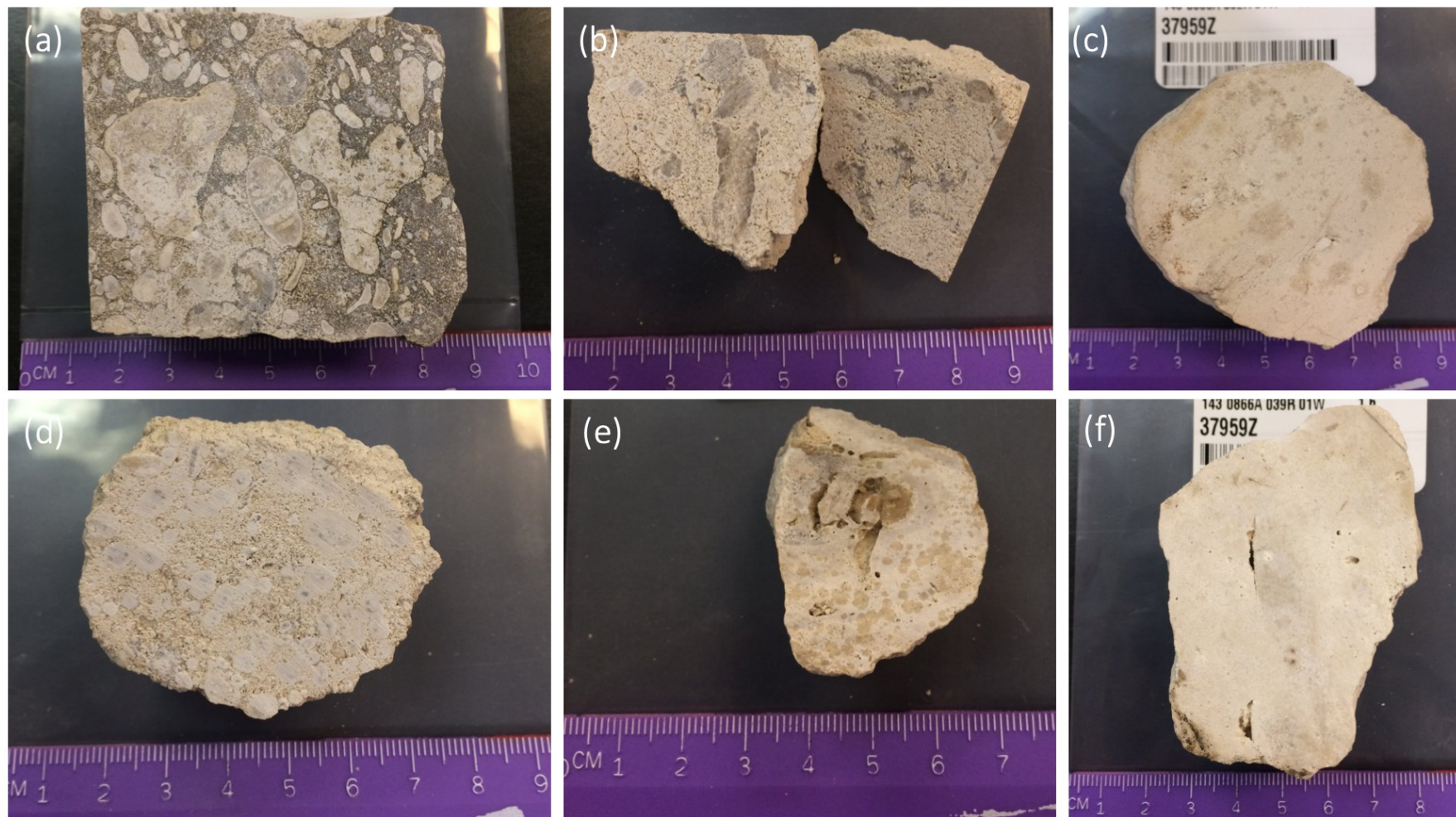


Figure 3.3. Photographs of the selected core from Hole 866, Leg 143 illustrating textural difference between lithological units. Detailed description is presented in the text.

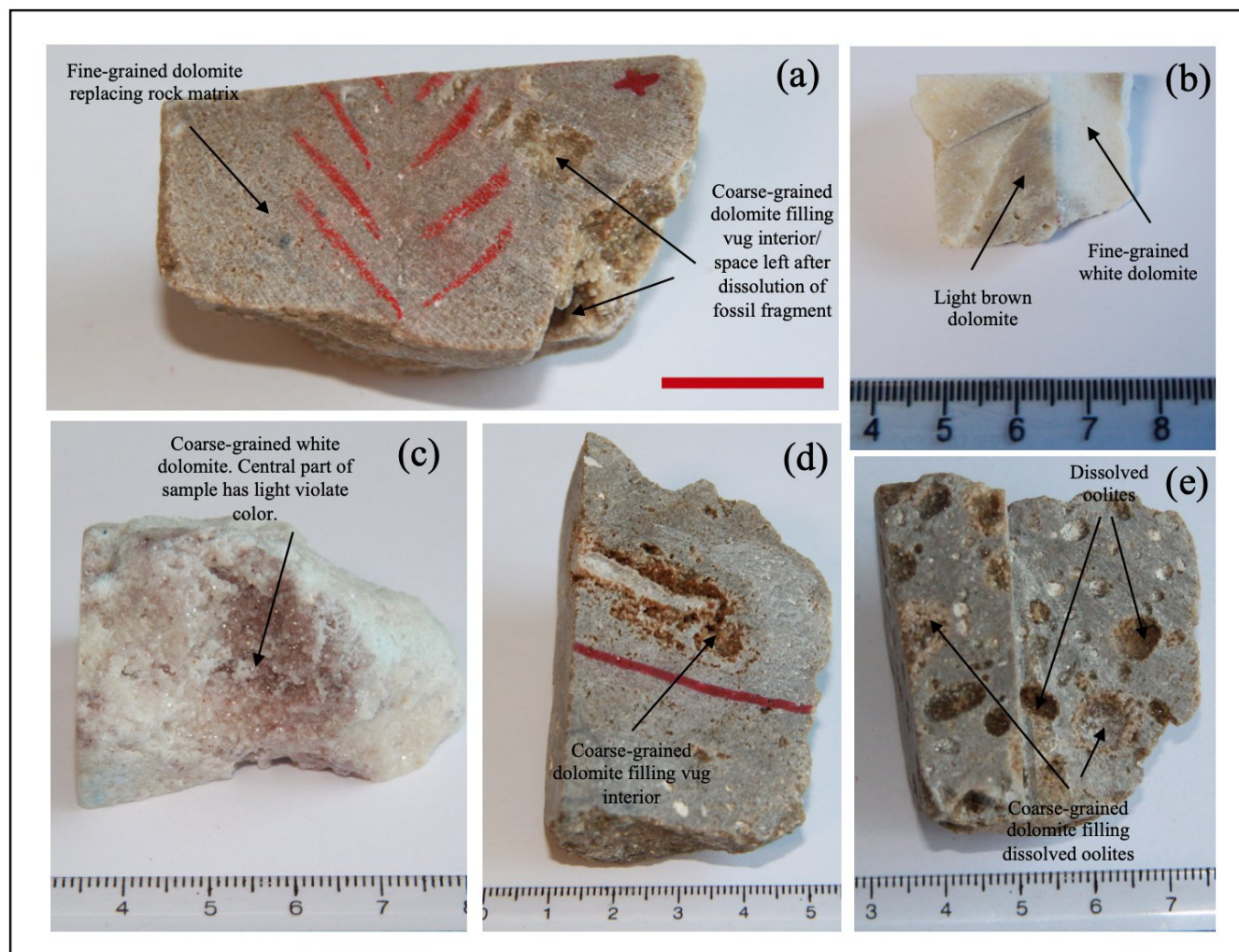


Figure 3.4. Photographs of macroscopic textures of brown and white dolomite samples. Sample 161-1(a-b) (a) illustrates the coarse-grained dolomite replacing dissolved fossil fragment. The core matrix is fully dolomitized with fine-grained dark brown dolomite. Red triangle represent scale. Its length equals 2cm. Samples 133-2-136-137 (b) and 133-2-136-137 (c) illustrates white colour dolomite. Sample 133-3-136-137 illustrates presence of light brown dolomite within white dolomite. Sample 165-2 (d) – dolomitized core matrix with coarse-grained light brown dolomite filling the vug interior. Sample 164-1-114-118 (e). Dolomitized core matrix with dissolved oolites.

PETROGRAPHIC TEXTURES OF
DOLOMITES FROM RESOLUTION GUYOT

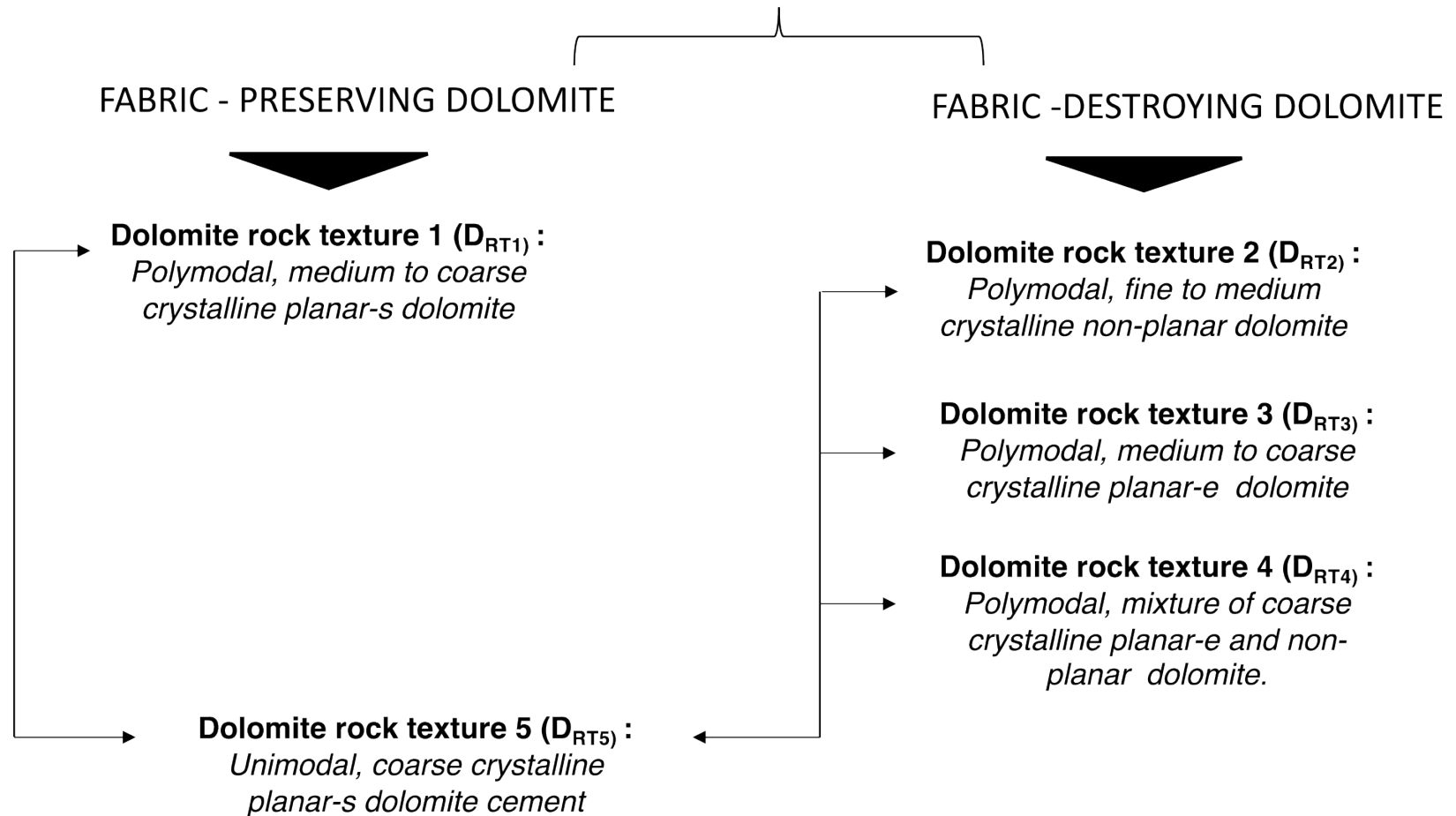


Figure 3.5. Schematic illustration of types and petrographic textures of dolomites from Resolution Guyot.

Fabric-preserving dolomitization:

Under “fabric-preserving” dolomitization it is usually understood the rocks showing selective replacement of original limestones by dolomite crystals without any destruction of the original relationships between the fabric components (Sibley, 1980; Sibley, 1982). The fabric-preserving dolomites from Resolution Guyot exhibit grain-supported textures. Initial rock textures were recognised and classified into oolitic wackstone-grainstone. Two main fabric components can be distinguished in the rocks: medium to coarse crystalline planar-s dolomite (D_{RT1})

- **Dolomite rock-texture 1: Polymodal medium to coarse crystalline planar-s dolomite (D_{RT1}):**

This type of dolomite is predominant in thin sections for samples 164-1-114-118 and 168-4-125-130 (Fig.3.6.a-b). It forms mosaic of subhedral to anhedral (planar-s) dolomite crystals. The crystals boundaries are clearly visible and have straight boundaries. Dolomite crystals are mostly tightly packed. The main characteristic of this type of dolomite that it is fabric-preserving and replaces oolitic grainstone-wackstone. Replaced by dolomite crystals oolites are easily recognised on thin sections (Fig.3.6.a-b) and they have clear, sharp boundaries. This type of dolomite was named D_{RT1} .

Fabric-destroying dolomitization:

Rocks displaying fabric-destroying dolomitization are crystalline dolomites. Petrographic observation shows that this type of the rock lacks relicts of previous rock-textures.

- **Dolomite rock-texture 2: Polymodal, fine to medium crystalline non-planar dolomite (D_{RT2}):**

This type of dolomite is predominant in samples 161-1(a-b), 162-2 (a-b), 165-2-79-81 (Fig.3.6.c-e), as well as minor presence was observed in samples 134-2-40-42. (Fig.3.6.g). Compare to dolomite D_{RT1} , dolomite with this rock-textures is fabric destroying, has smaller size of the dolomite crystals and different shape of the crystal boundaries. This dolomite represents dense, tightly packed mosaics of fine to medium crystalline non-planar dolomite. The pre-dolomitization rock textures are almost completely lost, in rare cases ghosts are visible.

(Fig.3.6.c). Besides, dolomite crystals often exhibit cloudy, inclusion rich cores (Co) and clean, inclusion-free rims (Ri). This type of dolomite was further named as D_{TR2} .

- **Dolomite rock-texture 3: Polymodal, medium to coarse crystalline planar-e dolomite (D_{RT3}):**

This type of dolomite was observed in sample 165-2-79-81. The main distinctive characteristic of this type of dolomite compare to the previous types of dolomites is its planar-e textur.

Dolomite crystals have clear euhedral- rhombic form (Fig.3.6.f). The intracrystalline space is not filled with dolomite cement. Crystals are mostly inclusion-free. In some rare cases, crystals exhibit clean rim (R_i) and inclusion-rich cores (Co). This dolomite was classified as type 3 dolomite and further named as D_{TR3}

- **Dolomite rock-texture 4: Polymodal, coarse-crystalline non-planar-a dolomite to coarse-crystalline planar-e dolomite (D_{RT4}):**

This type of dolomite is predominant in samples of white colour dolomite : 134-2-40-41 and 134-2-27-28 and represent the dolomite with biggest size of the crystal (Fig.3.6.g-h). It forms a mixture of coarse-crystalline non-planar-a dolomite and coarse-crystalline, planar-e dolomite. Planar-e dolomite consists of scattered rhombs of euhedral/subhedral form. Rare crystals have cloudy, inclusion reach cores (Co) and clean rims (R_i). The intercrystalline space is not filled with dolomite cement.

- **Dolomite rock-texture 5: unimodal, coarse crystalline planar-s dolomite cement D_{RT5} :**

Dolomite cement are dolomite crystals found in filling the intergranular, intragranular, vein and vug porosity in both fabric-preserving and fabric-destroying dolomites. It is a unimodal, coarse crystal planar -s dolomite. Dolomite crystals are inclusion-free. This dolomite was named as D_{TR5} . Its presence is noticed in samples 134-2-40-42, 164-1-114-118 , 167-2-114-118. (Fig.3.6.e,i-j).

In total, core samples description revealed presence of two types of dolomite, which can be distinguished by colour (brown versus white) and crystal size. The core description also revealed that white dolomite sometimes contains patches of brown dolomite. Thin section analysis revealed that samples of brown dolomite predominately have types 1 to 3 dolomite

rock textures (D_{RT1-3}). The white dolomite predominately consists of type 4 dolomite rock texture (D_{RT4}) with small amount of D_{RT2} dolomite (sample 134-2-27-28). Current observation is consistent with core sample description. The dolomite cement which was described as dolomite rock texture 5 (D_{RT5}) and it has been observed both in samples of brown dolomite as well as in samples of white dolomite. Name of the samples and predominant rock textures are summarised in Table.3.2. Parallel to thin section observation, samples were used to study their mineral composition.

Table 3.2. Name of dolomite samples of Resolution Guyot and corresponding identified petrographic rock textures.

Sample name	Corresponding dolomite rock texture
164-1-114-118	D_{RT1}/ D_{RT5}
168-4-125-130	D_{RT1}
161-1 (a-b)	D_{RT2}
162-2 (a-b)	D_{RT2}
165-2-79-81	$D_{RT2}/D_{RT3}/ D_{RT5}$
133-2-136-137	D_{RT4}
134-2-27-28	$D_{RT4}/ D_{RT2}/ D_{RT5}$
134-2-40-42	D_{RT4}
137-1-43-44	D_{RT4}
137-2-73-74	D_{RT4}

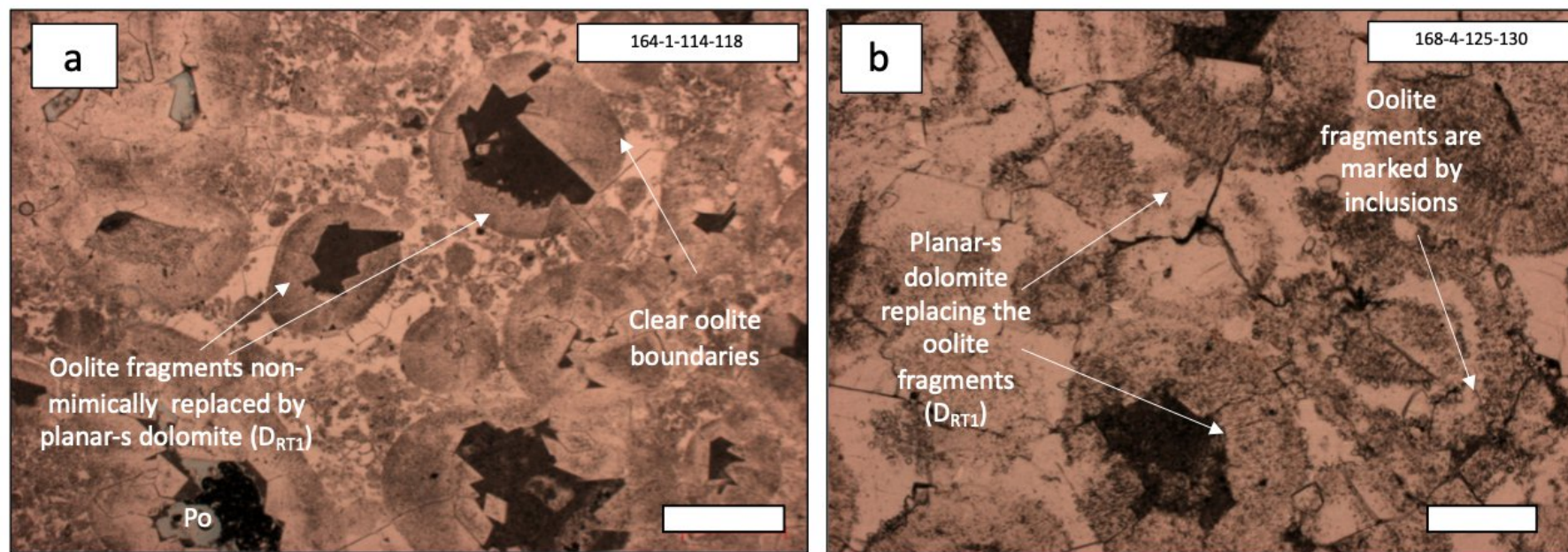


Figure 3.6. Dolomite rock-texture 1 (D_{RT1}): unimodal medium to coarse crystalline planar-s dolomite replacing oolites. Dolomite in sample 164-1-114-118 is non-mimetically replaces the oolites (a). More advanced level of dolomitization in sample 168-4-125-130-125-130. Oolite fragments are marked by solid inclusions (b) The scale of the picture is shown by a white rectangle at the bottom right corner that equals 500 μm .

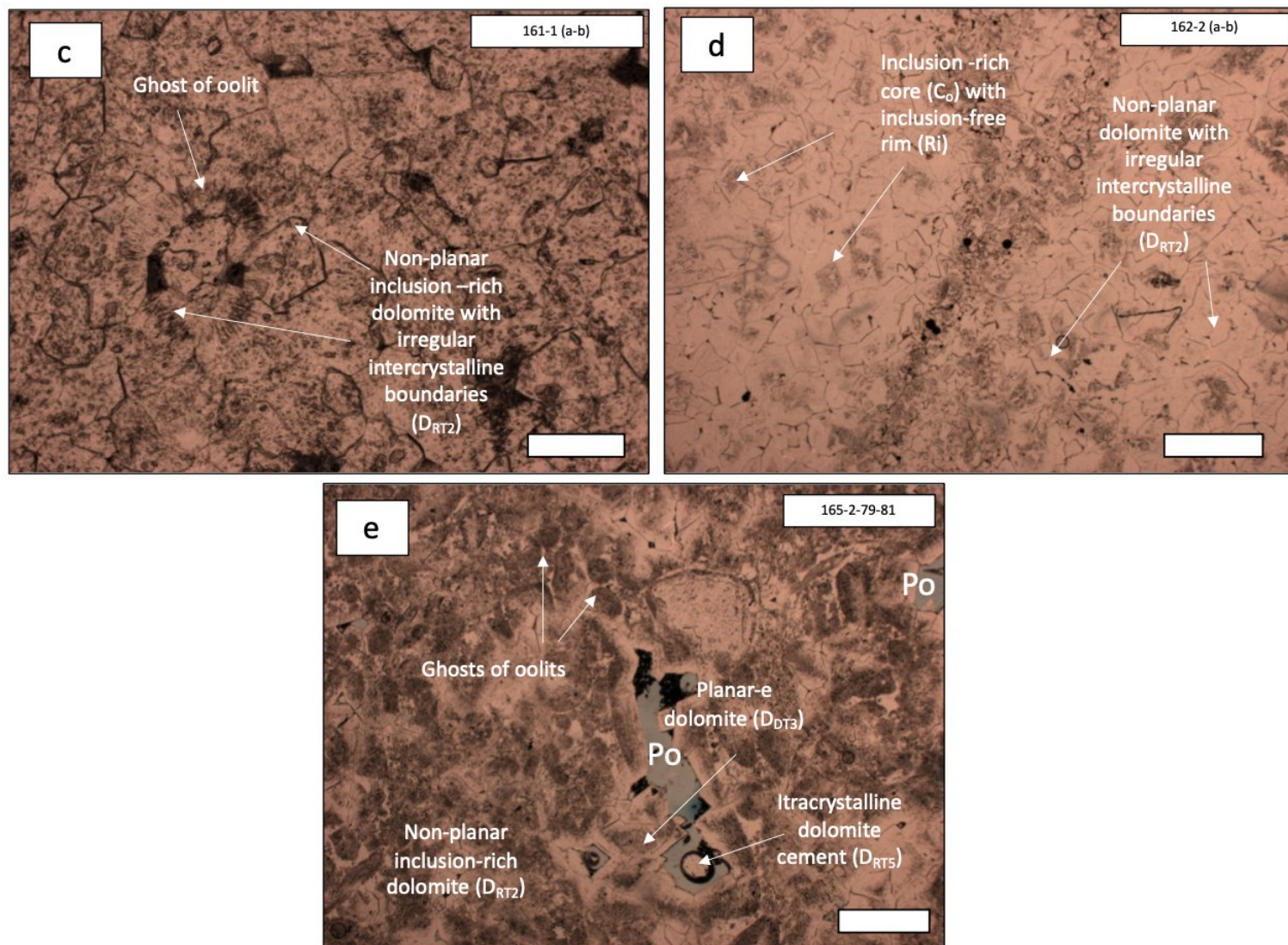


Figure 3.6 (Continued). Dolomite rock-texture 2 (D_{RT2}): fine to medium crystalline non-planar dolomite (c,d) with relict of oolite fragment (c). Dolomite crystals exhibit the cloudy, inclusion-rich centres and clean rims (d) e) Sample 165-2-79-81 with minor presence of planar-e dolomite and intracrystalline dolomite cement. Predominance of non-planar-a inclusion-rich dolomite. The scale of the picture is shown by a white rectangle at the bottom right corner that equals 500 μm .

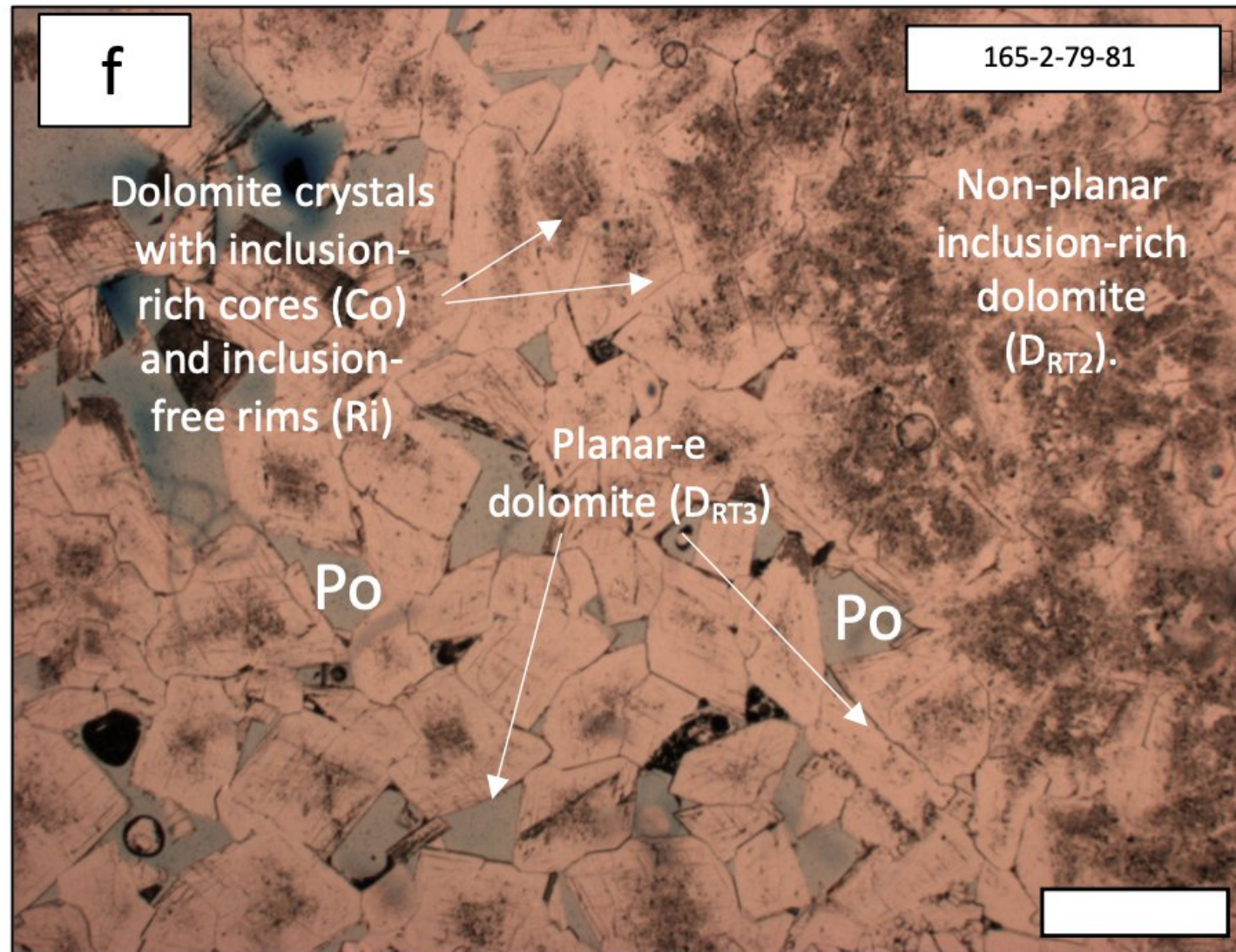


Figure 3.6. (Continued). Dolomite rock-texture 3 (D_{RT3}): and unimodal, medium coarse-crystalline planar-e dolomite (f). Presence of non-planar-a inclusion-rich dolomite of type 2. The scale of the picture is shown by a white rectangle at the bottom right corner that equals 500 μm .

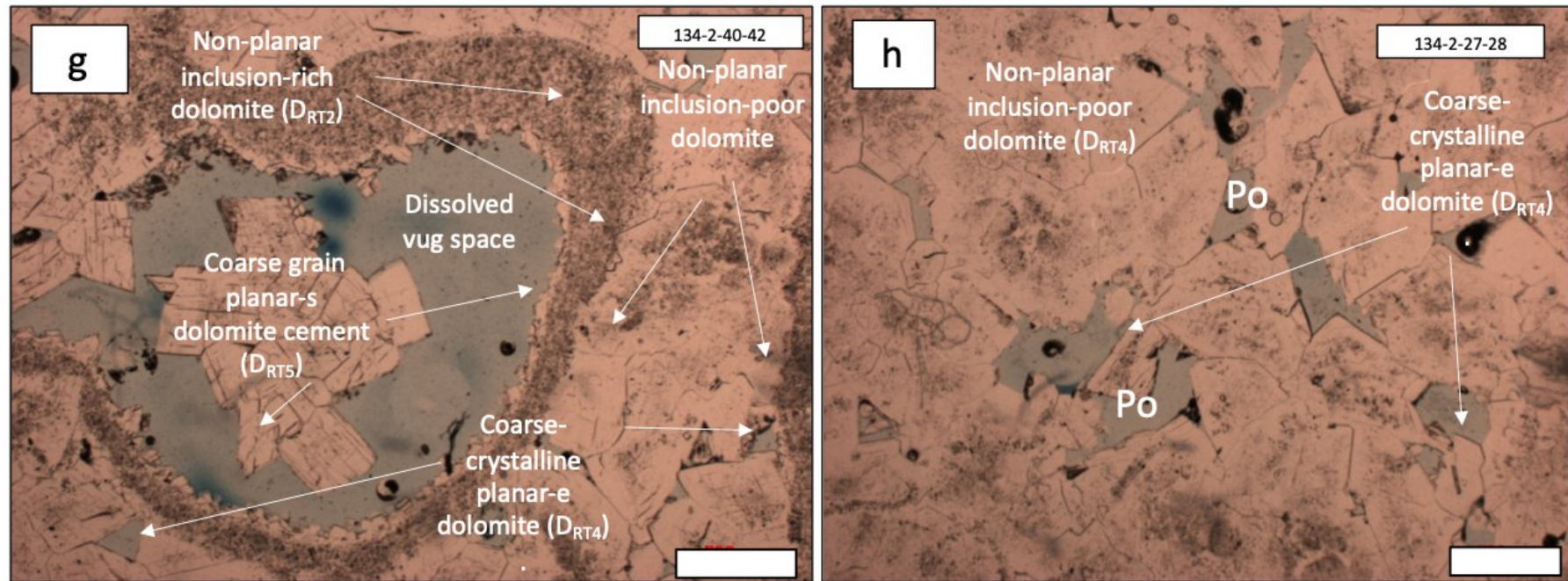


Figure 3.6 (Continued). Dolomite rock-texture 4 (D_{RT4}): coarse-crystalline, non-planar, inclusion-poor dolomite (g) and coarse-crystalline planar-e dolomite (h). The dissolved vug space is filled with coarse grain planar-s dolomite cement (h). The scale of the picture is shown by a white rectangle at the bottom right corner that equals 500 μm .

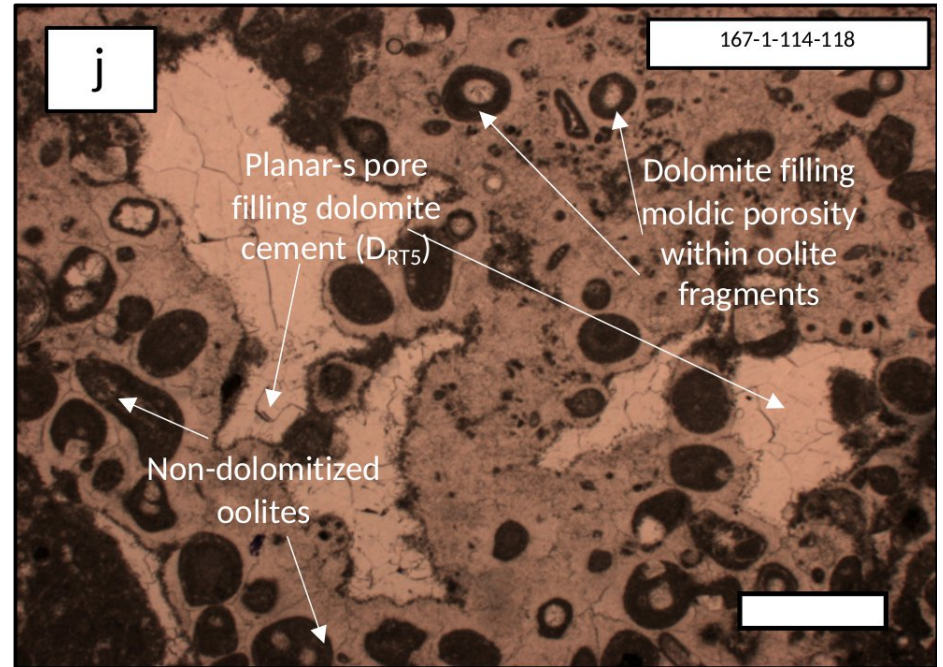
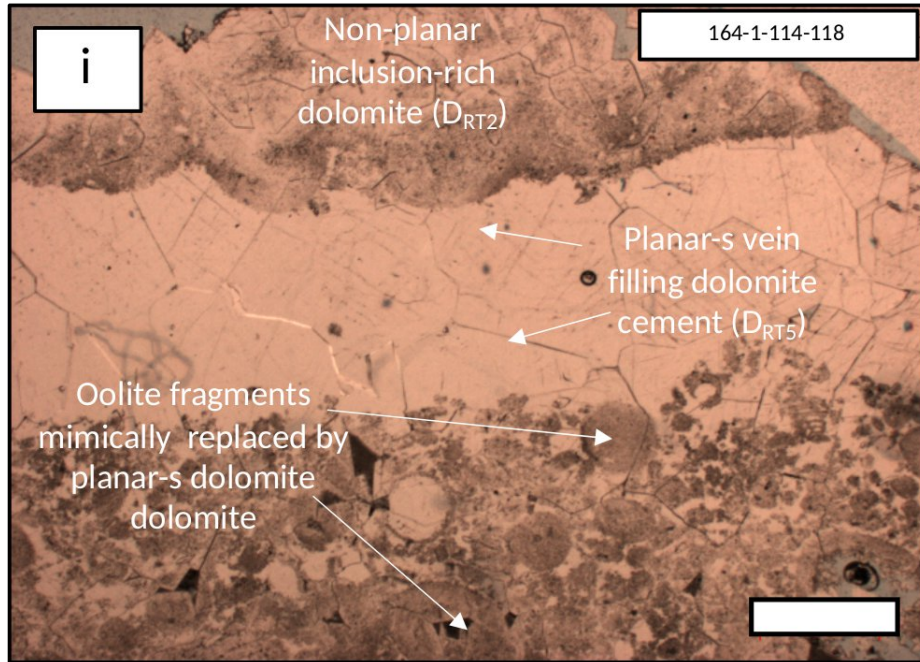


Figure 3.6 (Continued). Dolomite rock-texture 5 (D_{RT5}): coarse grain planar-s dolomite cement filling vein interior (e) or pore space (f). The scale of the picture is shown by a white rectangle at the bottom right corner that equals 500 μm .

Table.3.3. Petrographic characteristics of the five types of Resolution Guyot dolomites.

Type of dolomite	Occurrence	Grain size	Morphology	Remarks	Predominance in samples
D_{RT1}	Fabric-preserving	Medium to coarse crystalline	Planar-s	Initial rock-textures: oolitic wackstone-grainstone. Presence of D _{RT5} dolomite cement.	164-1-114-118 168-4-125-130
D_{RT2}	Fabric -destroying	Fine to medium crystalline	Non-planar	Inclusion rich crystals. Some of the dolomite crystals have inclusion rich cores and inclusion poor rims. Presence of D _{RT5} dolomite cement.	161-1(a-b) 162-2(a-b) 165-2-79-81 134-2-40-42
D_{RT3}	Fabric -destroying	Medium to coarse crystalline	Planar-e	Porous space is not filled with cement. Dolomite crystals with inclusion rich cores and inclusion poor rims.	165-2-79-81
D_{RT4}	Fabric -destroying	Coarse crystalline	Non-planar and planar-e	Low amount of inclusions within dolomite crystals. Dissolution vug filled with D _{RT5} dolomite cement. Core samples sometimes have small amount of DRT ₁₋₃ visible as brown dolomite patches.	134-2-40-42 134-2-27-28
D_{RT5}	Cementing pores	Coarse crystalline	Planar-s	Mostly inclusion free dolomite crystals	134-2-40-42 164-1-114-118 167-2-114-118 164-1-114-118

Mineralogy and grain size

Results of both the FTIR and X-Ray diffraction methods allow the determination of mineral composition of the samples. Example of both types of diagram is presented in Fig.3.7 (a-b). Samples with mixt phases (calcite and dolomite) were removed from the study and were not used for clumped isotope measurements because the heterogeneous mineral composition is likely to cause mixture of clumped isotope results. Out of 17th studied samples (Table.3.1), only one sample revealed a mixt mineralogy : Sample 167-1-114-118. The rest of the samples showed homogeneous concentration of dolomite and were used for clumped isotopes and U-Pb measurements.

Stable and clumped isotope measurements.

In total, 10 samples were studied using clumped isotope method. Powder for clumped isotope analysis was selected from the predominate dolomite textures, which were identified using thin section analysis (Table.3.2). Powder was also taken from the core matrix avoiding dolomite cement from the vug cavities or dissolved ooid/fossil fragments. In order to simplify the clumped isotope analysis, studied samples were divided into groups according to predominant dolomite rock texture. The first group includes sample 168-4-125-130 with predominant dolomite rock texture 1 (D_{RT1}). Corresponding symbol of this group on clumped isotope diagrams is red rhomb. The second group includes samples with second type of dolomite rock texture (D_{RT2}). These are samples 161-1(a-b) and 162-2(a-b) with corresponding symbol of black square. The third group includes only samples of white colour dolomite with predominant rock textures 4 (D_{RT4}). Corresponding symbol is green circle. The last group includes samples with a mixture of rock textures. These are samples 164-1-114-118 (D_{RT1}/D_{RT5}), 165-2-79-81 ($D_{RT2}/D_{RT3}/D_{RT5}$), and 143-2-40-42 ($D_{RT2}/D_{RT4}/D_{RT5}$) with corresponding symbol of grey triangle and used annotation D_{mix} . Clumped isotope results are summarised in Table. 3.4anf graphically presented in Fig.3.8.

The oxygen isotopic composition ($\delta^{18}O_{VPDB}$) is -3.77 ± 0.21 ‰ VPDB for sample 168-4-125-130 (D_{RT1} dolomite), -2.02 ± 0.21 ‰ and -3.3 ± 0.13 ‰ VPDB for samples 161-1 (a-b) and 162 (a-b) (D_{RT2} dolomite). Samples with a mixture of dolomite rock textures have values for the oxygen isotopic composition equals to -4.18 ± 0.17 ‰ VPDB for sample 165-2-79-81 ($D_{RT2}/D_{RT3}/D_{RT5}$ dolomite), -3.66 ± 0.20 ‰ VPDB for sample 164-1-114-118 (D_{RT1}/D_{RT5} dolomite), and 0.95 ± 0.16 ‰ VPDB for sample 134-2-40-42 81 ($D_{RT2}/D_{RT4}/D_{RT5}$ dolomite). The

values for $d^{18}\text{O}_{\text{VPDB}}$ for the rest of the samples of white dolomite (D_{RT4}) are ranging between $-0.69 \pm 0.22\text{‰}$ and $2.15 \pm 0.12\text{‰}$ VPDB. Values are presented with one standard deviation error.

The carbone isotopic composition ($d^{13}\text{C}_{\text{VPDB}}$) is $+2.4 \pm 0.07\text{‰}$ VPDB for sample 168-4-125-130 (D_{RT1} dolomite), $+1.89 \pm 0.01\text{‰}$ and $+2.55 \pm 0.03\text{‰}$ VPDB for samples 161-1 (a-b) and 162 (a-b) (D_{RT2} dolomite). Samples with a mixture of dolomite rock textures have values for the carbone isotopic composition equals to $+2.46 \pm 0.07$ VPDB for sample 165-2-79-81 ($D_{\text{RT2}}/D_{\text{RT3}}/D_{\text{RT5}}$ dolomite), $+2.34 \pm 0.26\text{‰}$ VPDB for sample 164-1-114-118 ($D_{\text{RT1}}/D_{\text{RT5}}$ dolomite), and $3.31 \pm 0.03\text{‰}$ VPDB for sample 134-2-40-42 81 ($D_{\text{RT2}}/D_{\text{RT4}}/D_{\text{RT5}}$ dolomite). The values for $d^{13}\text{C}_{\text{VPDB}}$ for the rest of the samples of white dolomite (D_{RT4}) are in the range between $2.68 \pm 0.08\text{‰}$ and $3.37 \pm 0.07\text{‰}$ VPDB. Values are presented with single standard deviation error.

The values of $D_{47\text{ CDES}}$ is $0.652 \pm 0.010\text{‰}$ for sample 168-4-125-130 (D_{RT1} dolomite), $0.638 \pm 0.008\text{‰}$ and $0.663 \pm 0.008\text{‰}$ for samples 161-1 (a-b) and 162 (a-b) (D_{RT2} dolomite), $0.617 \pm 0.003\text{‰}$ for sample 165-2-79-81 ($D_{\text{RT2}}/D_{\text{RT3}}/D_{\text{RT5}}$ dolomite), $0.654 \pm 0.011\text{‰}$ for sample 164-1-114-118 ($D_{\text{RT1}}/D_{\text{RT5}}$ dolomite), and $0.697 \pm 0.008\text{‰}$ for sample 134-2-40-42 ($D_{\text{RT2}}/D_{\text{RT4}}/D_{\text{RT5}}$ dolomite). The values of $D_{47\text{ CDES}}$ for samples of white dolomite (D_{RT4}) are in the range between $0.692 \pm 0.003\text{‰}$ and $0.708 \pm 0.006\text{‰}$. The errors are calculated as a single standard error calculated by replicate standard deviation divided by square root of number of replicates.

The $D_{47\text{ CDES}}$ values when converted to temperatures using the calibration of Davies and John (2019) corresponds to temperatures of $39 \pm 4\text{ °C}$ for sample 168-4-125-130 (D_{RT1} dolomite), $35 \pm 4\text{ °C}$ and $44 \pm 3\text{ °C}$ for samples 161-1 (a-b) and 162 (a-b) (D_{RT2} dolomite), $53 \pm 1\text{ °C}$ for sample 165-2-79-81 81 ($D_{\text{RT2}}/D_{\text{RT3}}/D_{\text{RT5}}$ dolomite), $38 \pm 4\text{ °C}$ for sample 164-1-114-118 ($D_{\text{RT1}}/D_{\text{RT5}}$ dolomite), and $23 \pm 3\text{ °C}$ for sample 134-2-40-42 ($D_{\text{RT2}}/D_{\text{RT4}}/D_{\text{RT5}}$ dolomite). . Temperatures for samples of white dolomite (D_{RT4}) vary between $20 \pm 2\text{ °C}$ and $25 \pm 1\text{ °C}$. Temperature error are calculated using 1SE errors for $D_{47\text{ CDES}}$ values.

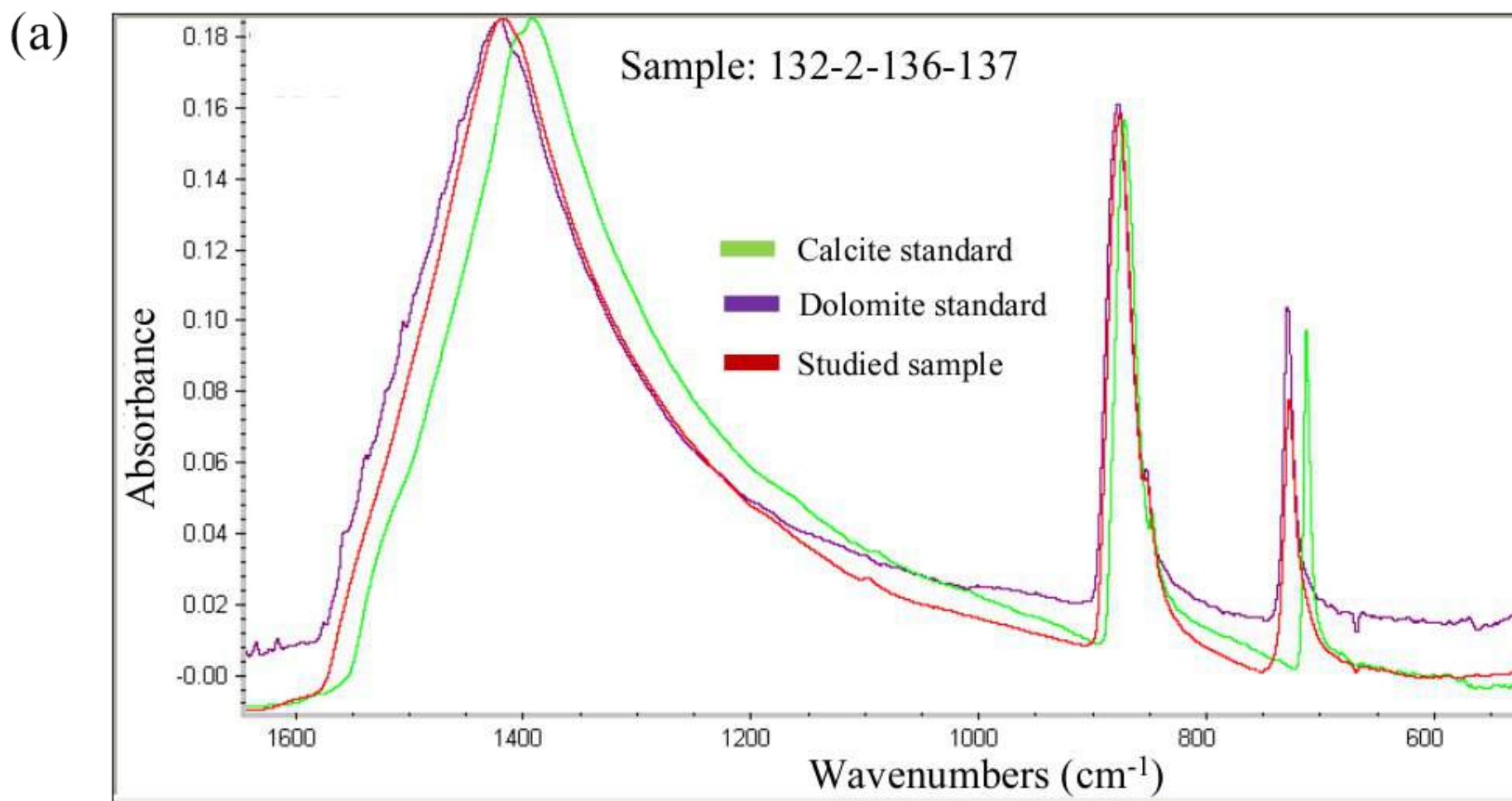


Figure 3.7 Example of results received for FTIR measurement of white dolomite sample 132-2-136-137. Current measurement shows pure dolomite concentration.

(b)

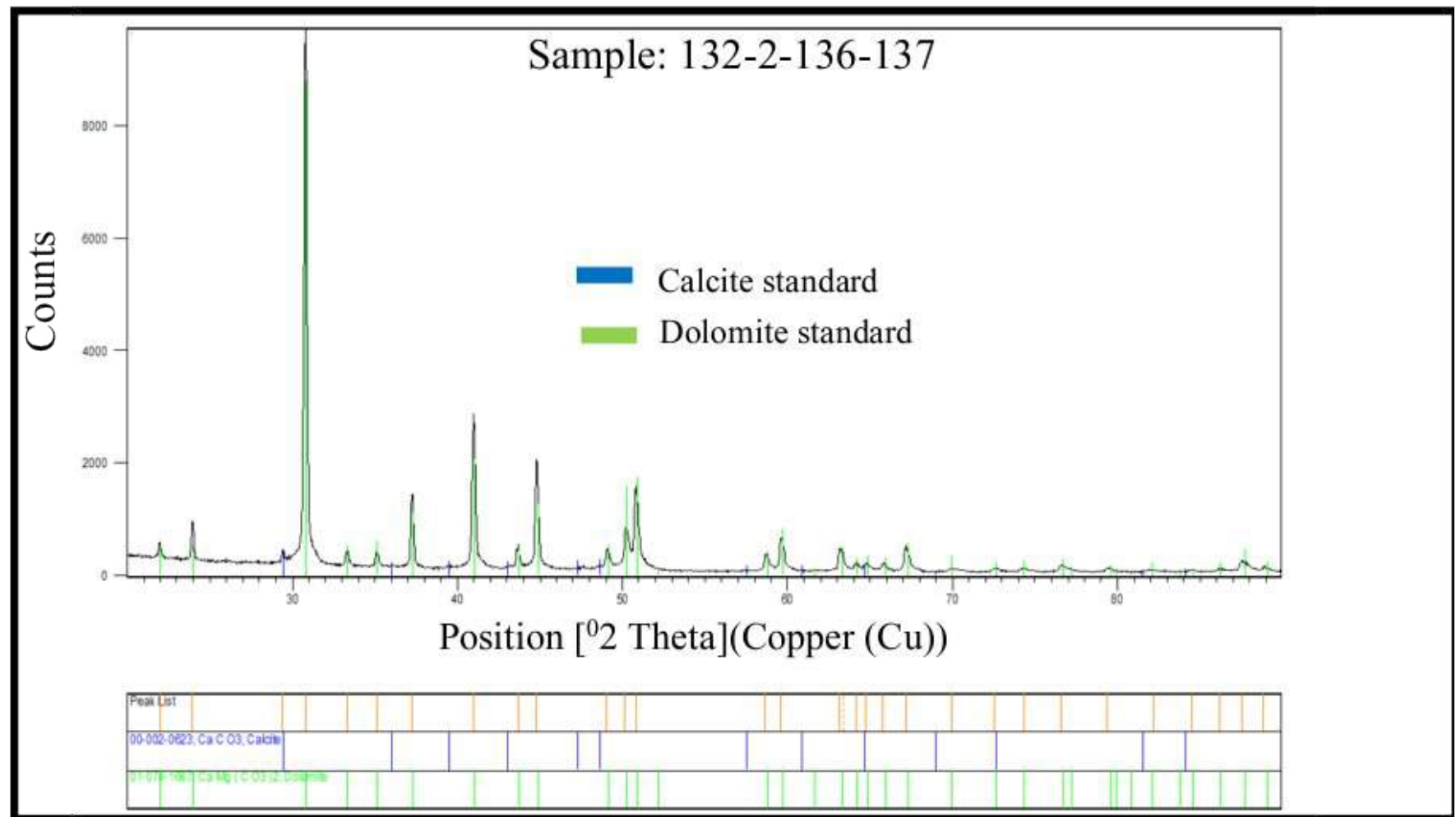


Figure 3.7 (Continued). Example of results received for X-Ray measurement of white dolomite sample 132-2-136-137. Current measurement shows pure dolomite concentration.

Table 3.4. Clumped isotope results for dolomite samples measured in this study.

Sample	Dolomite rock textures*	Δ_{48} offset	49 parameter	$\delta^{18}\text{O}$ PDB	$\delta^{13}\text{C}$ PDB	Δ_{47} CDES (‰)	$\pm 1\text{SE}$	Temperature (°C)	± 1 SE	$\delta^{18}\text{O}$ fluid (‰ VSMOW)
168-4-125-130	D_{RT1}									
		0.166	0.111	-3.53	2.48	0.691				
		0.167	0.117	-4.05	2.44	0.644				
		0.170	0.070	-3.74	2.55	0.646				
		0.287	0.107	-3.59	2.46	0.651				
		-0.094	0.102	-3.94	2.37	0.629				
			Averages:	-3.77	2.46	0.652		39	4	-1.32
			SD:	0.22	0.07		0.010			
164-1-114-118	D_{RT1}/ D_{RT5}									
		0.246	0.142	-3.71	2.46	0.686				
		0.340	0.106	-3.54	1.88	0.669				
		0.063	0.098	-3.93	2.44	0.634				
		-0.342	-0.050	-3.41	2.43	0.627				
		0.130	0.043	-3.69	2.47	0.656				
			Averages:	-3.66	2.34	0.654		38	4	-1.35
			SD:	0.20	0.26		0.011			
161-1(a-b)	D_{RT2}									
		-0.094	0.045	-2.17	1.88	0.655				
		0.174	0.093	-1.88	1.90	0.670				
			Averages:	-2.02	1.89	0.663		35	3	-0.21
			SD:	0.21	0.01		0.008			

Sample	Dolomite rock textures*	Δ_{48} offset	49 parameter	$\delta^{18}\text{O}$ PDB	$\delta^{13}\text{C}$ PDB	Δ_{47} CDES (‰)	$\pm 1\text{SE}$	Temperature (°C)	± 1 SE	$\delta^{18}\text{O}$ fluid (‰ VSMOW)
162-2(a-b)	D_{RT2}									
		0.135	0.057	-3.16	2.53	0.650				
		0.178	0.109	-3.42	2.54	0.624				
		0.032	0.108	-3.31	2.59	0.640				
			Averages:	-3.3	2.55	0.638		44	3	0.13
			SD:	0.13	0.03		0.008			
			SD:	0.20	0.26		0.011			
165-2-79-81	D_{RT3}/ D_{RT2}/ D_{RT5}									
		1.043	0.081	-4.07	2.34	0.622				
		0.033	0.079	-4.10	2.42	0.613				
		0.121	0.130	-4.38	2.33	0.617				
			Averages:	-4.18	2.36	0.617		53	1	0.62
			SD:	0.17	0.05		0.003			
133-2-136-137	D_{RT4}									
		0.297	0.172	1.85	3.13	0.703				
		0.078	0.154	1.75	3.15	0.709				
		-0.063	0.088	1.51	3.19	0.695				
		0.063	0.019	1.64	3.09	0.725				
			Averages:	1.69	3.14	0.708		20	2	0.53
			SD:	0.15	0.04		0.006			

Sample	Dolomite rock textures*	Δ_{48} offset	49 parameter	$\delta^{18}\text{O}$ PDB	$\delta^{13}\text{C}$ PDB	Δ_{47} CDES (‰)	$\pm 1\text{SE}$	Temperature (°C)	± 1 SE	$\delta^{18}\text{O}$ fluid (‰ VSMOW)
134-2-27-28	D_{RT4}									
		-0.026	0.134	0.14	3.30	0.698				
		0.123	0.167	0.27	3.36	0.731				
		0.068	0.061	0.31	3.44	0.679				
			Averages:	0.24	3.37	0.703		21	5	-0.60
			SD:	0.09	0.07		0.015			
134-2-40-42	D_{RT2}/ D_{RT4}/ D_{RT5}									
		0.149	0.094	1.07	3.30	0.712				
		0.150	0.131	0.77	3.35	0.694				
		0.025	0.023	1.01	3.29	0.684				
			Averages:	0.95	3.31	0.697		23	3	0.54
			SD:	0.16	0.03		0.008			
137-1-43-44	D_{RT4}									
		-0.263	-0.051	2.28	2.69	0.693				
		-0.147	0.056	2.04	2.75	0.708				
		-0.136	-0.018	2.14	2.60	0.719				
			Averages:	2.15	2.68	0.707		20	2	1.10
			SD:	0.12	0.08		0.008			
137-2-73-74	D_{RT4}									
		0.030	0.080	-0.92	3.29	0.695				

Sample	Dolomite rock textures*	Δ_{48} offset	49 parameter	$\delta^{18}\text{O}$ PDB	$\delta^{13}\text{C}$ PDB	Δ_{47} CDES (‰)	$\pm 1\text{SE}$	Temperature (°C)	± 1 SE	$\delta^{18}\text{O}$ fluid (‰ VSMOW)
		0.051	0.101	-0.65	3.3	0.686				
		0.133	0.071	-0.49	3.22	0.696				
			Averages:	-0.69	3.27	0.692		25	1	-0.86
			SD:	0.22	0.04		0.003			

Sample name and dates for each runs are indicated. 49 parameter and Δ_{48} offset are two parameters used to monitor the level of contamination. Values for each acquisition are averaged per sample. Error for Δ_{47} is given as a single standard error, calculated by the replicate standard deviation divided by square root of number of replicates. Δ_{47} temperatures are calculated using the equation of Davies and John (2018) and 1SE errors for Δ_{47} CDES values. $\delta^{18}\text{O}_{\text{VSMOW}}$ is calculated using averaged $\delta^{18}\text{O}_{\text{dol}}$ value, Δ_{47} temperature and the equation of Horita, (2014). Error for $\delta^{18}\text{O}_{\text{VSMOW}}$ is calculated using single standard deviation error of $\delta^{18}\text{O}_{\text{carbonate}}$ and single standard error of Δ_{47} temperature.

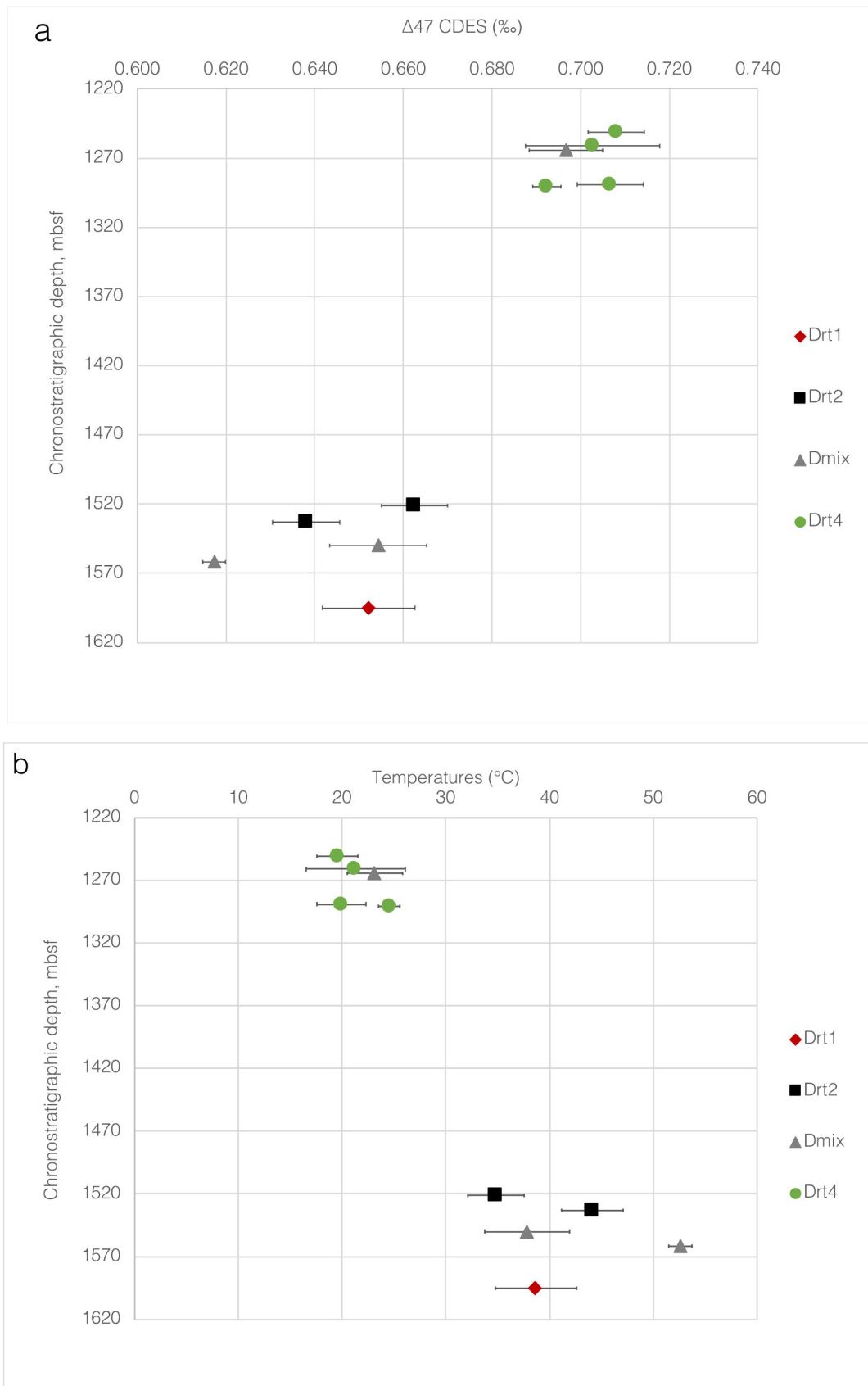


Figure 3.8. (a) Graphic of $\Delta 47$ (%) versus stratigraphic depth (mbsf). Mbsf- meters below sea floor. $\Delta 47$ values are plotted with single standard error. (b) Calculated clumped isotope temperatures ($T^{\circ}\text{C}$) versus stratigraphic depth (mbsf). Error for $\Delta 47_{\text{CDES}}$ is given as a single standard error, calculated by the replicate standard deviation divided by square root of n. Temperatures are calculated using 1SE for $\Delta 47_{\text{CDES}}$ values.

Table 3.5. Description of samples studied using U-Pb method, corresponding dolomite textures and mean U, Pb and Pb_{com} concentrations along with calculated U-Pb ages.

<i>Sample name</i>	<i>Description of the rock sample within the resin disk and position of data points</i>	<i>Dated dolomite textures</i>	<i>Variation in concentrations (ppm)</i>		<i>Pb_{com}, %</i>	<i>U-Pb ages, Ma</i>
			<i>U</i>	<i>Pb</i>		
168-4-125-130	Coarse grain dolomite of homogeneous brown colour. Small scale vug. Data points were placed randomly.	D _{RT1}	5.13-1.90	0.019 – 0.170	1.9 – 32	109.4±5.3
161-1(a-b)	The main part of the sample has dark brown dolomite (D _{RT2}). Vugs were filled with light brown to white, coarse dolomite. Data points were placed within the fine-grained matrix to date D _{RT2} dolomite and within the vug to date dolomite cement D _{RT5} .	D _{RT2} / D _{RT5}	D _{RT2} (Dark brown dolomite): 1.61-1.24 D _{RT2} (Light brown dolomite): 1.50-2.27 D _{RT5} :0.81-2.39	D _{RT2} (Dark brown dolomite): 0.002-0.008 D _{RT2} (Light brown dolomite): 0.04-0.018 D _{RT5} :0.001-0.016	D _{RT2} (Dark brown dolomite): 0-6.4 D _{RT2} (Light brown dolomite): 3.9-11 D _{RT5} : 0-8.4	D _{RT2} (Dark brown dolomite): 122±6.9- 116.3±7.1 D _{RT2} (Light brown dolomite): 120.6±6.2- 111.1±6.2- D _{RT5} : 120.6±7.2- 94.2±7.0
162-2(a-b)	Sample represents a mixture of dark and light brown dolomite. Data points were placed to date both types of dolomite.	D _{RT2}	D _{RT2} (Dark brown dolomite) : 6.65-3.34 D _{RT2} (Light brown	D _{RT2} (Dark brown dolomite):0. 325-0.001	D _{RT2} (Dark brown dolomite):53-5 D _{RT2} (Light	D _{RT2} (Dark brown dolomite): 117.9±4.6- 87.1±4.4-

Sample name	Description of the rock sample within the resin disk and position of data points	Dated dolomite textures	Variation in concentrations (ppm)		Pb _{com} , %	U-Pb ages, Ma
			U	Pb		
			dolomite): 4.80-2.35	D _{RT2} (Light brown dolomite):0.159—0.005	brown dolomite):40-0.5	D _{RT2} (Light brown dolomite): 118.5±5.2-110.2±5.2
165-2-79-81	Sample represents a mixture of dark and light brown dolomite. Data points were placed to light and brown dolomites.	D _{RT2} / D _{RT3}	5.02-2.53	0.16-0.003	37-2.8	117.8±7.5
134-1-123-124	Coarse grain, pale brown-white dolomite replacing porous carbonate matrix. Data points were placed within dolomite crystals to avoid dating the rock matrix.	D _{RT4}	24.12-1.63	0.774-0.034	50-12	57.6±3.8
133-2-136-137	Mixture of white dolomite and light brown dolomite. Based on thin section analyses, D _{RT4} contains D _{RT2} dolomite. For this reason, light brown dolomite was identified as D _{RT2} dolomite.	D _{RT4} with some amount of D _{RT2}	D _{RT4} :13.32-7.10. Overall < 0.01 D _{RT2} : 7.10-2.52	D _{RT4} :0.101-0.136 D _{RT2} <0.029	D _{RT4} : 28 and 57%. Overall >90-100 D _{RT2} : 12-45	D _{RT2} : 101 ±5.0 – 94.1 ±6.0 D _{RT4} : 51.9 ±8.8 – 66.1±5.1

U-Pb measurements

Out of 16th samples, 10 samples were dated using U-Pb method. However, 4 out of 6 samples of D_{RT4} dolomite revealed poor potential for dating due to low concentration of uranium (0.01-0.1 ppm) and overall high proportion of common Pb. These samples were excluded from data interpretation. Detailed results for these samples are still presented in Table 2 of Appendix.3.1. The summary of successfully dated samples with description of resin disks, corresponding dolomite textures, brief summary of variation in U, Pb, Pb_{com}, as well as U-Pb ages for each dolomite texture is presented in Table. 3.4. Calculated ages of single data points are then tabulated in Table 1. Appendix.3.2 and graphically presented in Fig 3.8-3.13.

Sample data is presented with independent dates within a textural context, any complexity is discussed in terms of a process of mineral crystallization over time and/or variability in common Pb composition. Sample data are presented along with other relative chronological information from textural data; complexities, where present, are discussed in terms of recrystallisation and diagenetic processes and their effect on the common Pb contained in analyzed crystals. The data are plotted in 8-6TW diagrams and in weighted mean diagrams of single spot ages for all points that are relatively radiogenic and texturally related. Overall, the studied dataset can be divided into four main groups: (i) highly radiogenic data with a reasonable fit of regression; (ii) highly radiogenic scattered data with variable ages of crystallisation; (iii) scattered data with variable age of crystallisation and variation in common Pb concentration; (iv) not-radiogenic data with a reset value of common Pb.

- **D_{RT1} dolomites (sample 168-4-125-130)**

Sample 168-4-125-130 with predominantly D_{RT1} dolomite texture (Fig.3.9.a) is an example of highly radiogenic material with good fit of regression. This sample has one of the highest concentrations of uranium (5.13-1.90 ppm) with overall low proportion of common Pb (13-1.9%), producing an array with limited scatter (MSWD=2.2). An isochron age of 109.4 ± 5.3 Ma was calculated, and can be compared to the weighted mean age of single spots of 108.2 ± 5.9 Ma with MSWD of 3.2 (Fig.3.9.b).

Sample: 168-4-125-130

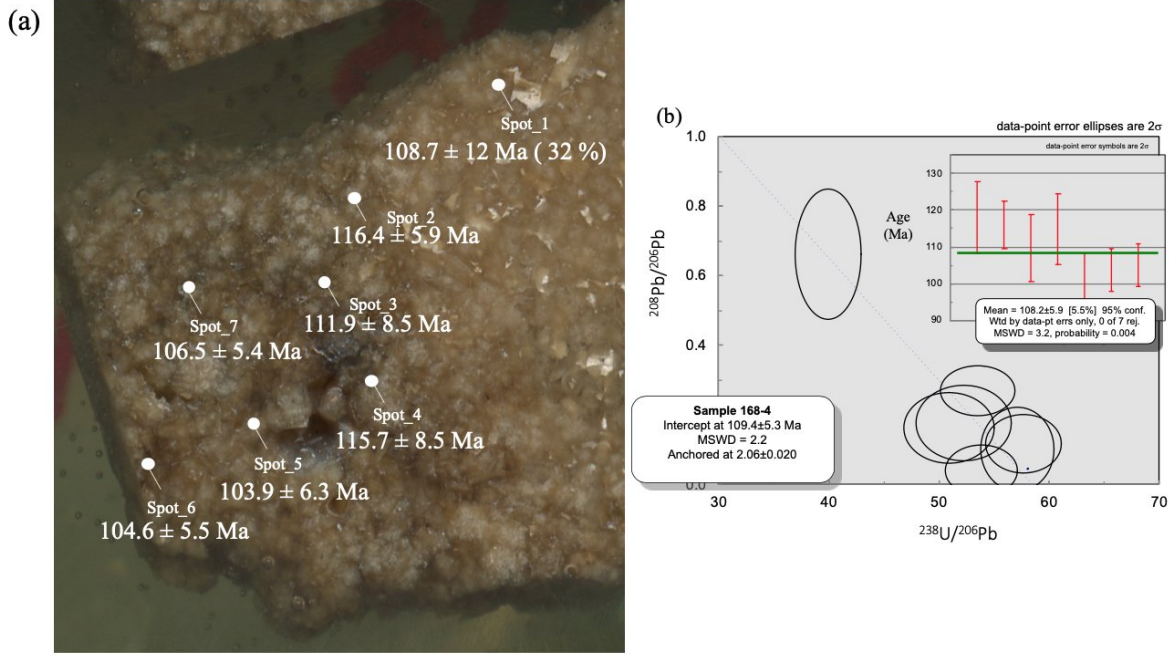


Figure 3.9. (a) Photograph of image of sample 168-4-125-130 as mounted, polished and analysed under normal lightning. The position of ablation data points and corresponding ages are indicated. The age is indicated for data points with low relative proportion of common lead. Otherwise, it is indicated in parentheses. b) 8-6T-W diagram for sample 168-4-125-130-125-130. Age was calculated using regression method. Detailed information is presented in Table 3.5.

- **D_{RT2} dolomite (samples 161-1(a-b) and 162-2 (a-b))**

Resin disk observations of samples 161-1 (a-b), as well as 162-2 (a-b) revealed presence of dark brown and light brown dolomite. Thin section analysis did not reveal any particular correlation between colour of dolomite and corresponding dolomite rock texture. Thus, both dark brown and light brown dolomites were classified as D_{RT2} dolomite based on thin section observation.

D_{RT2} dolomite from sample 161-1 (a-b) revealed uranium concentration in the range between 1.50 and 2.75 ppm (for both light and dark brown dolomites) with very low proportion of common Pb (<11%). The data set represents highly radiogenic data. The ellipses overlap in age and there essentially is no scatter in this sample along x-axis due suggesting a single age of crystallization (Fig.3.10.c-d). The ages were calculated for single data points. Their position and corresponding ages are presented in Fig.3.10 (a-b). Overall, the age for D_{RT2} dolomite (dark brown colour) from this sample 161 (a-b) is within the range between 122 ± 6.9 Ma and 116.3 ± 7.1 Ma, the age for D_{RT2} dolomite (light brown colour) is within the range between 120 ± 6.2 Ma and 111.1 ± 6.2 Ma

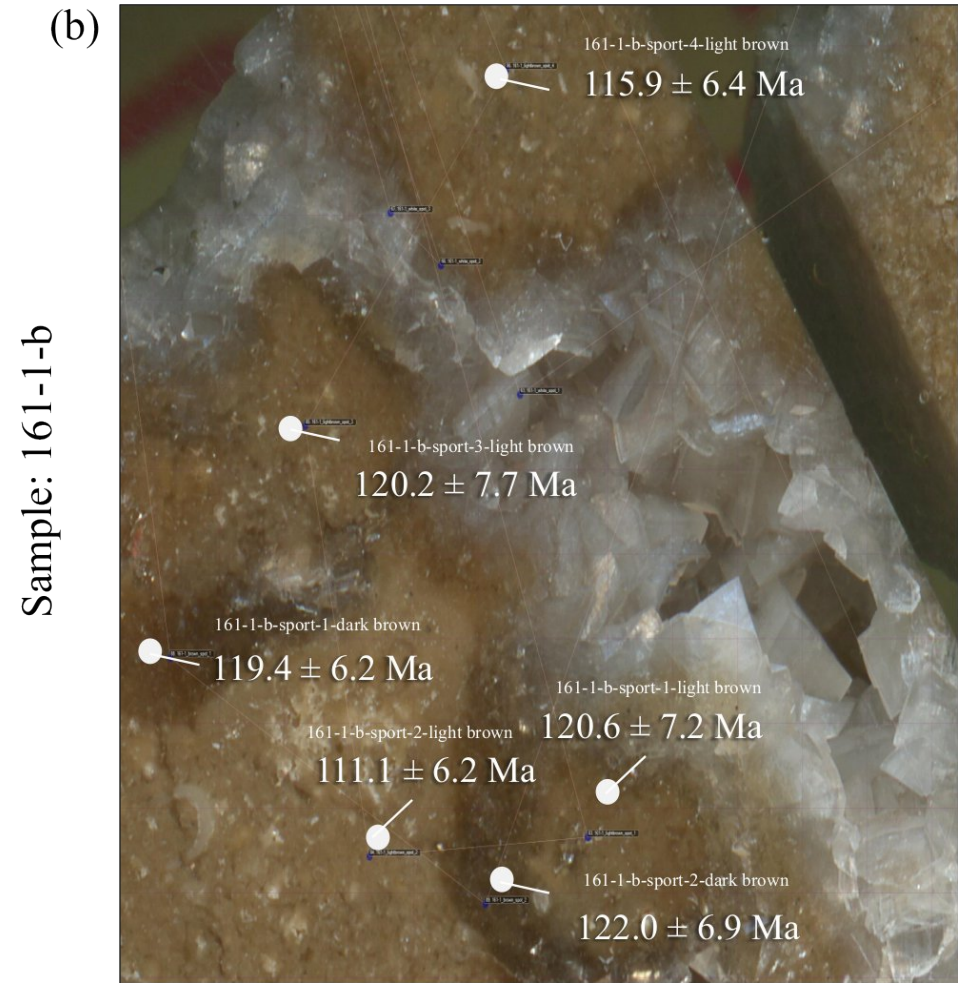
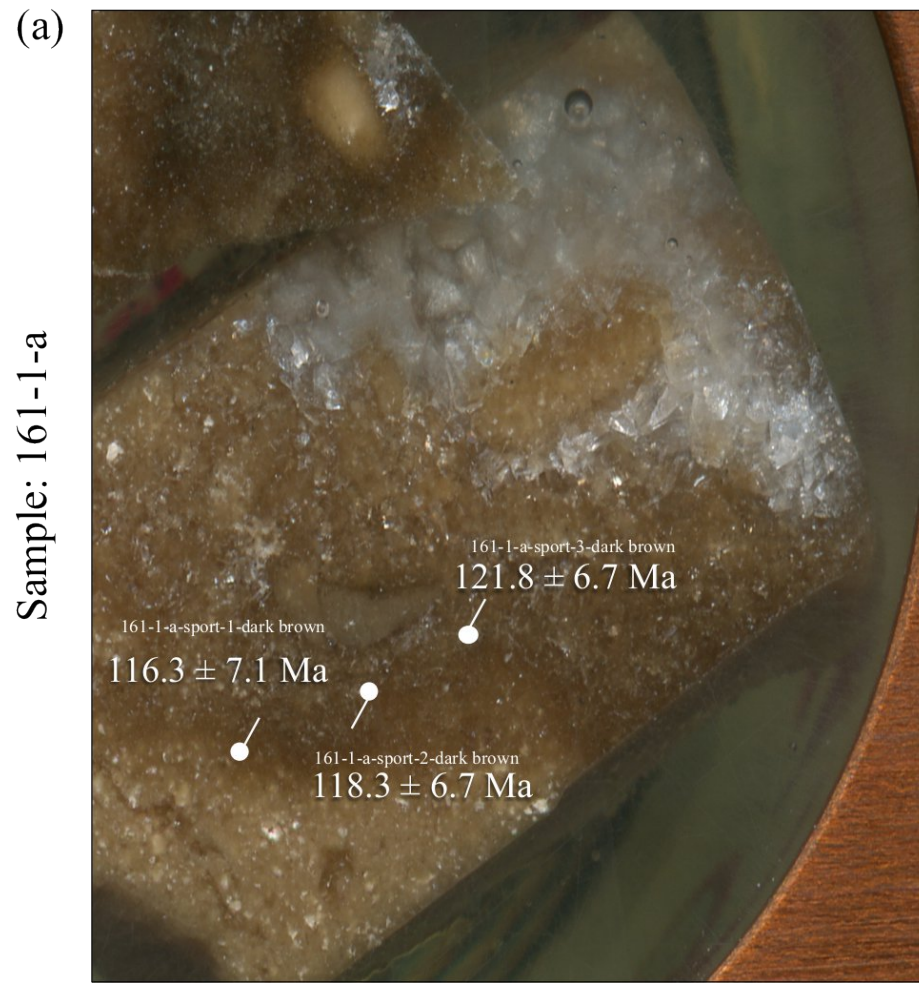


Figure 3.10. (a-b) Photographs of images of sample 161-1 (a-b) as mounted, polished and analysed under normal lightning. The position of ablation data points and corresponding ages are indicated. The age is indicated for data points with low relative proportion of common lead. Otherwise, it is indicated in parentheses.

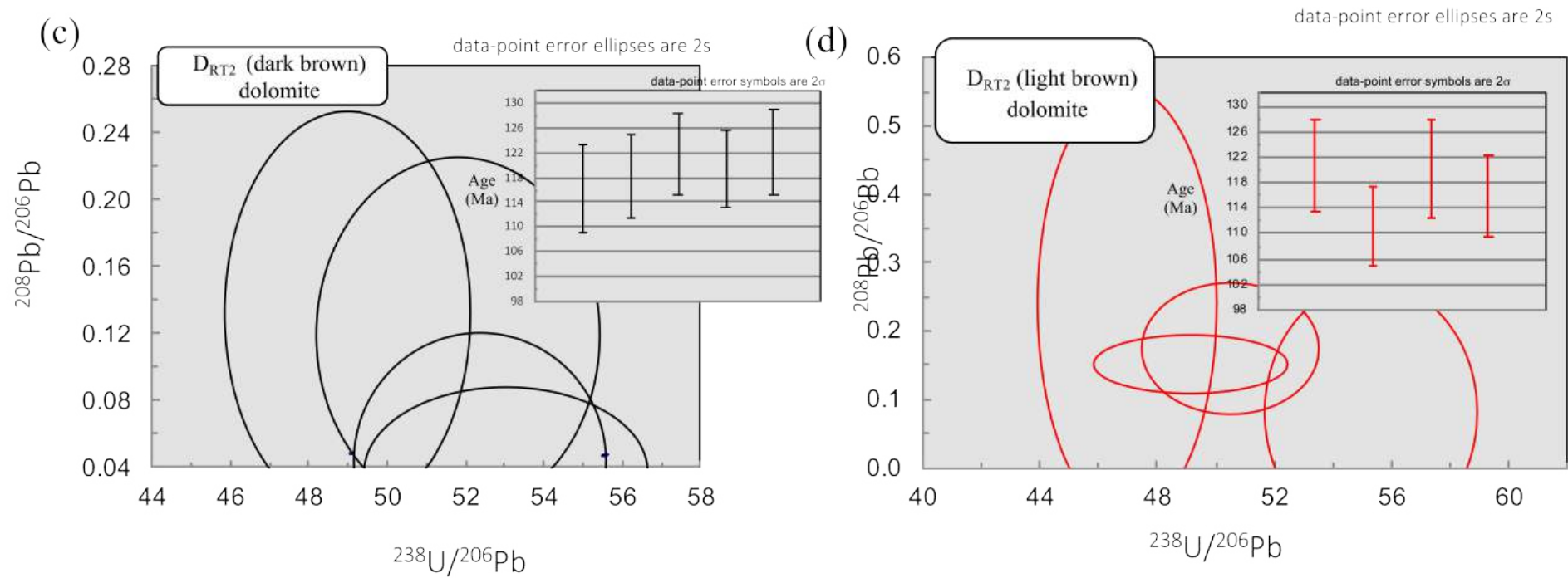


Figure 3.10. (Continued). (a-b) 8-6TW diagram for sample 161-1 (a-b) represent data for the D_{RT2} dolomite. Detailed information is presented in Table 3.5.

D_{RT2} dolomite from sample 162-2(a-b) have between 2.3-6.7 ppm U with show some scatter and are generally highly radiogenic. Amongst the very radiogenic analyses of both colours, there is a clear lack of overlap in uncertainties of uncertainty ellipses, implying a range in age of crystallisation of single spots of both colours from 122.0 ± 6.9 to 87.1 ± 4.4 Ma (Fig.3.11.c). Although a single regression could be calculated for each sample this would produce a large MSWD and obscure the real age variation from place to place within each dolomite group. Instead, single spot ages of radiogenic analyses are tabulated instead to illustrate that the precipitation of dark brown dolomite (black ellipses) range from 117.9 ± 4.6 Ma to 87.1 ± 4.4 Ma and that light brown dolomite (red ellipses) are between 110.2 ± 5.2 Ma and 118.5 ± 5.2 Ma.

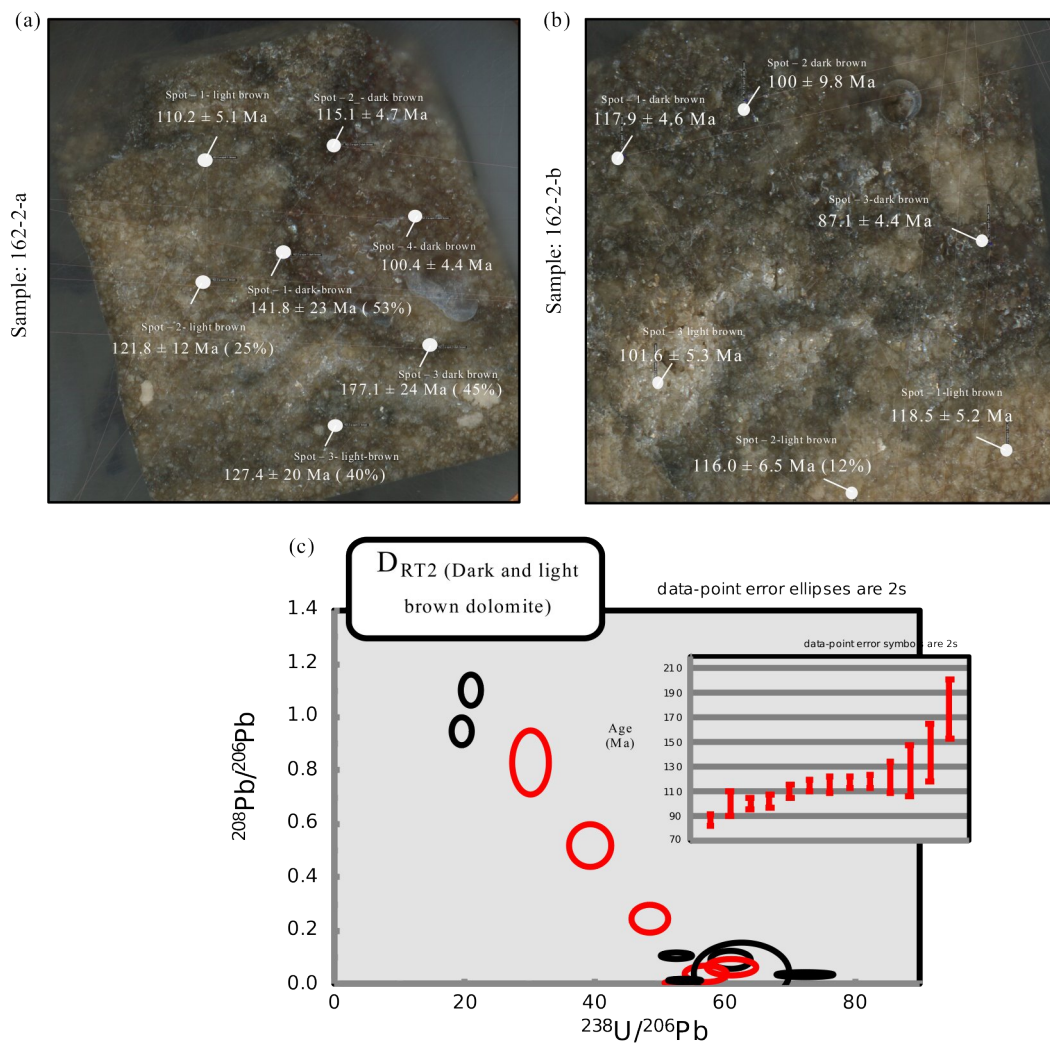


Figure 3.11. (a-b) Photographs of images of sample 162-2 (a-b) as mounted, polished and analysed under normal lightning. The position of ablation data points and corresponding ages are indicated. The age is indicated for data points with low relative proportion of common lead. Otherwise, it is indicated in parentheses. c) 8-6TW diagram for sample 162-2 (a-b) Black ellipses represent D_{RT2} dolomite of the dark brown colour. Red ellipses represent D_{RT2} dolomite of the light brown colour. Weighted mean plots represent individual age analyses for each type. The age for single data points were plotted accordingly their positions in Fig 3.9. Detailed information is presented in Table 3.5.

• Mixture of D_{RT2} / D_{RT3} dolomites (Sample 165-2-79-81)

Sample: 165-2-79-81

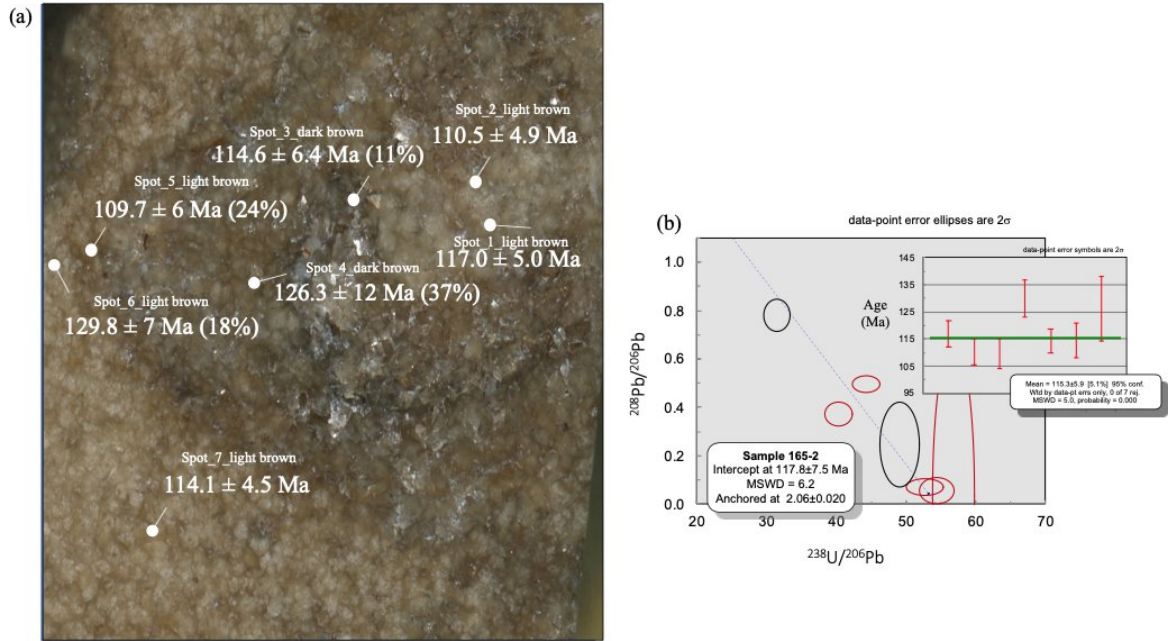


Figure 3.12. (a) Photograph of image of sample 165-2-79-81 as mounted, polished and analysed under normal lightning. The position of ablation data points and corresponding ages are indicated. The age is indicated for data points with low relative proportion of common lead. Otherwise, it is indicated in parentheses. (b) 8-6T-W diagram for 165-2-79-81. Black ellipses represent dark brown colour dolomite. Red ellipses represent light brown dolomite. Age was calculated using regression. Detailed information is presented in Table 3.5.

Thin section analysis revealed presence of two different types of dolomite textures in sample 165-2-79-81. Resin disk for sample 165-2-79-81 shows presence of two colours of dolomite: dark and light brown. As it was not possible to establish correlation between the colour of the dolomite and rock textures. Samples 165-1-79-81 was interpreted as a mixture of two rock textures: D_{RT2} and D_{RT3} . Data points for age measurements were placed according to the colour of the dolomite.

Data set represent an example of scattered data along y-axis due to input of common Pb. The proportion of common Pb is between 2.8-37%. However, the absence of scatter along x axis suggest single age of mineral crystallization and was calculated using regression. The age is equal 117.8 ± 7.5 Ma (Fig. 3.12. b) (MSWD = 6.2). For data points with low common lead concentration the ages for single data points were calculated (Fig. 3.12.a). The age is in the range between 110.5 ± 4.9 Ma- 117.0 ± 5 Ma with MSWD of 5.

- **D_{RT4} dolomites (Sample 143-1-123-124 and 133-2-136-137)**

Samples with predominance of D_{RT4} type of dolomite rock texture revealed high variation of uranium. It varies between 24.12 and 1.63ppm in sample 134-1-123-124, and between 13.32 and 7.10 in sample 133-1-136-137. The proportion of common Pb is variable as well and is overall very high: 12-50% in sample 134-1-123-124, and 57-28% for sample 134-1-123-124. In the majority of samples (4 out of 6) there is very low concentration of U (<0.01) along with high proportion of common Pb (90-100%). For this reason, ages were calculated only for two samples: 133-1-136-137 and 134-1-123-124.

Interestingly, in these two samples, the maximum proportion of common Pb appears to be less radiogenic than the predicted by Stacey and Kramers model (1975). Single spot ages are calculated twice using two values for common $^{208}\text{Pb}_{\text{com}}/^{206}\text{Pb}$ ratio. The first value is the “reset” value. It is calculated by taking mean for $^{208}\text{Pb}_{\text{com}}/^{206}\text{Pb}$ for data points with high concentration of common lead (Fig.3.13). The second value is the one predicted by Stacey and Kramers model (1975) and equals 2.06 ± 0.02 . Results are tabulated in Table 3.5. Below results are presented for ages calculated with the “reset” value.

Sample 134-1-123-124 represents a complex set of data. On one hand, there is scattered data with variable age of crystallisation and variation in common Pb proportion. On the other hand, there is not-radiogenic data set where the maximum common Pb ratio appears to be less radiogenic than the predicted by Stacey and Kramers model (1975). In this case, the high proportion of common Pb does not allow calculating of the single data point ages of cementation with a high level of certainty. In this case, it is more reasonable to calculate the mean age using regression.

When ages are calculated using regression, upper intercept is usually anchored using Stacey and Kramers' (1975) ratios calculated for Pb of 100 Ma old equals to value of 2.06 ± 0.020 $^{208}\text{Pb}/^{206}\text{Pb}$ ratios. However, results for sample 134-1-123-124 show that the maximum $^{208}\text{Pb}/^{206}\text{Pb}$ ratios is lower than the one predicted by Stacey and Kramers' (1975) model. The wrong use of $^{208}\text{Pb}/^{206}\text{Pb}$ ratios would normally lead to older ages of recrystallization. In this case, the new value for $^{208}\text{Pb}/^{206}\text{Pb}$ ratio was calculated by taking the mean of $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of data points with a very high concentration of common Pb. This value was name “reset” value of $^{208}\text{Pb}/^{206}\text{Pb}$ ratios and then used as an anchor to calculate either the regression age.

Regressed data revealed the age of white dolomite precipitation of 57.6 ± 3.8 Ma (Fig.3.13.b) (MSWD =22). The single data points ages were also calculated. (Table 3.5; Fig.3.13.a). The data points with low - medium proportion of common Pb show the time of precipitation between 51.3 ± 3.7 Ma (31%) and 66.6 ± 4.5 Ma (20%). The single data points with the lowest proportion of common Pb (0.7 %) indicates the age of dolomitization to be 57.2 ± 1.9 Ma.

Sample 133-2-136-137 represents mixture of white and light brown dolomite (potentially D_{RT2-3}). The measurements for sample 133-2-136-137 were done for both types of dolomite. Similar to sample 134-1-123-124 , sample 133-2-136-137 represents a complex data set with not-radiogenic data set and “reset” value of $^{208}\text{Pb}/^{206}\text{Pb}$ ratio equals to 0.96 ± 0.05 (Fig.3.13.e), as well as more radiogenic data points with low proportion of common Pb and highly variable U concentration. This suggest different ages of crystallization. For this reason, the regression would not be representable, as it will only show mean age. Thus, it is more reasonable to calculate the single data points using reset value of $^{208}\text{Pb}/^{206}\text{Pb}$ ratio.

The results suggest D_{RT2-3} dolomites precipitated between 101.0 ± 5 Ma (13%) to 76.4 ± 9 Ma (46%). The results for white dolomite showed single ages of cementation between 66.1 ± 5.1 Ma (29%) and 51.9 ± 8.1 Ma (56%) with MSWD = 5.1 (Fig.3.13.d-e).

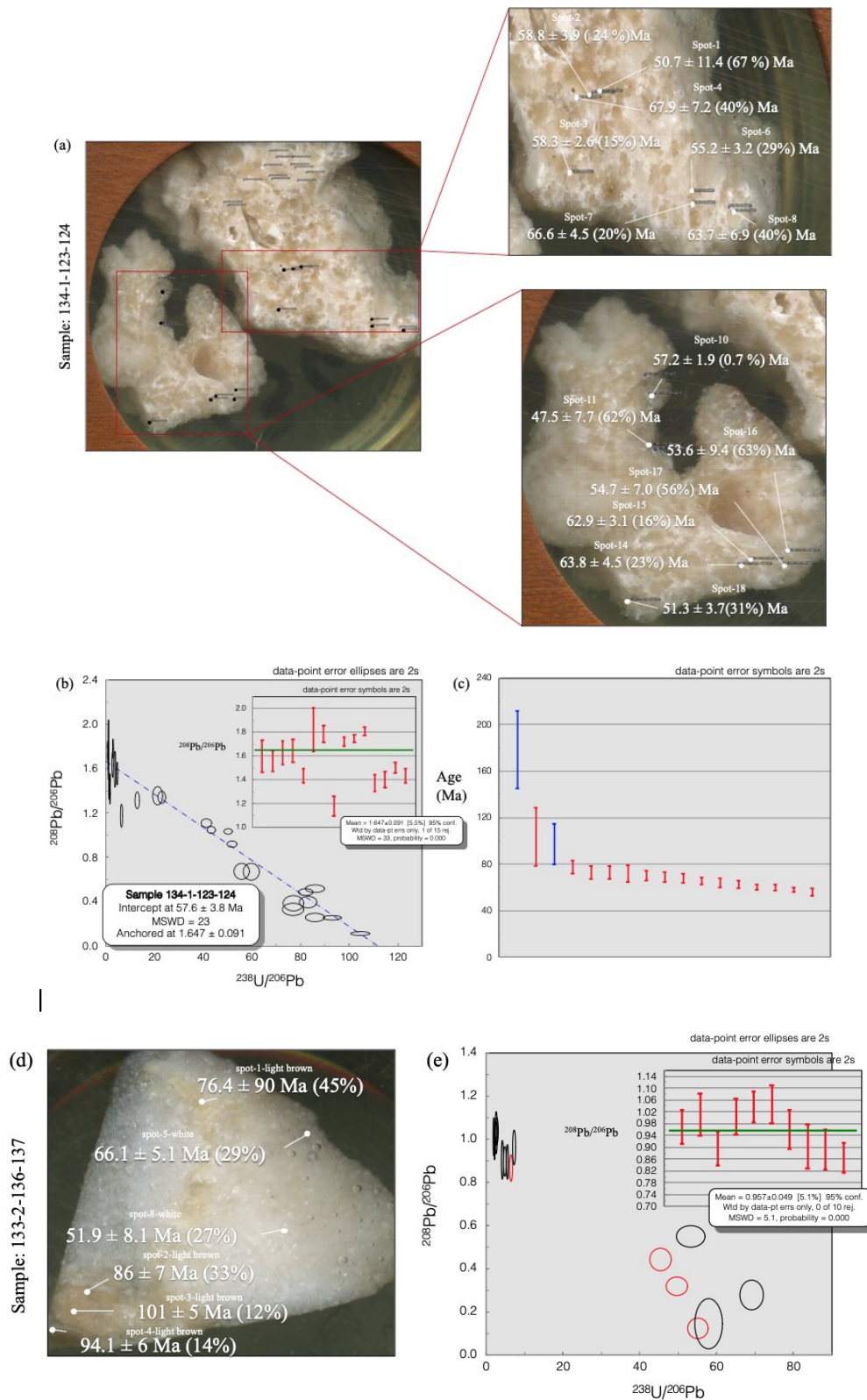


Figure 3.13. a) Photograph of image of sample 134-1-123-124 as mounted, polished and analysed under normal lightning. The name of individual data points, corresponding ages and relative proportion of common lead is indicated. Presented single data point ages were calculated using reset value for $^{208}\text{Pb}/^{206}\text{Pb}$ ratio equals 1.647 ± 0.091 . b) Regressed data for sample 134-1-123-124. The plot in the upper right corner represents mean value for $^{208}\text{Pb}/^{206}\text{Pb}$ ratio. c) Weighted mean plot for individual analyses. d) Photograph of image of sample 134-1-136-137 as mounted, polished and analysed under normal lightning. The name of individual data points, corresponding ages and relative proportion of common lead is indicated. Presented single data point ages were calculated using reset value for $^{208}\text{Pb}/^{206}\text{Pb}$ ratio equals 0.96 ± 0.05 . e) 8-6TW diagram for sample 133-2-136-137. Mean value of $^{208}\text{Pb}/^{206}\text{Pb}$ ratio is calculated and plotted in the right corner of 8-6TW diagram. Detailed information for each data point is presented in Table 3.4 in section for white dolomite.

- **D_{RT5} dolomite (Sample 161-1(a-b))**

Data points were placed on single crystals of white colour dolomite filling the vug interior. The dataset comprises an array of highly radiogenic data with no scatter along X-axis. Ellipses for 6 data points are overlapping (Fig.3.14.b). This suggest single age of crystallization. The low proportion of common Pb in the sample allowed calculation of single data points with ages in the range from 117.9 ± 4.9 Ma to 94.2 ± 7.0 Ma.

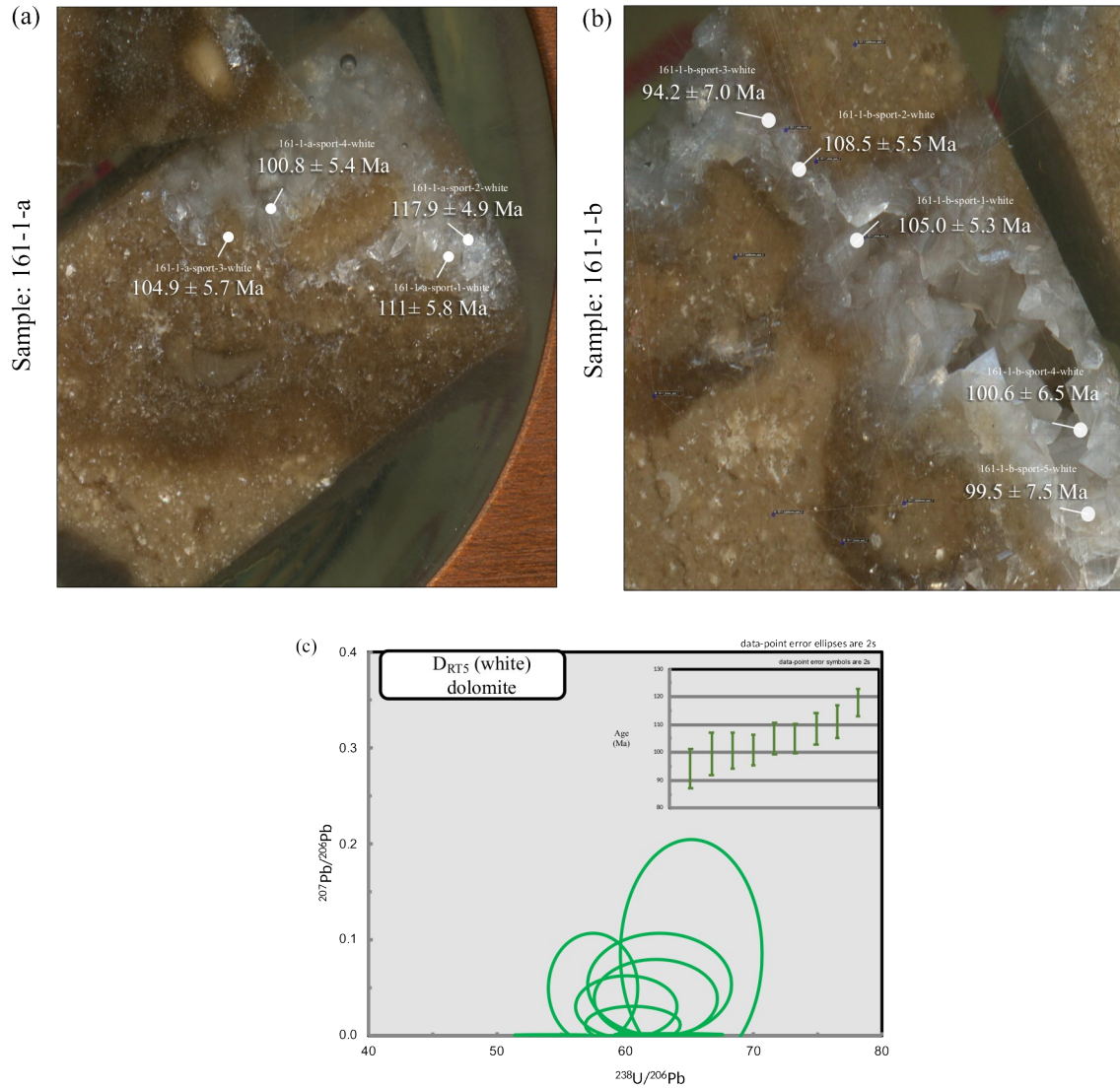


Figure.3.14. (a-b) Photograph of images of D_{RT5} dolomite cement from sample 161-1 (a-b) as mounted, polished and analysed under normal lightning. The position of ablation data points and corresponding ages are indicated. The age is indicated for data points with low relative proportion of common lead. Otherwise, it is indicated in parentheses. (c) 8-TWdiagram for D_{RT5} dolomite cement from sample 161-1 (a-b). Detailed information is presented in Table 3.5.

3.5. Discussion

Early sedimentary dolomites tend to recrystallize due to their unstable mineralogy shortly after mineral precipitation at shallow burial conditions via dissolution and re-precipitation process (Machel et al., 1993; Machel, 1997; Kaczmarek and Sibley, 2014; Veillard et al., (2019). In case dolomite minerals were recrystallised and are not primary dolomite, clumped isotope signal would record the environment of recrystallization and not the environment of primary dolomitization. For this reason, it was important to screen studied samples for presence of recrystallization. The evaluation was made using petrographical analyses coupled with bulk isotopic composition and clumped isotope temperatures. Petrography was used to reveal recrystallization textures (presence of dissolution features, growth rims, increase size of crystals), whereas clumped isotope temperatures were used as indicator of recrystallization in case they were higher than depositional temperatures, and/or reveal low water/rock fluid recrystallization.

3.5.1. Petrographic consideration and reconstruction of paragenetic dolomite types.

Based on identified five main types of dolomite rock-textures (D_{RT1-5}) (Fig.3.5; Fig.3.6) it was possible to reconstruct the paragenetic history. Paragenetic history was built based on level of preservation of initial rock texture visible from thin section analysis, crystal size of dolomite crystals and any changes in crystals boundary shape (planar-non-planar). Paragenetic history is presented in Figure.3.15.

Preservation of initial rock textures in dolomite minerals is normally explained by precursor mineralogy and grain/crystal size. Previously, it was also suggested that high magnesium calcite tends to be dolomitized with retention of the primary fabrics, whereas low magnesium calcite is more resistant to dolomitization and replacement results in fabric-destroying textures (Murray and Lucia, 1967; Sibley, 1982; 1990)..

The preservation of original rock textures in D_{RT1} dolomite points out that it is the closest example of primary dolomite and was not recrystallized. Otherwise, the recrystallization of dolomite would lead to destruction of preserved rock textures (Warren, J., 2000; Machel, H.G., 2005;). D_{RT1} dolomites have similar characteristics to the fabric preserving dolomites described by Al-Languani (2006), oolitic dolomites from the Feixianguan Formation (Sijing et al., 2014), as well as type II dolomite from the Upper Jurassic Hacialabaz formation in the

Bagbasi area (Turkey) studied by Özkan and Dinc (2011). The preservation of original textures during dolomitization also indicates shallow depths conditions of dolomitization (Sijing et al., 2014).

D_{RT2} and D_{RT3} dolomites is an example of fabric destructive dolomites with non-planar (D_{RT2}) and planar-s (D_{RT3}) crystal boundary shapes. The destruction of original dolomite textures is usually a characteristic of recrystallization processes in dolomite (Warren, J., 2000; Machel, H.G., 2005; Bidgoli and Navidtalab, 2020). Additionally, predominance of non-planar boundary shapes in D_{RT2} dolomite is an indicator of dolomite growth at elevated temperatures ($>50\text{ }^{\circ}\text{C}$) or/and rarely of higher level of supersaturation (Gregg and Sibley, 1987; Amthor and Friedman, 1991; Bidgoli and Navidtalab, 2020). Planar-s boundaries in D_{RT3} dolomite crystals suggest that crystal growth took place under shallow-medium burial conditions. Similar dolomite type was described by Özkan and Dinc (2011).

Additionally, the both types of dolomite exhibit the increase of crystal size from fine-medium to coarse grained. One possible explanation for increase of crystal size may be continuous recrystallization process. The increase of crystal size with recrystallization was experimentally proved by Kaczmarek and Sibley, (2014) and Kaczmarek, (2017). Another possible explanation may be that D_{RT2} and D_{RT3} dolomites were continuously precipitated from high-temperature fluids. Higher temperatures could affect the mode of crystal growth. Some evidence exists in the literature (Brice, 1973; Lewis, 1980; Kirkpatrick, 1981) to support this view. However, at the stage of thin section analysis, it is still difficult to state which scenario is more plausible.

Core samples description coupled with thin section analysis suggest that brown dolomite predominately have D_{RT1-3} dolomite textures, when white colour dolomite predominately consist of D_{RT4} dolomite. Based on this division, the patches of brown dolomite visible on core samples of white dolomite can be interpreted as D_{RT1-3} dolomites (Fig.3.4.b and Fig.3.6.d). this observation is proved by thin section analysis. As an example, thin section observation of D_{RT4} dolomite revealed presence of D_{RT2} dolomite in sample 134-2-27-28.

D_{RT4} dolomites exhibits fabric destructive textures with mixture of non-planar and planar-e crystal boundaries. Compare to D_{RT1-3} dolomites, D_{RT4} dolomites exhibit the biggest crystal size. Presence of D_{RT1-3} dolomites within the D_{RT4} dolomites in core samples indicates a

potential genetic relationship between these dolomites. One possible scenario for precipitation of D_{RT4} dolomite could be recrystallization of D_{RT2} and D_{RT3} dolomites. Preservation of prior to dolomitization rock textures in D_{RT1} dolomite suggests that it was not recrystallized. However, further evidence from geochemistry is needed to support this observation (see next section). Finally, D_{RT5} dolomite is mainly filling vug and porous spaces and largely cross-cut the rest of the dolomite rock textures (D_{RT1-4}). D_{RT5} dolomite was interpreted as a dolomite cement.

Based on the above observations, it was possible to build the paragenetic history of dolomite rock-texture from Resolution Guyot (Fig.3.15). Preservation of rock textures in D_{RT1} suggests that it was not recrystallized and is an example of primary dolomitization. Thin section observation of D_{RT2} and D_{RT3} dolomites suggest that either they were recrystallized or were precipitated from fluids with high temperatures. The presence of D_{RT1-3} dolomites in the D_{RT4} dolomite points out that it was formed after D_{RT1-3} and potentially due to recrystallization of D_{RT2} and D_{RT3} dolomites. Finally, presence of D_{RT5} dolomite in D_{RT1-4} dolomites suggest that it was precipitated as the last one.

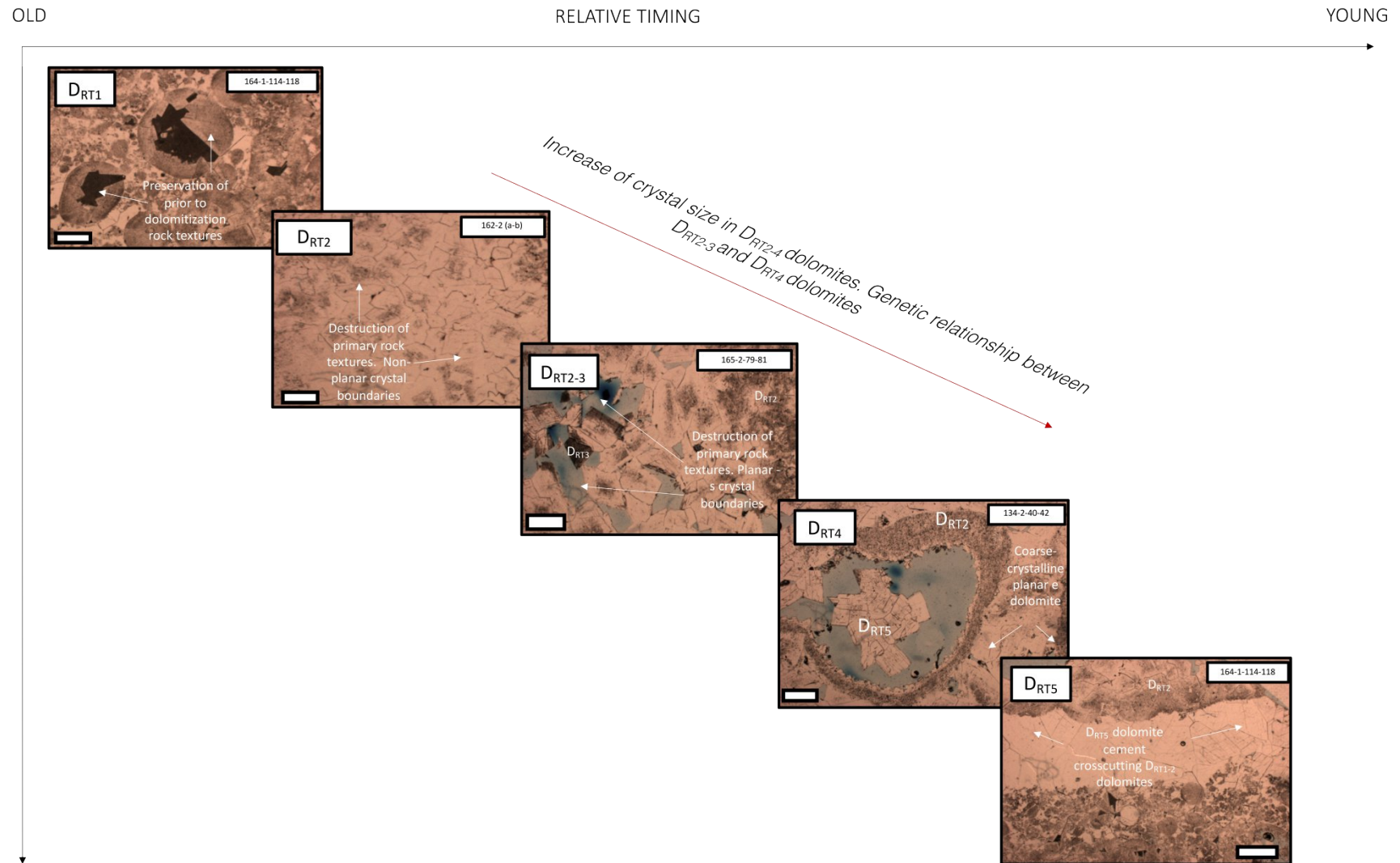


Figure 3.15. Paragenetic history of five dolomite types from Resolution Guyot based on thin section analysis.

3.5.2. Recrystallized versus pristine early dolomite: evidence from clumped isotope data.

The origin of dolomites was further evaluated using clumped isotope data. Clumped isotope temperature for sample 168-4-125-130 with predominant D_{RT1} dolomite is $39(\pm 4) ^\circ\text{C}$ with $\delta^{18}\text{O}_{\text{fluid}} - 1.32 (\pm 0.80) \text{‰}$. Interestingly, clumped isotope results for sample 164-1-114-118 with mixture of dolomite textures (D_{RT1} and D_{RT5}) revealed temperature of precipitation and isotopic composition of dolomitized fluids within the same range as sample 168-4-125-130 (Fig.3.16). Measured clumped isotope temperature for sample 164-1-114-118 equals to $38 (\pm 2) ^\circ\text{C}$ with $\delta^{18}\text{O}_{\text{fluid}} - 1.35 (\pm 0.83) \text{‰}$. On the plot of clumped isotope temperature versus $\delta^{18}\text{O}_{\text{fluid}}$ (Fig.3.16) values for these two samples are plotting close to each other suggesting similar origin of dolomite minerals. Observation of clumped isotope data is supported by similarity in thin section (Fig.3.6). Based on these observations these two samples will be analysed together.

Three scenarios are possible to explain the clumped isotope data for these two samples and they are summarised in Table.3.6. Scenario 1 – seawater dolomitization in a near-surface to shallow burial setting. Scenario 2 – dolomitization by geothermally heated sea waters (geothermal endo-upwelling) Scenario 3- shallow burial recrystallization.

Table 3.6. Argument for and against different scenarios for the formation of D_{RT1} dolomite.

Potential scenarios for precipitation D_{RT1} dolomite	Data supporting the scenario	Data not supporting the scenario
<i>Scenario 1: Near surface seawater dolomitization</i>	Calculated $\delta^{18}\text{O}_{\text{fluid}}$ is within error with Cretaceous sea waters;	Temperatures of dolomitization are slightly higher than expected for sea surface temperatures ($30 - 32 ^\circ\text{C}$);
<i>Scenario 2: Dolomitization by geothermally heated sea waters (geothermal</i>	- Elevated $T_{\Delta 47}$ of mineral precipitation. $\delta^{18}\text{O}_{\text{fluid}}$ is within error with Cretaceous sea waters;	High $T_{\Delta 47}$ may also represent temperatures of recrystallization process at shallow

<i>endo-upwelling)</i>		burial depth (Scenario 3).
Scenario 3: shallow burial recrystallization	• Elevated $T_{\Delta 47}$ of mineral precipitation • Under assumption of a high F/R ratio $\delta^{18}\text{O}_{\text{fluid}}$ is within error with Cretaceous sea waters;	• Fabric-retentive textures;

Seawater itself can also be a source of dolomite precipitation because it contains the sufficient amount of Mg ions with little modification if a good pumping process exists. The near sea surface dolomitization also explains $\delta^{18}\text{O}_{\text{fluid}}$ values of - 1.32 ($\pm$ 0.80) and - 1.35 ($\pm$ 0.83) ‰, which are within error of the estimated isotopic composition of Cretaceous sea waters (- 1 ‰, Cramer et al. 2011;Dennis et al.2013). However, in order to support this scenario, it is necessary to compare measured clumped isotope temperature with age of crystallization and the depth of mineral precipitation. If D_{RT1} dolomite was precipitated at the surface from Cretaceous sea waters, it is expected that the age for D_{RT1} dolomite crystals would be close to the chronostratigraphic age for this lithological unit (127.6-127 Ma).

The first scenario is partially consistent with clumped isotope data. Based on previous studies, the age of $D_{\text{RT1-3}}$ dolomites was interpreted as Early Cretaceous (Flood and Chivas, 1995). In this case, the expected surface seawater temperatures for Early Cretaceous tropical sea surface can be expected to be in the range between 30 and 32 °C (Dumitrescu, 2006). Clumped isotope temperature for sample of D_{RT1} is slightly higher than expected but are close to the upper end of this range taking into account the temperatures error of 4 °C. As an example, clumped isotope temperature of 37 ($\pm$ 2) °C for oysters from Lower Cretaceous Qishn formation was interpreted compatible with a Lower Cretaceous shallow, tropical sea by John (2015).

The second potential scenario implies precipitation of D_{RT1} dolomite from sea waters heated by the geothermal gradient – geothermal endo - upwelling. Due to basal heating from the volcanic basement and the thermal contrast between the cold and the warm platform top, cold seawater is thought to invade the platform along its slope, advect laterally and vertically upwards, and discharges at the top of the platform (Budd et al., 1997). This scenario would explain warmer than ocean sea surface clumped isotope temperatures, and

$\delta^{18}\text{O}_{\text{fluid}}$ close to Cretaceous sea waters. The second scenario is compatible with the interpretation of the mechanism of dolomitization at Resolution Guyot (Flood and Chivas, 1995). However, in order to support this scenario, it would be necessary to demonstrate that the depth of D_{RT1} dolomite precipitation cannot justify the measured clumped isotope temperatures. In case of dolomitization due to geothermal upwelling, measured temperature should be colder compare to temperatures of host rock, but still hotter than the sea surface temperature.

For the third scenario, the measured clumped isotope temperatures and negative isotopic composition of the dolomitized fluids may be characteristic of shallow dolomite recrystallization at high water -to- rock ratio (Huntington and Lechler, 2015). The preservation of original textures in this case can be related to incomplete recrystallization process. Again, in order to assess further the third scenario it is also necessary to determine the age of D_{RT1} dolomites. This would allow to calculate the depth of recrystallization and build burial model. Thus, burial model will indicate if D_{RT1} dolomite was buried deep enough to explain clumped isotope temperatures. In this case, expected burial temperatures should be equal to the clumped isotope temperatures. As can be seen above, determination of the U/Pb ages will be key to distinguish which one of the mechanisms is more likely (see section 3.5.3).

Clumped isotope temperatures for samples with predominate D_{RT2} dolomite rock textures (Samples 161-1(a-b) and 162-2 (a-b)) are equal $35(\pm 3)^\circ\text{C}$ and $44(\pm 3)^\circ\text{C}$. Calculated values of $\delta^{18}\text{O}_{\text{fluid}}$ are equal to $-0.21 (\pm 0.66) \text{‰}$ and $0.13 (\pm 0.59) \text{‰}$ (Table.3.4). Due to lack of suitable sample, it was not possible to measure clumped isotope temperatures separately for D_{RT3} dolomite. Single sample 165-2-79-81 which represents the mixture of D_{RT2} and D_{RT3} dolomite (Fig.3.6.f). Clumped isotope results for $D_{\text{RT2-3}}$ dolomite is $53(\pm 1)^\circ\text{C}$ with $\delta^{18}\text{O}_{\text{fluid}}$ of $0.62 (\pm 0.28) \text{‰}$.

High clumped isotope temperatures and fabric-destructive textures for D_{RT2} and D_{RT3} dolomites can be explained by continuous seawater dolomitization due to geothermal endo-upwelling. In this case, it is expected that dolomite mineral would record the isotopic composition of seawaters, which is the main dolomitizing fluid. Expected value for $\delta^{18}\text{O}_{\text{seawater}}$ in Cretaceous time equals -1‰ (Cramer et al. 2011; Dennis et al.2013). However, calculated values of $\delta^{18}\text{O}_{\text{fluid}}$ for D_{RT2} and D_{RT3} dolomites are heavier. Alternative explanation

for high clumped isotope temperatures may be solid -state reordering process. However, maximum burial temperatures at Resolution Guyot (Flood and Chivas, 1995) are lower than the expected temperatures for solid -state reordering for dolomites (200-300°C; Bonifacie et al., 2016). Thus, solid-state reordering processes can be ignored in this case and will not be discussed.

The plot of clumped isotope temperature versus $\delta^{18}\text{O}_{\text{fluid}}$ reveal presence of increasing Trend 1 (Fig.3.16) of $\delta^{18}\text{O}_{\text{fluid}}$ versus clumped isotope temperatures for D_{RT2} and $D_{\text{RT2-3}}$ dolomites. Such trend is a characteristic of recrystallization at low water -to- rock ratio (Huntington and Lechler, 2015). During low water-rock ratio recrystallization, the increase of cementation with burial, stagnant condition of pore space causes equilibration of the isotopic composition of the pore fluids with isotopic composition of surrounded rocks. In this case, the values for $\delta^{18}\text{O}_{\text{fluid}}$ are expected to be invariant during the process of recrystallization, whilst temperature increases. This causes an artificial increase of the calculated values $\delta^{18}\text{O}_{\text{fluid}}$ along with increasing temperatures. Thus, $\delta^{18}\text{O}_{\text{fluid}}$ values do not represent the real composition of the diagenetic fluids and are artificial. Based on the observations in thin sections and discussed clumped isotope data, we suggest that D_{RT2} and $D_{\text{RT2-3}}$ dolomites likely underwent recrystallization. However, in order to assess the measured temperature and whether it corresponds to recrystallization temperatures it is necessary to compare it with expected burial temperature and age of mineral precipitation.

However, it should be taken into account that end data point for Trend 1 ($T=53(\pm 1) ^\circ\text{C}$; $\delta^{18}\text{O}_{\text{fluid}} = 0.62 (\pm 0.28) \text{‰}$) was measured for sample 165-2-79-8 with mixture of textures of both D_{RT2} and D_{RT3} dolomites (Fig.3.16). This could cause an offset for Δ_{47} values (Defliese et al.,2015) which is controlled by the difference in bulk isotope composition of the two phases. In our case, it is unlikely that the two dolomite textures would be several tens of permil apart in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, and this process is thus deemed unlikely.

Clumped isotope temperatures for D_{RT4} dolomites (including sample with addition of D_{RT2} and D_{RT5} dolomite textures) and are in the range between 19-25°C (Fig.3.16). The plot of clumped isotope temperatures versus $\delta^{18}\text{O}_{\text{fluid}}$ reveal Trend 2 of variation in $\delta^{18}\text{O}_{\text{fluid}}$ versus temperature similar to the Trend 1 previously observed for $D_{\text{RT2-3}}$ dolomites (Trend 2, Fig.3.15.a). The variation of $\delta^{18}\text{O}_{\text{fluid}}$ versus temperature is potential indicator for recrystallization origin of D_{RT4} dolomite at low water -to- rock ratio (Huntington and Lechler,

2015). However, several data points from D_{RT4} samples revealed more negative values for $\delta^{18}\text{O}_{\text{fluid}}$ and suggest recrystallization at higher water-to-rock ratio.

Another interesting observation for D_{RT4} dolomites is increase of concentration of Fe in D_{RT4} dolomite compare to D_{RT1}- D_{RT3}. Reported values for Fe change from 91-2051ppm for D_{RT1}- D_{RT3} dolomite till 38 ppm in D_{RT4} (Flood and Chivas, 1995). The decrease of Fe concentration in D_{RT4} compare to D_{RT1}- D_{RT3} dolomites suggest that Fe was lost from mineral structure. The loss of Fe likely happened during recrystallization process during dissolution - reprecipitation reaction at high water-to rock ratio. The release of Fe into pore space and its further removal from the site of recrystallization during open -system recrystallization process was previously described by Renard et al., (2017) on the example of siderite mineral and by Debure et al., (2017) on the example of Fe-bearing dolomites. Study of Debure et al., (2017) demonstrates that dissolution of Fe-bearing dolomite involves two-step process with release of Fe and its further precipitation as a separate phase in the form of (nano)hematite, ferrihydrite, and an ankerite minerals. However, at this stage of analysis there is still not enough evidence to prove that D_{RT4} dolomite was recrystallized. One of the potential strong evidence can be younger ages for D_{RT4} dolomite, which would overlap with ages for D_{RT1}- D_{RT3} dolomites. Additionally, it is worth to check if measured clumped isotope temperatures correspond to expected burial conditions for D_{RT4} dolomite.

In summary, based on petrographic analysis and clumped isotope data, it is hard to say if D_{RT1} dolomite represents a recrystallized dolomite or was precipitated from either normal surface seawaters or from the seawaters heated by Kohout circulation. Three scenarios were discussed and summarised in Table.3.6. Further observations are needed. The thin section analyses and clumped isotope data suggest that D_{RT2} and D_{RT2-3} dolomites represent recrystallized dolomites at lower water-to-rock ratio. Furthermore, based on loss of Fe, presence of D_{RT2-3} dolomites within D_{RT4} dolomite (based on core and thin section observations), variation in $\delta^{18}\text{O}_{\text{fluid}}$ versus $T_{\Delta 47}$ and trend towards more negative values of $\delta^{18}\text{O}_{\text{fluid}}$ (Trend 2) suggest that D_{RT4} is potentially a product of recrystallization of D_{RT2-3} dolomites in water-buffered system. However, the interpretation of the recrystallization origin of D_{RT4} may be strengthened by U-Pb data and correspondence of age of D_{RT4} dolomite to expected burial depths.

In order to assess the origin of the D_{RT1} dolomite and support the interpretation D_{RT2-4} dolomites, it is necessary to determine the precipitation and/or recrystallization ages, depths of recrystallization/precipitation and thus, place these processes in the context of a burial model. We can determine which process is more likely to be happened based on whether the measured clumped isotope temperatures are compatible with expected burial temperatures within each stratigraphic interval. The age of dolomite may also help to understand if D_{RT1} dolomite was precipitated at the surface by normal sea waters or from the seawaters heated by Kohout circulation. It is expected that in case of Scenario 1, the age for D_{RT1} dolomite would be close to the age for the stratigraphic interval where D_{RT1} dolomite is sampled (127.6-127 Ma).

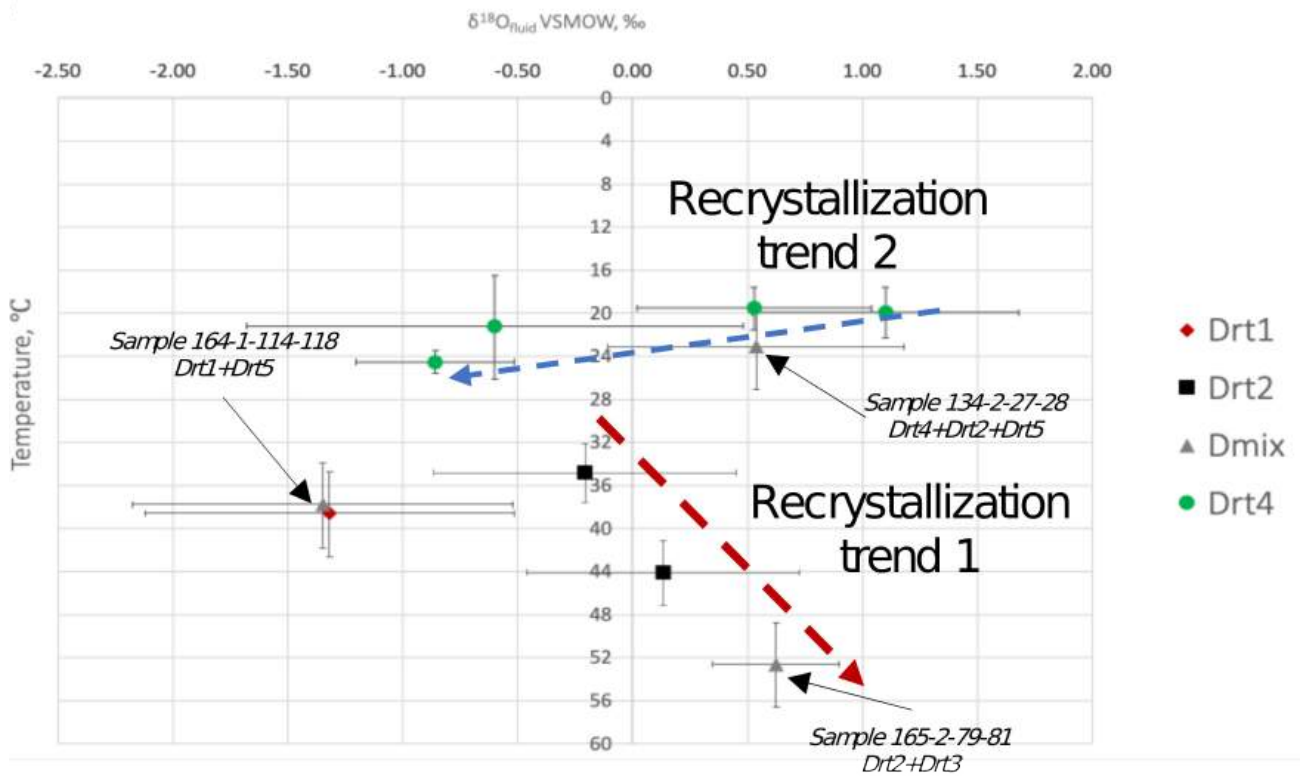


Figure. 3.16. The temperature of dolomite mineral precipitation (T , °C) versus calculated isotopic composition of dolomitised fluid ($\delta^{18}O_{fluid}$ VSMOW, ‰). The clumped isotope temperatures are calculated using Davies and John's (2019) equation. The fluid composition was calculated using Horita's (2014) equation. The temperature error was calculated using a single standard error for D_{47} CDES value. The error for fluid composition was calculated using maximum and minimum temperatures values and a single standard error of $\delta^{18}O_{dol}$ PDB (‰) values.

3.5.3. Reconstruction of formation ages for D_{RT1} – D_{RT3} dolomites using the LA-ICPMS U-Pb method.

Having established 5 diagenetic types of dolomite along with some relative timing and environment of dolomite precipitation and recrystallization based on thin section analysis and clumped isotope data (Fig.3.15, Fig.3.16), we can now build a paragenetic history in absolute time using U-Pb method of dating. This will also allow us to support or reject some of the hypothesis we formed in the previous section.

D_{RT1} dolomite is an example of highly radiogenic data with low scatter along the $^{238}\text{U}/^{206}\text{Pb}$ -axis and $^{207}\text{Pb}/^{206}\text{Pb}$ axis (Fig.3.8.b). Low ratio of $^{207}\text{Pb}/^{206}\text{Pb}$ suggests that proportion of common Pb is very low. Absence of scatter along $^{238}\text{U}/^{206}\text{Pb}$ axis suggests single age of mineral crystallization. Calculated age for D_{RT1} is 109.4 ± 5.3 Ma. Calculated age shows the precipitation of D_{RT1} dolomite happened at the late stage of the Resolution Guyot growth and does not correlate with the lithostratigraphic age of studied sample 168-4-125-130: 127.6 and 127 Ma. This observation rules out the first scenario for the near syn-sedimentary precipitation of D_{RT1} dolomite at the surface of the carbonate platform straight from sea waters (Table.3.6). However, it is still unclear whether D_{RT1} dolomite was precipitated from seawaters percolating Resolution Guyot enforced by geothermal endo-upwelling process or D_{RT1} dolomite is an example of burial recrystallization at higher burial temperatures. In order to resolve the interpretation problem, as the next step, burial model will be built and it will allow to draw final conclusions (See 3.5.5).

D_{RT2} dolomite is an example of highly radiogenic data. The Terra-Wasserburg diagram for sample 161-1 (a-b) exhibits scatter of data along $^{238}\text{U}/^{206}\text{Pb}$ axis with no scatter along $^{207}\text{Pb}/^{206}\text{Pb}$ axis (Fig.3.10.a). The measured ages for this sample equals to 122 ± 6.9 – 116.3 ± 7.1 Ma. The Terra-Wasserburg diagram for second sample 162-2 (a-b) of D_{RT2} dolomite exhibits scatter of data along both axes: $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ (Fig.3.11.c) with calculated ages between 122 ± 6.7 Ma and 87.1 ± 4.4 Ma. Similar to clumped isotope data, it was not possible to separate D_{RT3} dolomite from D_{RT2} dolomite during U-Pb measurements. Sample 165-2-79-81, which represents mixture of D_{RT2} and D_{RT3} dolomites, was studied and will be discussed together with samples with predominant D_{RT2} dolomite rock textures. The Terra-Wasserburg diagram for sample 165-2-79-81 (Fig.3.12.b) exhibits scatter along $^{238}\text{U}/^{206}\text{Pb}$ axis with no scatter along $^{207}\text{Pb}/^{206}\text{Pb}$ axis. Calculated age equals

117.8± 5.2 Ma and overlaps with recrystallization ages received for pure D_{RT2} dolomites from samples 162-2 (a-b) and 161-1 (a-b). Overall, U-Pb ages for D_{RT2} and D_{RT3} dolomites show dolomite precipitation within time interval between 122 ± 6.7 Ma and 87.1 ± 4.4 Ma. Long period of mineral growth is consistent with earlier interpreted recrystallization origin of D_{RT2} and D_{RT3} dolomites based on clumped isotope data and observed recrystallization Trend 1 (Fig. 3.16.a), as well as thin section observations (Fig.3.15). Thus, calculated U-Pb ages represent ages of recrystallization.

3.5.4. Reconstruction of age of D4 dolomite and new approach to date recrystallized carbonate.

D_{RT4} dolomite was the hardest to date due to the lowest amount of U along with highest proportion of Pb_{com} 28-100% (Fig.3.13.b,c,e). Although single data points revealed exceptionally high concentration of Uranium: between 24.12 and 1.63 ppm in sample 134-1-123-124 and between 13.32 and 7.10 ppm in sample 133-2-136-137, the overall uranium concentration in D_{RT4} dolomite is extremely low (< 0.01ppm). Calculated ages for most prolific samples 134-1-123-124 and 133-2-136-137 show that precipitation of D_{RT4} dolomite took place in time interval between 66.1± 5.1 and 51.9± 8.8 Ma and are younger compared to the one calculated for D_{RT1-3} dolomites.

Additionally, D_{RT2-3} dolomites from sample 133-2-136-137 have ages of precipitation between 101± 5.0 Ma and 94.1 ± 6 Ma. This time interval overlaps with measured ages for recrystallized D_{RT2} and D_{RT3} dolomites: 122 ± 6.7 Ma and 87.1 ± 4.4. Presence of D_{RT2} dolomite in D_{RT4} was also observed on thin sections (Fig.3.6.g). Furthermore, overlapping of calculated ages between D_{RT2} and D_{RT3} and D_{RT4} in sample 133-2-136-137 supports the previous interpretation of clumped isotope data and recrystallization origin of D_{RT4} dolomites from D_{RT2}-D_{RT3}.

The difficulty to extract the age from data points measured in D_{RT4} dolomite was mostly related to very high proportion of common Pb in all studied samples. The general approach for Pb_{com} correction is to use an estimated value for $^{208}\text{Pb}_{\text{com}}/^{206}\text{Pb} = 2.06 \pm 0.02$ typically derived from Stacey and Kramer model (1975) (Palin et al., 2013; Regis et al., 2016). Multiple studies show that the value for Pb ratio derived from other minerals such as feldspar, biotite, apatite is within the same value as suggested by the Stacey and Kramers

model (e.g. Stübner et al., 2014; Warren et al., 2014). Thus, the estimates of common Pb based on the Stacey- Kramer model (1975) was considered a reasonable approach for dating carbonate minerals (Li and Parrish, 2014; Parrish et al., 2017; Mangenot et al., 2018; Roberts et al., 2019). For D_{RT4} dolomite, however, we find that this is not a such a suitable approach. Our results demonstrate that values for $^{208}\text{Pb}_{\text{com}}/^{206}\text{Pb}$ ratio are lower than predicted by the Stacey and Kramers model (Fig.3.12b,e). Similar behaviour was also noticed in calcite cement from fractures in Proterozoic crystalline crust of Sweden, as well as in calcite cement from fractures in the Bighorn Basin (Roberts et al., 2019).

Lower than expected values for Pb_{com} suggests that age values calculated using assumed Pb_{com} compositions from S.K model are inaccurate. Anchoring the upper intercept of the T-W diagram at the value close to the terrestrial lead model composition will lead to calculation of apparent ages older than formation ages. For this reason, a new approach to calculate the ages was used. A new value for the initial $^{208}\text{Pb}_{\text{com}}/^{206}\text{Pb}$ ratios was calculated by taking the mean $^{208}\text{Pb}_{\text{com}}/^{206}\text{Pb}$ ratios of points with high concentration of Pb_{com} . These Pb_{com} ratios were then used as an anchor to calculate the age of re-precipitated mineral (Fig.3.13.b.e). This approach was considered more robust, and is demonstrated by the fact that calculated ages for D_{RT4} dolomite are 20-40 Ma younger compare to the one calculated using ratio predicted by the Stacey and Kramers model. As an example, single data point ages for sample 133-2-136-137 of D_{RT4} dolomite calculated using assumed value of common Pb for $^{208}\text{Pb}_{\text{com}}/^{206}\text{Pb}$ ratio equal 2.06 ± 0.02 based on the Stacey and Kramers model indicate age of recrystallization in the range between 88.4 ± 7.0 and 80.4 ± 3.7 Ma. The ages for similar data point calculated using reset value for $^{208}\text{Pb}_{\text{com}}/^{206}\text{Pb}$ ratio equals 0.96 ± 0.05 suggest recrystallization in time interval between 66.1 ± 5.1 and 51.9 ± 8.8 Ma. As it can be seen, age calculation using reset value for $^{208}\text{Pb}_{\text{com}}/^{206}\text{Pb}$ ratios gives more accurate results and more precise dating.

On the example of sample 133-2-136-137 (Fig.3.17) we will explain the behaviour of radiogenic system during dolomite recrystallization. Assuming that primary dolomite precipitated at certain time T_0 in the past. This dolomite will contain certain amount of isotopes of U with initial ratio of radiogenic and common Pb equals to approximately 2.06 ± 0.020 . During certain period of time there will be decay of U and formation of daughter isotope of Pb. Graphically, this will give increase of U/Pb ration on the X-axis of the T-W diagram. Now, let's imagine that at some time T_1 dolomite was recrystallized. Assuming that recrystallization process happened via dissolution -reprecipitation process, it can be then

expected that dissolution of primary dolomite caused release of all isotopes of U and Pb into pore space. After reprecipitation of dolomite, the new crystal will then either gain (from pore waters) or lose (some amount of isotopes will be lost from pore space during dissolution process) some amount of isotopes of U and/or Pb. Such behaviour of radiogenic system is visible graphically on the example of sample 133-2-136-137 (Fig.3.17). Some data points show complete loss of U and gain of Pb_{com} . These data points are not datable. However, they show that the Pb ratio in newly formed mineral was no more equal to the one predicted by S.K model. On the other hand, we can observe data points with gain of U with low proportion of Pb. These are data the points which we were able to data using reset value for Pb ratio.

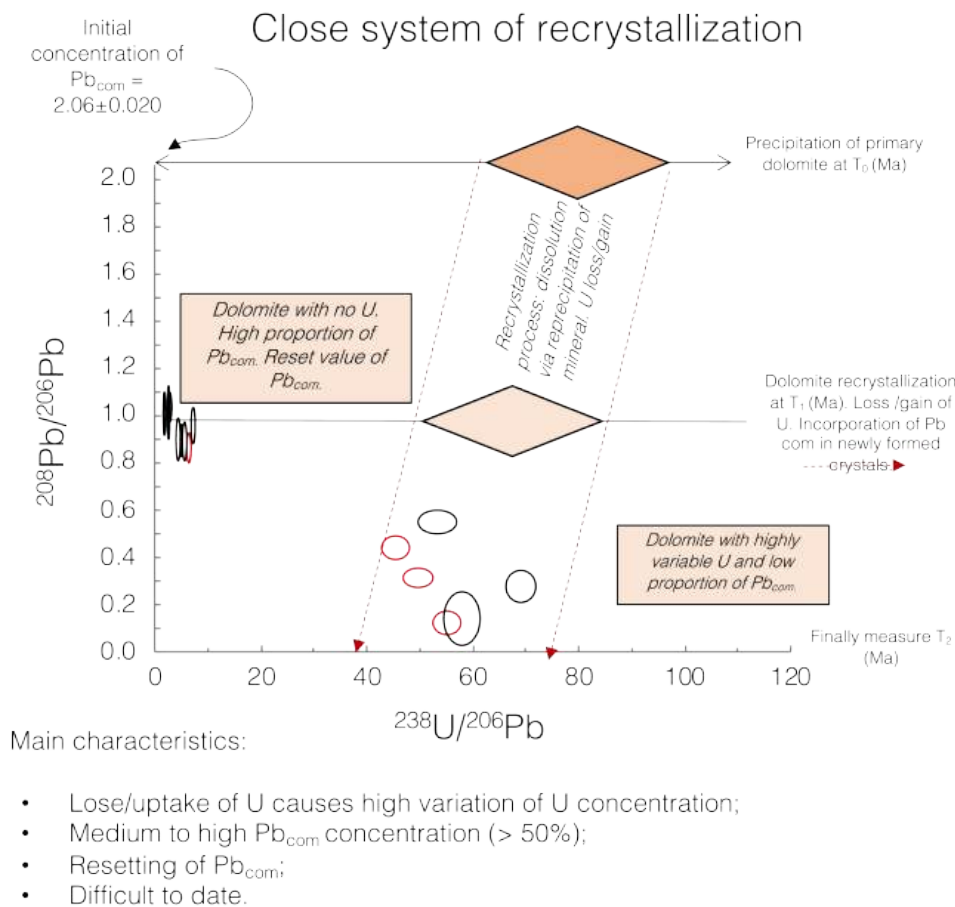


Figure 3.17. Diagram illustrating behaviour and main characteristics of radiogenic system during closed system recrystallization process explained on the example of the D_{RT4} dolomite (Sample 133-2136-137).

Expulsion of U from D_{RT4} could be also favoured by lose of Fe during recrystallization of process. Co-precipitation of U and Fe under different geochemical conditions was previously discussed by Murakami et al., 1997; Dabous, 2002; Pett-Ridge et al., 2007). Association of Fe with Uranium is explained by scavenging of U out of solution by Fe and its further immobilization (Nico et al., 2009; Stewart et al., 2009; Roberts et al., 2007). The studies of Luo and Gu (2011) and Eagling et al., (2013) demonstrated that the dissolution of Fe bearing

mineral phase can cause the release of U into porewaters. It was also demonstrated that Fe complexes overall tend to be more soluble in the presence of carbonate ligands (Byrne and Kester, 1976), as well as carbonate contributes to the mobilization of Fe (Bruno et al., 1991; Bruno et al., 1992; Grivé et al., 2014).

Furthermore, it is worth to discuss the dolomite cement D_{RT5} . The U-Pb ages for dolomite cement were received for filling vug dolomite from sample 161-1(a-b) (Fig.3.14). D_{RT5} is an example of highly radiogenic data with low proportion of common Pb. The scatter of data points along the X-axis ($^{238}\text{U}/^{206}\text{Pb}$) indicates variation in age of dolomite cement precipitation. Measured ages are in the range between 120.6 ± 7.2 Ma and 94.2 ± 7.0 Ma and they are overlap with ages for D_{RT2} - D_{RT3} dolomites. This observation is consistent with thin section and reconstructed paragenetic history of five dolomite types illustrated in Fig.3.15. However, measured U-Pb ages for D_{RT4} and D_{RT5} dolomites do not overlap. The discrepancy is likely explained by low amount of measured material: D_{RT5} dolomites was measured only in one sample, as well as low quality of radiogenic data of D_{RT4} dolomite. As a next step, U-Pb ages will be paired with clumped isotope temperatures to build a thermal history model.

3.5.5. Reconstruction of thermal history of Resolution Guyot dolomitization using clumped isotope and U-Pb methods.

After we established the age for all five dolomite types and constrained paragenetic history, it is logical to compare the measured clumped isotope temperatures with received U-Pb ages in order to assess the origin of D_{RT1-4} dolomites and support clumped isotope data. The assessment could be done by building the burial model using depths of recrystallization and clumped isotope temperatures.

A subsidence model was built in four steps. Step 1 includes building subsidence curve based on using the main parameters from Roh and Ogg (1996). The age estimates for stage boundaries and corresponding thickness of the Guyot were taken from Jenkyns et al., (1995). Step 2 includes choosing temperature-age samples pairs and calculation of depth of recrystallization. Only samples with clumped isotope and U-Pb dating data were used, as well as ages which correspond to data points with lowest level of common Pb were used (Table.3.9). At step 3 geothermal gradient was calculated (Table.3.10). At the final step 4 building thermal model was build using approximate variation of sea surface temperature within 30°C in Cretaceous time up to 28 °C at the present time. Linearly approximated temperature depth profile for equatorial Pacific Ocean (Levitus and Boyer, 1994) was used to calculate temperatures the top of the platform. The resulting model is presented in Figure.3.18.

The shipboard scientific party reported a measured geothermal gradient of 0.0057 °C /m but also that that it was likely underestimated due to presence of colder seawaters in the well during shipboard measurements (Winter and Sager, 1995). This is confirmed by clumped isotope data, which demonstrate a geothermal gradient of 0.0140 °C /m during platform growth, twice higher than the shipboard gradient. This value was calculated using maximum recrystallization depth for studied samples and corresponding clumped isotope temperature (Table.3.10).

The reconstructed subsidence model (Fig.3.18) demonstrates that D_{RT1} dolomite plots off the expected temperature of recrystallization for the stratigraphic datum at 127 Ma. According to the model, measured clumped isotope temperatures correspond to horizon of 121 Ma. This observation supports the interpretation that D_{RT1} that it is not a product of recrystallization, but likely was precipitated from seawaters internally heated by local geothermal gradient. This

would explain why clumped isotope temperatures are still hotter than expected sea surface temperatures, but still colder than expected burial temperatures.

Dolomites D_{RT2} and D_{RT3} have similar lithostratigraphic age to D_{RT1} dolomite and are expected to be plotted at horizon of 127 Ma. One of two data points for dolomite D_{RT2} plots within expected temperature for stratigraphic datum at 127 Ma proving the previous interpretation of its recrystallization origin. Second data points for D_{RT2} plots slightly off the 127 Ma horizon, but still within the error. The discrepancy may be explained by incomplete recrystallization of studied sample. Sample 161-1(a-b) exhibits minor presence of preserved limestone textures on thin section (Fig.3.6.c). The variation of recrystallization may be also explained by different porosity and permeability characteristics, as well chemical or crystallographic differences in the initial dolomite. In this case, incomplete recrystallization leads to minimum rather than actual temperatures of recrystallization. Sample with mixture of D_{RT3} and D_{RT2} dolomites D_{mix} exhibits much higher clumped isotope temperatures and are plotted way off expected age horizon. One of the possible explanation for hotter than burial temperatures for this data point may be dolomite precipitation from hydrothermal fluids. However, there is no evidence for presence of hydrothermal fluids from the geological description and previous studies do not support this theory (Winter, 1996).

Younger in age D_{RT4} dolomite was recrystallized at temperatures 10/20 degrees colder than D_{RT2-3} dolomites. Colder temperatures are explained by later stage of recrystallization of D_{RT4} dolomite. Drowning of platform caused decrease of temperature at the top of the platform. The results of clumped isotope and U-Pb ages for D_{RT4} dolomite are consistent with modelled values and plot within error with expected age horizon temperature for stratigraphic datum at 121 Ma.

As a final step, it will be usefully to summarise the diagenetic history of dolomites from Resolution Guyot based on U-Pb ages and coupled with thin section analysis and clumped isotope data. Graphically, the summary is presented in Figure.3.19. D_{RT1} occurred shortly after carbonate matrix precipitation. Calculated U-Pb data suggest that it was precipitated around 109.4 ± 5.3 Ma from geothermally heated seawaters with temperatures 38-39 °C. Based clumped isotope data coupled, U-Pb dating and supported by burial model it was concluded that D_{RT2} dolomite was recrystallized in time interval between 122.5 ± 6.9 and 87.1 ± 4.4 M

at temperatures in the range between 35-44°C. Clumped isotope data and thin section analysis suggest that D_{RT3} dolomite is also a product of recrystallization, however there is discrepancy between expected measured U-Pb age and expected burial temperature and clumped isotope temperature. It appears to be too hot. Recrystallization process continued up to 51.9 and 66.1 Ma with precipitation of Fe-free coarse grained D_{RT4} dolomite in at temperatures around 19-25 °C. Along with recrystallization there was continuous process of dolomite cementation D_{RT5} from 120.6 ± 7.0 up to 94.2 ± 7.0 Ma .

Table 3.9. Samples pairs and corresponding U-Pb ages, clumped isotope temperatures, chronostratigraphic and recrystallization depths.

Sample	Age of recrystallization (Ma)	T Δ 47, °C	Thickness of Guyot during time of recrystallization (m)	Lithostratigraphic depth, mbsf	Distance between sample and the basement, m	Recrystallization depth (mbsf)
<i>161-1 (a-b)</i>	119.25 ($\pm$ 4.15)	35 ($\pm$ 3)	713.66	1521.1	100.82	613
<i>165-2</i>	117.8 ($\pm$ 7.50)	53($\pm$ 1)	796	1561.79	60.13	736
<i>162-2 (a-b)</i>	111.55 ($\pm$ 1.75)	44($\pm$ 3)	1101.83	1533.1	88.82	1013
<i>168-4</i>	109.4 ($\pm$ 5.30)	39($\pm$ 4)	1194	1595.12	26.80	1167
<i>133-2-136-137-</i>	60.85 ($\pm$ 0.10)	20($\pm$ 2)	1622	1251.13	370.79	1251

Table 3.10. Geothermal gradients calculated using clumped isotope data and recrystallization depths.

Geothermal gradients	°C/m
Shipboard data (Winter and Sager, 1995)	0.0057
Geothermal gradient, °C/m	0.0140

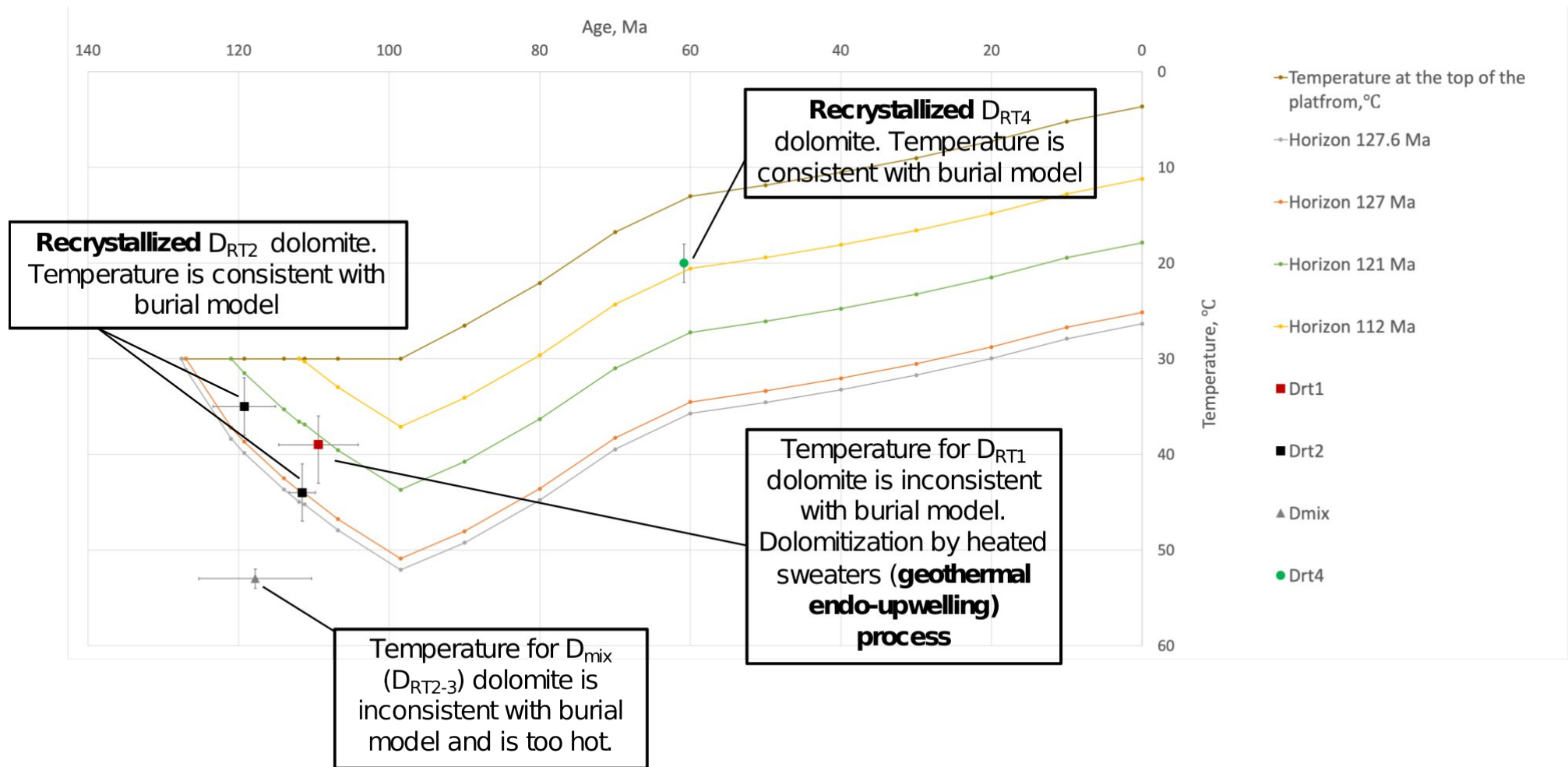


Figure 3.18. Subsidence model for Resolution Guyot.

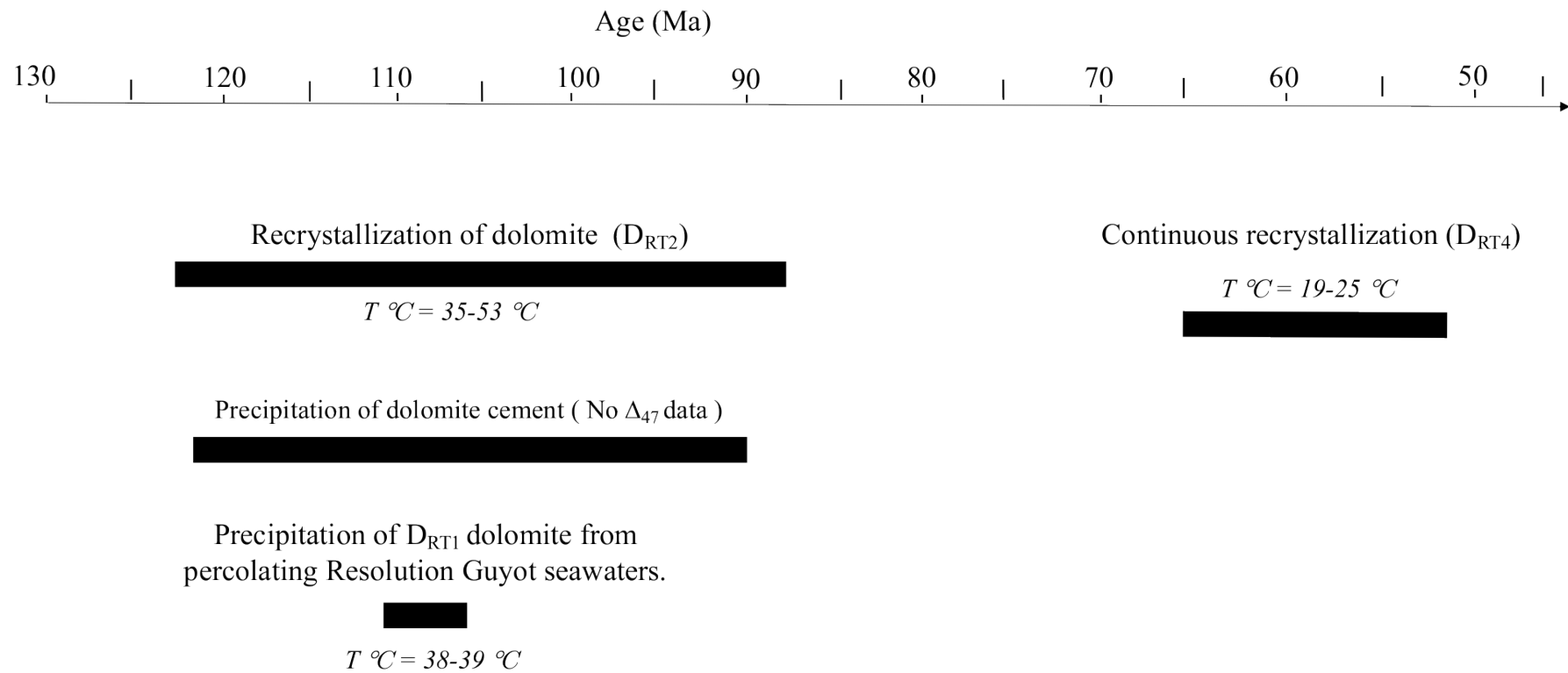


Figure 3.19. Summary of diagenetic history of dolomite minerals from Resolution Guyot. Interpretation is based on thin section, clumped isotope analyses and U-Pb data

Chapter 4: Thesis Outcomes and Conclusions

4.1. Conclusions

Clumped isotope paleo telethermometry is a useful tool for reconstruction of the environment of cementation of carbonate rocks (Huntingtoen et al. 2011; Dale et al. 2014; Vandeginste et al. 2014; MacDonald et al. 2017; Honlet et al. 2018). Understanding of temperatures of cementation and isotopic composition of cementing fluids allow predicting the petrographic characteristics of carbonate reservoir (Roehl and Choquette, 1985; Chilingarian et al. 1996; Moore and Wade, 2013). On the other hand, recent advances in U-Pb dating allow to date cement precipitation of carbonate rocks with high level of precision on a very small scale (Li et al. 2014; Lawson et al. 2017; Honlet et al. 2018; Mangenot et al. 2018., Parrish et al. 2018). Pairing these two methods allows constraining the temperature-time history of the sedimentary basin, which is essential not only to understand tectonic processes but also to predict porosity-permeability characteristics of carbonate reservoirs.

This study focuses on applying two methods of clumped isotope palaeothermometry and U-Pb dating to reconstruct the diagenetic history of carbonate rocks using examples of case study from Resolution Guyot (Pacific Ocean). The pairing of these two methods allows us to understand better the temporal and spatial resolution at which diagenetic processes can be reconstructed. The research also studies the behaviour of the U-Pb radiogenic system during carbonate cementation and recrystallisation (incorporation of initial Pb, loss and uptake of parent /daughter isotopes).

Finding 1: Pairing clumped isotope and U-Pb methods is an effective tool to reconstruct the diagenetic history of carbonate platforms

The Resolution Guyot was considered as a good case study due to its remote position, simple cementation history and gaps left in the interpretation of dolomitisation events (Flood and Chivas, 1995; Flood et al. 1996).

The age of cementation was successfully constrained using the U-Pb method and innovated approach in data processing. Dolomite samples were successfully dated with a high level of precision. The low common Pb concentration in some of the studied samples allowed calculating single data point ages (unique age) instead of regressed age (mean age). U-Pd dating proves to be

a more effective way to date carbonate cement compared to the Sr isotope method, which is based on comparing measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with a variation of Sr isotopes in seawater through time. The accuracy of the Sr isotope approach is questionable as there may be multiple sources of Sr in measured cement and not only seawater (for example, volcanic basement). Also, it is sometimes difficult to calculate the unique age of a data point. Furthermore, the Sr isotope approach is not effective to date recrystallisation minerals. Overall, pairing clumped isotope and U-Pb data proves to be an effective tool, especially in case one of the two methods does not work (for instance, samples are too small for clumped isotope analysis or do not contain enough Uranium for radiogenic dating).

Finding 2: The recrystallisation process mostly causes complete loss of radiogenic material with partial preservation of common Pb

The results for dolomite bodies (brown ($D_{\text{RT1-3}}$) and white dolomite((D_{RT4})) from the Resolution Guyot revealed the presence of recrystallisation event. The measured ages and core description suggested that white dolomite was most likely formed by recrystallisation of brown dolomite. The opening of the radiogenic system during recrystallisation caused almost complete loss of radiogenic material. Interestingly, the white dolomite showed an almost pure concentration of common Pb. A very high concentration of common Pb compared to a very low concentration of uranium allowed to study the behaviour of common Pb during the mineral recrystallisation process which is generally poorly understood. Received results and made observations have never been demonstrated before and indeed improve our understanding of the behaviour of the U-Pb system.

It was concluded that the recrystallisation process likely caused resetting of common Pb. The results for white dolomite samples (D_{RT4}) showed continues change in common lead composition. The new values of common Pb were then used to calculate the age of cement precipitation. The U-Pb data showed almost complete loss of radiogenic material during the recrystallisation process. However, it was noticed that common Pb remained preserved and reflected the concentration of common Pb at the moment of recrystallisation of the mineral.

Along with the more traditional approach of data processing using 7-6TW diagrams, the recently developed method for common Pb correction and age calculation using 8-6T-W diagrams (Parrish et al. 2018) were used in this study. This approach allowed to date samples with an initially high concentration of common Pb and low concentration of uranium. This method was applied to such

low-quality samples as white dolomite. Additionally, the recalculation of the initial concentration of common Pb for recrystallised samples allowed dating the time of the recrystallisation event with a higher level of precision. I believe that data points with such a high concentration of common Pb should not be neglected in the future and have to be used to constrain the age of mineral re-crystallization.

Finding 3: Pairing clumped isotope and U-Pb dating has its limitation

The ambiguity of pairing clumped isotope and U-Pb data to reconstruct the diagenesis of carbonate rocks was observed in the recrystallised cement of the white dolomite samples from Resolution Guyot, which were difficult to date. The opening of the radiogenic system during the recrystallisation process revealed mostly complete loss of radiogenic material, causing difficulty when attempting to extract the age. The paired approach, however, allowed to extract additional information using a clumped isotope palaeothermometry approach.

4.2. Future work

The results of the study successfully demonstrated that the pairing of these two methods is a useful tool to reconstruct the dolomitisation history of carbonate rock, however, the current work has also highlighted the gaps in knowledge which future studies can address through the following research topics:

Investigation of factors which control preservation and release of radiogenic material during the recrystallisation process within carbonate minerals.

Chapter 3 of this study was focused on dating brown dolomite precipitation and its further recrystallisation to white dolomite. The analysis of U-Pb data suggested that the recrystallisation process from dark brown dolomite into white dolomite caused the opening of the radiogenic system and almost complete loss of radiogenic material (mostly isotopes of uranium). Further work could focus on understanding the factors which control the incorporation of radiogenic material into the mineral structure of carbonate minerals (dolomite and calcite), as well as its loss during the recrystallisation process. The behaviour of uranium in marine conditions has been studied intensively for the past fifty years (Ku and Broecker, 1967; Krishnaswami and Turekian, 1982; Klinkhammer and Palmer, 1991; Morford et al. 2009). Additionally, the mobility of

uranium, its sorption capacity and uptake by carbonate mineral during precipitation process have been understood (Murakami et al. 1997; Reeder et al. 2000; 2001; Bernhard et al. 2001; Kelly et al. 2003). However, it would be interesting to understand how the presence of different chemical elements (Mg, Fe) or different chemical conditions of seawaters influence not only preservation but more importantly stability and release of uranium during the recrystallisation process of carbonate minerals. The change of colour of brown dolomite into white dolomite allowed to suggest that the recrystallisation process caused a loss of Fe. However, it remained unclear if the expulsion of Fe led to the expulsion of isotopes of uranium. Another factor which could also be taken into account is the pH and oxidation conditions of marine waters. The role of pH in the preservation of radiogenic material during carbonate mineral precipitation remains poorly understood. Although it was possible to find several studies related to this topic (Anderson, 1987; Barnes and Cochran, 1989; Eagling et al. 2013), they were mostly focused on synthetic calcite; no research was done on dolomite samples.

A better understanding of the behaviour of common lead during the mineral recrystallisation process

The recrystallisation process of brown dolomite into white dolomite caused re-setting of common Pb. Although the newly formed mineral of white dolomite contained a high concentration of common Pb, the common Pb concentration was no longer equal to the one suggested by Stacey and Kramers (1975). In this case, the reset value was calculated using the data points with the highest concentration of common Pb following Parrish et al. (2017). More work could be done to understand what factors control the preservation and re-setting of common lead during the recrystallisation process.

Application of clumped isotope and U-Pb dating methods to hydrocarbon-bearing carbonate rocks (reservoirs and source rocks)

Chapter 3 of this study proved that pairing clumped isotope and U-Pb dating may be successfully used to reconstruct the environment and time of dolomitisation events. The results of Chapter 5 also demonstrated that these both methods might be successfully applied to areas of more complex geology. The studied Morocco basin represents the buried carbonate platform with a complex tectonic history of multiple episodes of faulting. Unfortunately, both set of data may not be considered as a direct analogue of reservoir rocks. Further studies could test the application of

these two methods on hydrocarbon-bearing carbonate rocks (both reservoir and source rocks, e.g. Upper Cretaceous La Luna formation and Jurassic age Hanifa formation of Arabian basin). The recent study by Manguot et al. (2018) demonstrated that clumped isotope and U-Pb dating could be successfully applied to a carbonate sediments basin to reconstruct basin thermal and fluid-flow history. However, no work was done on carbonate source rocks. Overall, I believe the geological society, as well as the oil and gas industry, will benefit from more studies in this area.

References

- Affek, H. P. and Eiler, J. M. (2006) Abundance of mass 47 CO₂ in urban air, car exhaust, and human breath. *Geochimica Et Cosmochimica Acta*, 70(1), 1–12.
- Amthor, J.E and Friedman, G.M. (1991) Geochemistry and dolomite textures in the Ellenburger Group (Lower Ordovician), West Texas and southeastern New Mexico. *Sedimentology*, Volume 38, Issue 2, 343–362. <https://doi.org/10.1111/j.1365-3091.1991.tb01264.x>
- Anderson, H. and Jackson, J. (1987) Active tectonics of the Adriatic region. *Geophys. J. R. Astron. Soc.* 91, 937–983.
- Arnaud, H. M., Flood, P. G. and Strasser, A. (1995) Resolution Guyot (Hole 866, Mid-Pacific Mountains): Facies Evolution and Sequence Stratigraphy. *Geology*. DOI:10.2973/ODP.PROC.SR.143.230.1995
- Barnes C. E. and Cochran J. K. (1993) Uranium geochemistry in estuarine sediments: Controls on removal and release processes. *Geochim. Cosmochim. Acta.* 57, 555–569.
- Bernasconi S. M., Hu B., Wacker U., Fiebig J., Breitenbach S. F. M. and Rutz T. (2013) Background effects on Faraday collectors in gas-source mass spectrometry and implications for clumped isotope measurements. *Rapid Commun. Mass Spectrom.* 27, 603–612.
- Bernhard, G., Geipel, G., Reich, T., Brendler, V., Amayri, S. and Nitsche, H. (2001) Uranyl(VI) carbonate complex formation: Validation of the Ca₂UO₂(CO₃)₃(aq.) species. *Radiochimica Acta*, 89, 87–9. <http://doi.org/10.1524/ract.2001.89.8.511>
- Bidgoli and Navidtalab, (2020) Effects of progressive dolomitization on reservoir evolution: A case from the Permian–Triassic gas reservoirs of the Persian Gulf, offshore Iran. *Marine and Petroleum Geology*. 104480
- Bigeleisen, J., & Mayer, M. G. (1947). Calculation of equilibrium constants for isotopic exchange reactions. *The Journal of Chemical Physics*, 15(5), 261–267.
- Bigeleisen, J. (1955). Statistical mechanics of isotopic systems with small quantum corrections. I. General considerations and the rule of the geometric mean. *The Journal of Chemical Physics*, 23(12), 2264–2267.
- Bonifacie M., Calmels D., Eiler J. M., Horita J., Chaduteau C., Vasconcelos C., Agrinier P., Katz A., Passey B. H., Ferry J. M. and Bourrand J.-J. (2016) Calibration of the dolomite clumped isotope thermometer from 25 to 350 °C, and implications for a universal calibration for all (Ca, Mg, Fe)CO₃ carbonates. *Geochimica et Cosmochimica Acta*, 1– 53.
- Boggs, S. and Krinsley, D. (2006) Application of cathodoluminescence imaging to the Study of Sedimentary Rocks. 165 pp. Cambridge, New York, Melbourne: Cambridge University Press, 145(4). ISBN 9780 521 85878 6.

- Brand W. A., Assonov S. S. and Coplen T. B. (2010) Correction for the ^{17}O interference in $\delta^{13}\text{C}$ measurements when analyzing CO_2 with stable isotope mass spectrometry (IUPAC Technical Report). *Pure and Applied Chemistry*, 1719–1733.
- Brand W. A., Assonov S. S. and Coplen T. B. (2010) Correction for the ^{17}O interference in $\delta^{13}\text{C}$ measurements when analyzing CO_2 with stable isotope mass spectrometry (IUPAC Technical Report). *Pure and Applied Chemistry*.
- Brice J C. (1973) *The Growth of Crystals from Liquids*. New York: North- Holland Pub. Co..
- Lewis B. (1980) Nucleation and growth theory. *Crystal Growth*, 23-63
- Bruno, P and C. Chappert, C. (1991) Oscillatory coupling between ferromagnetic layers separated by a nonmagnetic metal spacer. *Phys. Rev. Lett.* 67, 1602. <https://doi.org/10.1103/PhysRevLett.67.1602>
- Bruno, P and C. Chappert. (1992) Ruderman-Kittel theory of oscillatory interlayer exchange coupling. *Phys. Rev. B* 46, 261. <https://doi.org/10.1103/PhysRevB.46.261>
- Budd, D.A. (1997) Cenozoic dolomites of carbonate islands: their attributes and origin. *Earth-Science Reviews*, 42(1–2), 1-4.
- Burchette, T. (2012). Carbonate rocks and petroleum reservoirs: A geological perspective from the industry. *Geological Society London Special Publications*, 370(1), 17–37. <http://doi.org/10.1144/SP370.14>
- Byrne, R.H. and Kester, R.K. (1976). A potentiometric study of ferric ion complexes in synthetic media and seawater. *Marine Chemistry* , 4(3), 275-287. [https://doi.org/10.1016/0304-4203\(76\)90013-X](https://doi.org/10.1016/0304-4203(76)90013-X)
- Chilingarian, C. V., Mazzulli, S. J. and Rieke, H. H. (1996). Carbonate reservoir characterization: A geologic-engineering analysis. part II. Elsevier.
- Coogan, L. A., Parrish, R. R. and Roberts, N. M. W. (2016) Early hydrothermal carbon uptake by the upper oceanic crust: Insight from in situ U–Pb dating. *Geology*, 44, 147–150.
- Cramer, B. S., Miller, K. G., Barrett, P. J. and Wright, J. D. (2011) Late Cretaceous–Neogene trends in deep ocean temperature and continental ice volume: Reconciling records of benthic foraminiferal geochemistry ($\delta^{18}\text{O}$ and Mg/Ca) with sea level history. *Journal of Geophysical Research*, 116(C12), C12023. <http://doi.org/10.1029/2011JC007255>
- Dabous, A. A. (2002) Uranium isotopic evidence for the origin of the Bahariya iron deposits, Egypt. *Ore Geology Reviews* 19(3), 165-186. [http://doi.org/10.1016/S0169-1368\(01\)00039-7](http://doi.org/10.1016/S0169-1368(01)00039-7)
- Dale, A. (2014). “Carbonate Clumped Isotopes: A New Tool to Assess Carbonate Cementation in Clastic Sediments”. PhD thesis.
- Davies, A. J. and John, C. M. (2018) The clumped ($^{13}\text{C}^{18}\text{O}$) isotope composition of echinoid calcite: Further evidence for “vital effects” in the clumped isotope proxy. *Geochimica Et Cosmochimica Acta*. 245, 172–189. <http://doi.org/10.1016/j.gca.2018.07.038>

Davies, A. J. (2018). “Vital effects” in the ^{13}C - ^{18}O clumped isotopic composition of marine macro-invertebrates: exploring biologically mediated disequilibrium effects in echinoids and cephalopods”. PhD thesis.

Debure, M., Andreazza, P., Canizarès, A., Grangeon, S., Lerouge, C., Mack, P., Madé, B., Simon, P., Veron, E., Warmont, F., and Vayer, M., (2017). Study of Iron-Bearing Dolomite Dissolution at Various Temperatures: Evidence for the Formation of Secondary Nanocrystalline Iron-Rich Phases on the Dolomite Surface. *ACS Earth and Space Chemistry* 1 (7), 442-454. DOI: 10.1021/acsearthspacechem.7b00073

Defliese, W. F., Hren, M. T. and Lohmann, K. C. (2015) Compositional and temperature effects of phosphoric acid fractionation on $\Delta 47$ analysis and implications for discrepant calibrations. *Chemical Geology*, 396(C), 51–60.
<http://doi.org/10.1016/j.chemgeo.2014.12.018>

Delaney, M. L. and Boyle, E. A. (1983) Uranium and thorium isotope concentrations in foraminiferal calcite. *Earth and Planetary Science Letters*, 62(2), 258–262.
[http://doi.org/10.1016/0012-821X\(83\)90088-2](http://doi.org/10.1016/0012-821X(83)90088-2)

Dennis, K. J. and Schrag, D. P. (2010). Clumped isotope thermometry of carbonatites as an indicator of diagenetic alteration. *Geochimica Et Cosmochimica Acta*, 74(14), 4110–4122.
<http://doi.org/10.1016/j.gca.2010.04.005>

Dennis, K. J., Affek, H. P., Passey, B. H., Schrag, D. P. and Eiler, J. M. (2011) Defining an absolute reference frame for “clumped” isotope studies of CO_2 . *Geochimica Et Cosmochimica Acta*, 75(22), 7117–7131. <http://doi.org/10.1016/j.gca.2011.09.025>

Dennis, K. J., Cochran, J. K., Landman, N. H. and Schrag, D. P. (2013) The climate of the Late Cretaceous New insights from the application of the carbonate clumped isotope thermometer to Western Interior Seaway macrofossil. *Earth and Planetary Science Letters*, 362, 51–65. <http://doi.org/10.1016/j.epsl.2012.11.036>

Denniston, R. F., Asmerom, Y., Polyak, V. Y., McNeill, D. F., Klaus, J. S., Cole, P. and Budd, A. F. (2008) Caribbean chronostratigraphy refined with U-Pb dating of a Miocene coral. *Geology*, 36(2), 151–5. <http://doi.org/10.1130/G24280A.1>

Dumitrescu, M., Brassell, S. C., Schouten, S., Hopmans, E. C., Sinninghe Damsté, J. S. (2006). Instability in tropical Pacific sea-surface temperatures during the early Aptian. *Geology*, 34, pp. 833-836.

Eagle, R. A., Schauble, E. A. and Tripathi, A. K. (2010) Body temperatures of modern and extinct vertebrates from ^{13}C - ^{18}O bond abundances in bioapatite. *Proc Natl Acad Sci U S A*, 107(23):10377-82. <http://doi.org/10.1073/pnas.0911115107>

Eagling, J., Worsfold, P. J., Blake, W. H. and Keith-Roach, M. J. (2013) Fate of Sr-90 and U(VI) in Dounreay sediments following saline inundation and erosion. *Chemosphere*, 92, 911–917.

Eiler, J. M. (2006) “Clumped” isotope geochemistry. *Geochimica Et Cosmochimica Acta*, 70(18), A156. <http://doi.org/10.1016/j.gca.2006.06.1379>

Eiler, J. M. (2007) “Clumped-isotope” geochemistry—The study of naturally-occurring, multiply-substituted isotopologues. *Earth and Planetary Science Letters*, 262(3–4), 309–327. <http://doi.org/10.1016/j.epsl.2007.08.020>

Eiler, J. M. and Schauble, E. (2004) $^{18}\text{O}^{13}\text{C}^{16}\text{O}$ in Earth’s atmosphere. *Geochimica Et Cosmochimica Acta*. 68(23), 4767–4777.

Engel, M. H. and Macko, S. A. (1993). *Organic Geochemistry. Principles and Application*. Springer Science and Business Media, LLC.

Epstein, E., Taylor, J.M., Chane, R.L. (1976) Effects of sewage sludge and sludge compost applied to soil on some soil physical and chemical properties. *Journal of Environmental Quality*, 5(4), 422-426. <http://doi.org/10.2134/jeq1976.00472425000500040021x>

Flood, P. G. and Chivas, A. R. (1995) Origin of Massive Dolomite, Leg 143, Hole 866. *Proceedings of the Ocean Drilling Program, Scientific Results*, 143. <http://doi.org/10.2973/odp.proc.sr.143.229.1995>

Flood, P. G., Fagerstrom, J. A. and Rougerie, F. (1996) Interpretation of the origin of massive replacive dolomite within atolls and submerged carbonate platforms: Strontium isotopic signature ODP Hole 866, Resolution Guyot, Mid-Pacific Mountains. *Sedimentary Geology*, 101(1-2), 9–13. [http://doi.org/10.1016/0037-0738\(95\)00098-4](http://doi.org/10.1016/0037-0738(95)00098-4)

Folk, R.L., (1962). Spectral subdivision of limestone types, *Amer. Assoc. Petrol. Geol. Mem.* 1, p. 62–84.

Gallagher K, Brown RW, Johnson C. (1998) Fission track analysis and its application to geological problems. *Annual Review of Earth and Planetary Science*, 26:519-572. *Planetary Science* 26: 519–572;

Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W., Schauble, E. A., et al. (2006) ^{13}C – ^{18}O bonds in carbonate minerals: A new kind of paleothermometer. *Geochimica et Cosmochimica Acta*, 70(6), 1439–1456. <http://doi.org/10.1016/j.gca.2005.11.014>

Goldstein, R. H. and Reynolds, T .J. (1994). *Systematics of Fluid Inclusions in Diagenetic Minerals*. SEPM Short Course. SEPM, Society for Sedimentary Geology. ISBN: 1-56576-008-5.

Grivé, M.; Duro, L.; Bruno, J. (2014). Fe(III) mobilisation by carbonate in low temperature environments: Study of the solubility of ferrihydrite in carbonate media and the formation of Fe(III) carbonate complexes. *Appl. Geochem.*, 49, 57– 67

Groot, P. A. (2009) *Handbook of stable isotope analytical techniques*. Elsevier.

Guo W., Daëron M., Niles P., Genty D., Kim S. T., Vonhof H., Affek H., Wainer K., Blamart D. and Eiler J. (2008) ^{13}C - ^{18}O bonds in dissolved inorganic carbon: Implications for carbonate clumped isotope thermometry. *Geochimica et Cosmochimica Acta* 72, A336–A336.

Haq, B. U. and Boersma, A. (1998). Introduction to Marine Micropaleontology. 2nd Edition. Elsevier B.V. <https://doi.org/10.1016/B978-0-444-82672-5.X5000-4>

He B., Olack, G. A. and Colman A. S. (2012) Pressure baseline correction and high-precision CO₂ clumped-isotope ($\Delta 47$) measurements in bellows and micro-volume modes. *Rapid Commun. Mass Spectrom.* 26, 2837–2853.

Henkes, G. A., Passey, B. H., Wanamaker, A. D., Jr, Grossman, E. L., Ambrose, W. G., Jr. and Carroll, M. L. (2013) Carbonate clumped isotope compositions of modern marine mollusk and brachiopod shells. *Geochimica Et Cosmochimica Acta*, 106(C), 307–325. <http://doi.org/10.1016/j.gca.2012.12.020>

Hess, H., Bender, M. L. and Schilling, J. G. (1986) Evolution of the Ratio of Strontium⁸⁷ to Strontium⁸⁶ in seawater from Cretaceous to present. *Science*, 231(4741), 979–984. <http://doi.org/10.1126/science.231.4741.979>

Hoffmann, D. L., Pike, A. W., García-Diez, M., Pettitt, P. B. and Zilhão, J. (2016). Methods for U-series dating of CaCO₃ crusts associated with Palaeolithic cave art and application to Iberian Sites. *Quaternary Geochronology*, 36, 104–119. <http://doi.org/10.1016/j.quageo.2016.07.004>

Honlet, R., Gasparrini, M., Muchez, P., Swennen, R. and John, C. M. (2018) New approach to geobarometry by combining fluid inclusion and clumped isotope thermometry in hydrothermal carbonates. *Terra Nova*, 30, 199–206, doi: <https://doi.org/10.1111/ter.12326>.

Horita J. (2014) Oxygen and carbon isotope fractionation in the system dolomite–water–CO₂ to elevated temperatures. *Geochimica Et Cosmochimica Acta*. 129, 111–124. <http://doi.org/10.1126/science.175.4023.795>

Honlet, R., Gasparrini, M., Muchez, P., Swennen, R. and John, C. M. (2018) New approach to geobarometry by combining fluid inclusion and clumped isotope thermometry in hydrothermal carbonates. *Terra Nova*, 30, 199–206, doi: <https://doi.org/10.1111/ter.12326>.

Huntington, K. W., Eiler, J. M. and Affek, H. P. (2009) Methods and limitations of “clumped” CO₂ isotope ($\Delta 47$) analysis by gas-source isotope ratio mass spectrometry. *Journal of Mass Spectrometry*, 44(9). <https://doi.org/10.1002/jms.1614>

Huntington K. W., Wernicke B. P. and Eiler J. M. (2010) Influence of climate change and uplift on Colorado Plateau paleotemperatures from carbonate clumped isotope thermometry. *Tectonics*, 29, n/a–n/a.

Huntington, K. W., Budd, D. A., Wernicke, B. P. and Eiler, J. M. (2011) Use of clumped-isotope thermometry to constrain the crystallization temperature of diagenetic calcite. *Journal of Sedimentary Research*, 81(9), 656–669. <http://doi.org/10.2110/jsr.2011.51>

Jenkyns, H. C. and Wilson, P. A. (1999) Stratigraphy, paleoceanography, and evolution of Cretaceous Pacific Guyots: Relics from a greenhouse Earth. *American Journal of Science*, 299, 341–392. <http://doi.org/10.2475/ajs.299.5.341>

Jenkyns, H. C., Paull, C. K. Cummins, D. I. (1995) Strontium-isotope stratigraphy of Lower Cretaceous atoll carbonates in the Mid-Pacific Mountains. *Proceedings of the Ocean Drilling Program, Scientific Results*, 143.

John, C. M. and Bowen, D. (2016) Community software for challenging isotope analysis: First applications of “Easotope” to clumped isotopes. *Rapid Communications in Mass Spectrometry*, 30(21), 2285–2300. <http://doi.org/10.1002/rcm.7720>

John, C. M. (2015) Burial estimates constrained by clumped isotope thermometry: Example of the lower Cretaceous Qishn Formation (Haushi-Huqf High, Oman). *Geological Society, London, Special Publications*, 435.

Kaczmarek S. E. and Sibley D. F. (2014) Direct physical evidence of dolomite recrystallization. *Sedimentology*, 61, 1862–1882.

Kaczmarek S. E. and Thornton B. P. (2017) The effect of temperature on stoichiometry, cation ordering, and reaction rate in high-temperature dolomitization experiments. *Chem. Geol.* 468, 32–41.

Kelly, S. D., Newville, M. G., Cheng, L., Kemner, K. M., Sutton, S. R., Fenter, P., Sturchio, N. C. and Spötl, C. (2003). Uranyl Incorporation in Natural Calcite. *Environ. Sci. Technol.* 37, 1284–1287. <http://doi.org/10.1021/es025962f>

Kim, S. T. and O'Neil, J. R. (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochimica Et Cosmochimica Acta*, 61(16), 3461–3475. [http://doi.org/10.1016/S0016-7037\(97\)00169-5](http://doi.org/10.1016/S0016-7037(97)00169-5)

Kirkpatrick M. (1981) Spatial and age dependent patterns of growth in New England black birch. *Am J Bot* 68:535–543. doi:10.2307/2443030

Klinkhammer, G. P. and Palmer, M. R. (1991) Uranium in the oceans: Where it goes and why. *Geochimica Et Cosmochimica Acta*, 55, 1799–1806. doi:10.1016/0016-7037(91)90024-Y

Krishnaswami S. and Turekian K. K. (1982) ²³⁸U, ²²⁶Ra and ²¹⁰Pb in some vent waters from the Galapagos Spreading Center. *Geophys. Res. Lett.* 9, 827–830.

Ku, T. and Broecker, W. (1967) Rates of sedimentation in the Arctic Ocean. *Progress in Oceanography*, 4, 95–104. [https://doi.org/10.1016/0079-6611\(65\)90043-1](https://doi.org/10.1016/0079-6611(65)90043-1)

Land, L. S. (1980) The isotopic and trace element geochemistry of dolomite: The state of the art. *SEPM Special Publication*, 28, 87–110.

Land, L. S. (1985) The Origin of Massive Dolomite: Summary and Suggestion. *Journal of Geological Education*, 33, 112–125. <http://dx.doi.org/10.5408/0022-1368-33.2.112>

Land, L. S. (1992) The quantum theory of dolomite stabilization: Does dolomite stabilize by ‘Ostwald steps’, Dolomite—from Process and Models to Porosity and Reservoirs. *National Conference of Earth Science, Banff, Alberta*.

- Lawson, M., et al. (2017) Deciphering the diagenetic history of the El Abra Formation of eastern Mexico using reordered clumped isotope temperatures and U-Pb dating. *Geological Society of America Bulletin*, 130, 617–629, <http://doi.org/10.1130/B31656.1>
- Levitus, S, and Boyer, T P. (1994) *World Ocean Atlas. Volume 4. Temperature*. United States: N. p., 1994. Web.
- Li, Q., Parrish, R. R., Horstwood, M. S. A. and McArthur, J. M. (2014) U–Pb dating of cement in Mesozoic ammonites. *Chemical Geology*, 376(C), 76–83. <http://doi.org/10.1016/j.chemgeo.2014.03.020>
- Li, QL, Li, XH, Liu, Y, Tang, GQ, Yang, JH & Zhu, WG.(2010). Precise U-Pb and Pb-Pb dating of Phanerozoic baddeleyite by SIMS with oxygen flooding technique', *Journal of Analytical Atomic Spectrometry*, vol. 25, no. 7, 1107-1113. <https://doi.org/10.1039/b923444f>
- Li, Q., Parrish, R.R., Horstwood, M.S.A. and McArthur, J.M. (2014). U–Pb dating of cements in Mesozoic ammonites. *Chemical Geology*, 376,76-83.
- Lohmann, K. C. (1988) Geochemical pattern of meteoric diagenetic systems and their application to the study of paleokarst. In: N.P. James and P.W. Choquette (Editors), *Paleokarst*. Springer-Verlag, New York, N.Y., 58–80.
- Ludwig, K. (2013) *Isoplot 4.13*. Berkeley Geochronology Centre Special Publication, 4.
- Luo, W and Gu,B (2011) Dissolution of Uranium-Bearing Minerals and Mobilization of Uranium by Organic Ligands in a Biologically Reduced Sediment. *Environ. Sci. Technol.* 2011, 45, 7, 2994–2999
- MacDonald, J. M., John, C. M. and Girard, J. P. (2017) Testing clumped isotopes as a reservoir characterization tool: A comparison with fluid inclusions in a dolomitized sedimentary carbonate reservoir buried to 2-4 km. *Geological Society, London, Special Publications*, 468, SP468. 7.
- Machel, H.G., Mason, R.A., Mariano, A.N. and Mucci, A. (1991) Causes and emission of luminescence in calcite and dolomite. *Luminescence Microscopy and Spectroscopy: Qualitative and Quantitative Applications*. SEPM Short Course, 25, 9–25.
- Machel, H. G. (1997) Recrystallization versus neomorphism, and the concept of ‘significant recrystallization’ in dolomite research. *Sedimentary Geology*, 113, 161–168.
- Machel, H. G., Mountjoy, E. W. and Amthor, J. E. (1993) Dolomitisation von devonischen Riff- und Plattformkarbonaten in West-Kanada. *Zentralblatt für Geologie und Paläontologie*, Teil I 7, 8.
- Machel H.G., (2005) *Investigations of Burial Diagenesis in Carbonate Hydrocarbon Reservoir Rocks*. *Geoscience Canada* 32, no. 3, 103–128.
- Mangenot, X., Gasparrini, M., Gerdes, A., Bonifacie, M. and Rouchon, V. (2018) An emerging thermochronometer for carbonate-bearing rocks: $\Delta 47$ (U-Pb). *Geology*, 46(12), 1067–1070. <http://doi.org/10.1130/G45196.1>

McCrea, J. M. (1950). On the Isotopic Chemistry of Carbonates and a Paleotemperature Scale. *J. Chem. Phys.* 18, 849. <https://doi.org/10.1063/1.1747785>

Merritt D. A. and Hayes J. M. (1994) Factors controlling precision and accuracy in isotope-ratio-monitoring mass spectrometry. *Anal. Chem.* 66, 2336–2347.

Methner, K., Mulch, A., Fiebig, J., Wacker, U., Gerdes, A., Graham, S. A. and Chamberlain, C. P. (2016) Rapid Middle Eocene temperature change in western North America. *Earth and Planetary Science Letters*, 450, 132–139, Elsevier.

Moore, C. H. and Wade, W. J. (2013) Carbonate Reservoirs - Porosity and Diagenesis. *Sequence*

Morford, J. L., Martin, W. R., Carney, C. M. (2009) Uranium diagenesis in sediments underlying bottom waters with high oxygen content. *Geochimica Et Cosmochimica Acta*, 73, 2920–2937. <http://doi.org/10.1016/j.gca.2009.02.014>

Murakami, T., Ohnuki, T., Isobe, H. and Sato, T. (1997) Mobility of uranium during weathering. *Am. Mineral*, 82(9), 888–899.

Nico, P. S., Stewart, B. D. and Fendorf, S. (2009) Incorporation of oxidized uranium into Fe (Hydr)oxides during Fe(II) catalyzed remineralization. *Environ. Sci. Technol.* 43, 7391–7396. <http://doi.org/10.1021/es900515q>

Nuriel, P., Weinberger, R., Kylander-Clark, A. R. C., Hacker, B. R. and Craddock, J. P. (2017) The onset of the Dead Sea transform based on calcite age-strain analyses. *Geology*, 45, 587–590, <http://doi.org/10.1130/G38903.1>

Ogg, J. G. (1996) Aptian–Albian sea level history from Guyots in the western Pacific. *Paleoceanography*, 11 (5), 513–648, <https://doi.org/10.1029/96PA01928>

Ozkan, A., & Dinç, S. (2011). Petrographic characteristics of the Hacialabaz formation dolomites (upper Jurassic) in the Bagbasi (Hadim-Konya/Turkey) area. *Ocean Journal of Applied Sciences* 4(3), 2011 ISSN 1943-2429

Pagel, M., et al. (2018) Improving paleohydrological and diagenetic reconstructions in calcite veins and breccia of a sedimentary basin by combining $\Delta 47$ temperature, $\delta 18\text{O}$ water and U-Pb age. *Chemical Geology*, 481, 1–17, <https://doi.org/10.1016/j.chemgeo.2017.12.026>

Palin, R.M., Searle, M.P., Waters, D.J., Parrish, R.R., Roberts, N.M.W., Horstwood, M.S.A., Yeh, M.W., Chung, S.L. and Anh, T.T. (2013) A geochronological and petrological study of anatectic paragneiss and associated granite dykes from the Day Nui C on Voi metamorphic core complex, North Vietnam: constraints on the timing of metamorphism within the Red River shear zone. *Journal of Metamorphic Geology*, 31, 359–387..

Parrish, R. R., Parrish, C. M. and Lasalle, S. (2017) Vein calcite dating reveals Pyrenean orogen as cause of Paleogene deformation in southern England. *Journal of the Geological Society*, 175(3), 425–442. <http://doi.org/10.1144/jgs2017-107>

Passey B.H. and Henkes G.A. (2012) Carbonate clumped isotope bond reordering and geospeedometry. *Earth and Planetary Science Letters* 351, 223–236.

Paton, C., Woodhead, J., Hellstrom, J., Hergt, J., Greig, A. and Maas, R. (2010) Improved laser ablation U–Pb zircon geochronology through robust downhole fractionation correction. *Geochemistry, Geophysics, Geosystems*, 11, <http://doi.org/10.1029/2009GC002618>

Paull, C. K., Fullagar, P., Bralower, T. J. and Röhl, U. (1995) Seawater ventilation of Mid-Pacific Guyots drilled during Leg 143. May 1995. *Proceedings of the Ocean Drilling Program: Scientific Results*, 143. <http://doi.org/10.2973/odp.proc.sr.143.222.1995>

Pett-Ridge, J. C., Monastera, V. M., Derry, L. A. and Chadwick, O. A. (2007) Importance of atmospheric inputs and Fe-oxides in controlling soil uranium budgets and behaviour along a Hawaiian Chronosequence. *Chemical Geology*, 244, 691–707. <http://doi.org/10.1016/j.chemgeo.2007.07.016>

Pike, A. W. G., Hoffmann, D. L., García-Diez, M., Pettitt, P. B., Alcolea, J., De Balbín, C., González-Sainz, Heras, C., J. Lasheras, J. A., Montes, R. and Zilhão, J. (2012). U-Series Dating of Paleolithic Art in 11 Caves in Spain. *Science*, 336(6087), 1409–1413. <http://doi.org/10.1126/science.1219957>

Polyakov, I. V., and Coauthors, (2005) One more step toward a warmer Arctic. *Geophys. Res. Lett.*, 32, L17605, doi:10.1029/2005GL023740.

Rasbury, E. T., Hanson, G. N., Meyers, W. J., Holt, W. E., Goldstein, R. H. and Saller, A. H. (1998) U-Pb dates of paleosols: Constraints on late Paleozoic cycle durations and boundary ages. *Geology*, 26(5), 403. [http://doi.org/10.1130/0091-7613\(1998\)026<0403:UPDOPC>2.3.CO;2](http://doi.org/10.1130/0091-7613(1998)026<0403:UPDOPC>2.3.CO;2)

Rasbury, E. T. and Cole, J. M. (2009) Directly dating geologic events: U-Pb dating of carbonates. *Reviews of Geophysics*, 47(3), RG3001–27. <http://doi.org/10.1029/2007RG000246>

Regis, D., Warren, C.J., Mottram, C.M. and Roberts, N.M.W. (2016). Using monazite and zircon petrochronology to constrain the P–T–t evolution of the middle crust in the Bhutan Himalaya. *Journal of Metamorphic Geology*, 34, 617–639.

Reeder, R. J., Nugent, M., Lamble, G. M., Tait, C. D. and Morris, D. E. (2000) Uranyl incorporation into calcite and aragonite: XAFS and luminescence studies. *Environ. Sci. Technol.*, 34, 638–644. <http://doi.org/10.1021/es990981j>

Reeder, R. J., Nugent, M., Tait, C. D., Morris, D. E., Heald, S. M., Beck, K. M., Hess, W. P. and Lanzirotti, A. (2001) Coprecipitation of uranium (VI) with calcite: XAFS, micro-XAS, and luminescence characterization. *Geochimica Et Cosmochimica Acta*. 65, 3491–3503.

F. Renard, C.V. Putnis, G. Montes-Hernandez, H.E. King (2017) Siderite dissolution coupled to iron oxyhydroxide precipitation in the presence of arsenic revealed by nanoscale imaging. *Chemical Geology*, 449, pp. 123–134.

- Richards, D. A., Bottrell, S. H., Cliff, R. A., Strohle, K. and Rowe, P. J. (1998) U–Pb dating of a speleothem of Quaternary age. *Geochimica Et Cosmochimica Acta*. 62, 3683–3688.
- Roberts, N. M. W. and Walker, R. J. (2016) U–Pb geochronology of calcite-mineralized faults: Absolute timing of rift-related fault events on the northeast Atlantic margin. *Geology*, 44, 531–534, <https://doi.org/10.1130/G37868>
- Roberts, N. M. W., Rasbury, E. T., Parrish, R. R., Smith, C. J., Horstwood, M. S. A. and Condon, D. J. (2017) A calcite reference material for LA-ICP-MS U-Pb geochronology. *Geochemistry, Geophysics, Geosystems*, 18(7), 2807–2814. <http://doi.org/10.1002/2016GC006784>
- Roberts, N., Drost, K., Horstwood, M., Condon, D., et al., (2019) LA-ICP-MS U-Pb carbonate geochronology: strategies, progress, and application to fracture-fill calcite. 10.5194/gchron-2019-15.
- Roehl, P. O. and Choquette, P. W. (1985) *Carbonate Petroleum Reservoirs*. 622 pp. Berlin, Heidelberg, New York, Tokyo. Springer. <https://doi.org/10.1017/S0016756800024365>
- Röhl, U. and Ogg, J. G. (2010) Aptian–Albian sea level history from Guyots in the western
- Röhl, Ursula; Ogg, James G. (1996). "Aptian-Albian sea level history from Guyots in the western Pacific". *Paleoceanography*. 11 (5): 595–624. Bibcode:1996PalOc..11..595R. doi:10.1029/96pa01928. ISSN 0883-8305.
- Rosenbaum J. and Sheppard S. M. F. (1986) An isotopic study of siderites, dolomites and ankerites at high temperatures. *Geochimica Et Cosmochimica Acta*. 50, 1147–1150.
- Sager, W.W., Winterer, E.L., Firth, J.V., et al., (1993) *Proc. ODP, Init. Repts.*, 143: College Station, TX (Ocean Drilling Program). doi:10.2973/odp.proc.ir.143.1993
- Schauble, E. A., Ghosh, P. and Eiler, J. M. (2006) Preferential formation of ^{13}C – ^{18}O bonds in carbonate minerals, estimated using first-principles lattice dynamics. *Geochimica Et Cosmochimica Acta*. 70(10), 2510–2529. <http://doi.org/10.1016/j.gca.2006.02.011>
- Sena, C. M., John, C. M., Jourdan, A. L., Vandeginste, V. and Manning, C. (2014) Dolomitization of lower Cretaceous peritidal carbonates by modified seawater constrained from clumped isotopic paleothermometry, elemental chemistry, and strontium isotopes. *Journal of Sedimentary Research*, 84, 552–566.
- Sibley, D. F., (1980) Climatic control of dolomitization, Seroe Domi Formation (Pliocene), Bonaire, N. A., in Zenger, D. H., Dunham, J. B., and Ethington, R. L., eds., *Concepts and Models of Dolomitization: Soc. Econ. Paleontologists Mineralogists Spec. Pub.* 28, 247-258.
- Sibley, D.F (1982). The origin of common dolomite fabrics: clues from the Pliocene. *Journal of Sedimentary Petrology*, vol 52 (4), 1087-1100.
- Sibley, D.F, Gregg, J.M. (1987). Classification of dolomite rock textures. *Journal of sedimentary petrology*, vol.57(6), 967-975.

Sijing, H., Huang, K., jie, L., Yefang, L. (2014) The relationship between dolomite textures and their formation temperature: a case study from the Permian-Triassic of the Sichuan Basin and the Lower Paleozoic of the Tarim Basin. *Pet.Sci*, 11, 39-51. DOI 10.1007/s12182-014-0316-7

Smalley, P. C., Higgins, A. C., Howarth, R. J., Nicholson, H., Jones, C. E., Swinburne, N. H. M. and Bessa, J. (1994) Seawater Sr isotope variations through time: A procedure for constructing a reference curve to date and correlate marine sedimentary rocks. *Geology*, 22(5), 431–434. [http://doi.org/10.1130/0091-7613\(1994\)022<0431:SSIVTT>2.3.CO;2](http://doi.org/10.1130/0091-7613(1994)022<0431:SSIVTT>2.3.CO;2)

Smith, P. E., Farquhar, R. M. and Hancock, R. G. (1991) Direct radiometric age determination of carbonate diagenesis using U-Pb in secondary calcite. *Earth and Planetary Science Letters*, 105(4), 474–491. [http://doi.org/10.1016/0012-821X\(91\)90186-L](http://doi.org/10.1016/0012-821X(91)90186-L)

Stacey, J. S. and Kramers, J. D. (1975) Approximation of terrestrial lead isotope evolution by a 2-stage model. *Earth and Planetary Science Letters*, 26, 207–221.

Stewart, B. D., Nico, P. S. and Fendorf, S. (2009) Stability of uranium incorporated into Fe (Hydr)oxides under fluctuating redox conditions. *Environ. Sci. Technol*, 43, 4922–4927. <http://doi.org/110.1021/es803317w>

Stübner, K., Grujic, D., Parrish, R.R., Roberts, N.M., Kronz, A., Wooden, J. and Ahmad, T (2014). Monazite geochronology unravels the timing of crustal thickening in NW Himalaya. *Lithos*, 210, 111-128.

Sweeney, J. J. and Burnham, A. K. (1990) Evaluation of a simple model of vitrinite reflectance based on chemical kinetics. *American Association of Petroleum Geologist Bulletin*, 74, 1559–1570.

Tera, F. and Wasserburg, G. (1972) U-Th-Pb systematics in 3 Apollo 14 basalts and the problem of initial Pb in lunar rocks. *Earth and Planetary Science Letters*, 14, 281–304, [https://doi.org/10.1016/0012-821X\(72\)90128-8](https://doi.org/10.1016/0012-821X(72)90128-8)

Thermo Fisher Scientific, Waltman, MA .(2002) Thermo Finningan DELTA^{plus} XP Operating Manual. Iden. No. 114 90 80, Issue 06/2002.

Thiagarajan, N., Adkins, J. and Eiler, J. (2011) Carbonate clumped isotope thermometry of deep-sea corals and implications for vital effects. *Geochimica Et Cosmochimica Acta*, 75(16), 4416–4425. <http://doi.org/10.1016/j.gca.2011.05.004>

Urey, H. C. (1947). The thermodynamic properties of isotopic substances. *Journal of the Chemical Society*

Vandeginste, V., John, C. M., Cosgrove, J. W. and Manning, C. (2014) Dimensions, texture-distribution, and geochemical heterogeneities of fracture-related dolomite geobodies hosted in Ediacarian limestones, northern Oman. *AAPG Bulletin*, 98, no. 9 , 1789–1809.

Veillard, C. J., John, C. M., Krevor, S. and Najorka, J. (2019) Rock-buffered recrystallization of Marion Plateau dolomites at low temperature evidenced by clumped isotope thermometry

and X-Ray diffraction analysis, *Geochimica Et Cosmochimica Acta*, 252, 190-212.
<https://doi.org/10.1016/j.gca.2019.02.012>.

Wacker U., Fiebig J. and Schoene, B. R. (2013) Clumped isotope analysis of carbonates: Comparison of two different acid digestion techniques. *Rapid Commun. Mass Spectrom*, 27, 1631–1642.

Wang, Z., Schauble, E. A. and Eiler, J. M. (2004) Equilibrium thermodynamics of multiply substituted isotopologues of molecular gases. *Geochimica Et Cosmochimica Acta*, 68(23), 4779–4797. <http://doi.org/10.1016/j.gca.2004.05.039>

Wang Z., Schauble E. A. and Eiler J. M. (2004) Equilibrium thermodynamics of multiply substituted isotopologues of molecular gases. *Geochimica et Cosmochimica Acta* 68, 4779–4797

Warren, C.J., Singh, A.K., Roberts, N.M.W., Regis, D., Halton, A.M. and Singh, R.B. (2014) Timing and conditions of peak metamorphism and cooling across the Zimithang Thrust, Arunachal Pradesh, India. *Lithos*, 200, 94-110,

Warren, J., (2000) Dolomite: occurrence, evolution and economically important associations. *Earth-Science Reviews*. 2000. 52(1-3): 1-81.

Swart P. K., Burns S. J. and Leder J. J. (1991) Fractionation of the stable isotopes of oxygen and carbon in carbon dioxide during the reaction of calcite with phosphoric acid as a function of temperature and technique. *Chemical Geology (Isotope Geoscience Section)*.

Winterer, E. L. and Sager, W. W. (May 1995) Synthesis of Drilling Results from the Mid-Pacific Mountains: Regional Context and Implications. *Proceedings of the Ocean Drilling Program*, 143 doi:10.2973/odp.proc.sr.143.245.1995. Retrieved 2018-09-30.

Winterer, E.L.; Sager, W.W. (1995). Synthesis of Drilling Results from the Mid-Pacific Mountains: Regional Context and Implications. *Proceedings of the Ocean Drilling Program*, 143 Scientific Results. *Proceedings of the Ocean Drilling Program*. 143. Ocean Drilling Program. doi:10.2973/odp.proc.sr.143.245.1995.

Woodhead, J., Hellstrom, J., Maas, R., Drysdale, R., Zanchetta, G., Devine, P. and Taylor, E. (2006) U–Pb geochronology of speleothems by MC-ICPMS. *Quaternary Geochronology*, 1, 208-221.

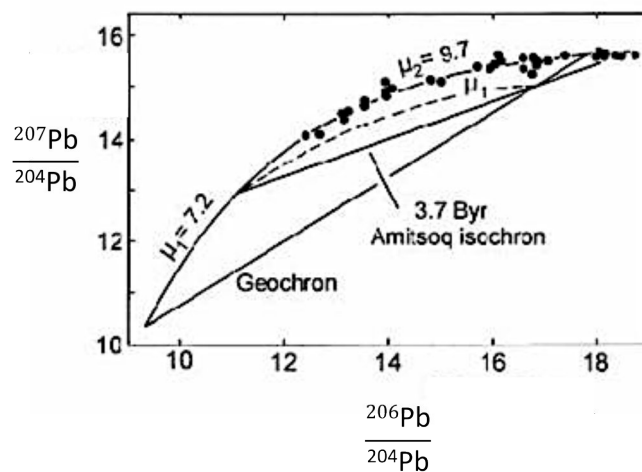
Zyakun, A. M., Schidlowski, M. (2003) Determination of ¹⁶O and ¹⁸O abundance ratios in natural carbon dioxide reservoirs. *International Journal of Mass Spectrometry* 203 (1-3):83-92.DOI: 10.1016/S1387-3806(00)00285-2

Additional material

Chapter 2

APPENDIX 2.1. Stacey and Kramers' model and estimation of common Pb ratio values

The galena mineral study by Stacy and Kramers (1975) measured the natural abundance of isotopes of Pb (206, 207 and 208), and their evolution through time on earth is illustrated in Figure 1 below. It was noticed that at this time point in earth history (around 3.7Ga), the ratio of leads abruptly changed. For this reason, it was decided to name the lead ratios before this data point as primordial and after the change as 3.7 Ga lead (Table 1).



Appendix 2.1. Figure 1. Stacey and Kramers' model illustrating the evolution of isotopes of lead on earth in time (Stacey and Kramers, 1975).

Using decay constant (λ) for isotopes of uranium (238, 235 and 232) and known ratios of isotopes of Pb, we can calculate the expected natural abundance of isotopes of lead at a specific time (Table 1). The assumed lead ratios are then used to correct the received data for common lead and calculate single data point ages. In this research, I used the ratios calculated for a time step of 100 Ma, which may be considered relevant as it is proximal to the age of the rock matrix of the core (132.9 Ma – 110 Ma).

The lead ratios are calculated using the following equations:

$$\frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} = \frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} \text{ at 3.7 Ga} + \frac{{}^{238}\text{U}}{{}^{204}\text{Pb}} (e^{\lambda_{238} \times 3.7 \times 10^9} - e^{\lambda_{238} \times 100 \times 10^6})$$

$$\frac{{}^{207}\text{Pb}}{{}^{204}\text{Pb}} = \frac{{}^{207}\text{Pb}}{{}^{204}\text{Pb}} \text{ at 3.7 Ga} + \frac{{}^{235}\text{U}}{{}^{204}\text{Pb}} (e^{\lambda_{235} \times 3.7 \times 10^9} - e^{\lambda_{235} \times 100 \times 10^6})$$

$$\frac{{}^{208}\text{Pb}}{{}^{204}\text{Pb}} = \frac{{}^{208}\text{Pb}}{{}^{204}\text{Pb}} \text{ at 3.7 Ga} + \frac{{}^{232}\text{U}}{{}^{204}\text{Pb}} (e^{\lambda_{232} \times 3.7 \times 10^9} - e^{\lambda_{232} \times 100 \times 10^6})$$

These calculated ratios are then used to calculate ${}^{208}\text{Pb}/{}^{206}\text{Pb}$, ${}^{207}\text{Pb}/{}^{206}\text{Pb}$, ${}^{206}\text{Pb}/{}^{208}\text{Pb}$, and ${}^{207}\text{Pb}/{}^{208}\text{Pb}$ ratios.

${}^{206}\text{Pb}/{}^{204}\text{Pb}$, ${}^{207}\text{Pb}/{}^{204}\text{Pb}$, and ${}^{208}\text{Pb}/{}^{204}\text{Pb}$ at 3.7 Ga are calculated similarly for the time period from 4.567 to 3.7 Ga.

Table 1.1. Stacey and Kramers' calculation of lead ratios

238U/235U	137.818	Primordial Pb				3.7 Ga Pb	
λ238	1.55125E-10	6/4	9.307	6/4	11.152		
λ235	9.9498E-10	7/4	10.294	7/4	12.998		
λ232	4.94E-11	8/4	29.487	8/4	31.23		
T_{earth}	4.57E+09	238/204	7.19	238/204	9.74		
		235/204	0.0522	235/204	0.0707		
		232/204	33.21	232/204	36.84		
From 4.567 to 3.7 Ga							
Age T (Ma)	6/4	7/4	8/4	8/6	7/6		
3700	657495546.555	12.998	12.998	0.000	0.000		
From 3.7 Ga to present							
Age t (Ma)	6/4	7/4	8/4	8/6	7/6	6/8	7/8
100	18.55	15.73	38.44	2.062	0.848	0.483	0.409

APPENDIX 2.2. LA-ICP-MS operating conditions

Table 1 was modified using an example from Parrish et al. (2017).

Table 1. LA-ICP-MS operating conditions

Laboratory & Sample Preparation	
Laboratory name	School of Earth and Environmental Sciences at the University of Portsmouth
Sample type/mineral	Calcite and dolomite samples
Sample preparation	Fragments of calcite and dolomite crystals of 2-3 mm in size, mounted in epoxy, polished
Imaging	Reflected light images
Laser ablation system	
Make, Model & type	ASI RESOlution SE ArF (Argon-Fluoride)
Ablation cell & volume	Laurin S155 (dual volume design)
Laser wavelength (nm)	193 nm
Pulse width (ns)	3 ns
Fluence (J.cm ⁻²)	3-4 J.cm ⁻²
Repetition rate (Hz)	8 Hz
Gas blank (s)	20 s
Ablation duration (s)	30 s
Washout and/or travel time in between analyses (s)	15 s
Spot diameter (µm)	80µm -100µm
Sampling mode/pattern	Static spot ablation
Cell Carrier gas (L/min)	He = 0.300 L/min, N2 = 0.003 L/min
ICP-MS Instrument	
Make, Model & type	PlasmaQuant MS Elite (quadrupole) from Analytik Jena
Sample introduction	Ablation aerosol
RF power (W)	1300W
Carrier gas (L/min)	Ar = 0.87 L/min
Masses measured	204, 206, 207, 208, 232, 235, 238

Integration time per peak/dwell times (ms); quadrupole settling time between mass jumps	10ms (204, 208, 232, 235, 238)
	20ms (206)
	30ms (207)
Scanning mode	Peak hopping
Acquisition mode	time-resolved analysis
Data Processing	
Calibration strategy	NIST612 used as primary reference material for downhole corrections, mass fractionation for Pb, and U-Pb drift correction and U-Pb initial normalisation; WC-1 was used for final U-Pb calibration
Reference Material info	NIST612 glass and 254±7 WC-1 for final Pb/U calibration
	Mud Tank zircon, 732 Ma
Data processing package used / Correction for LIEF	IOLITE 3.4 software, using the 'Linear spline' to correct for downhole fractionation and the 'Automatic spline' to correct for instrumental drift
Common-Pb correction, composition and uncertainty	Using a bespoke Excel spreadsheet as described in the text using both ^{207}Pb and ^{208}Pb methods
Quality control/Validation	Measurements of WC-1, Mud Tank zircon and NIST 614 were done along with samples throughout all analytical sessions; this data is presented in supplemental Appendix 3.2, Table 2.

APPENDIX 2.3. Additional Notes and Computational Formulas

Proximate age (T) is calculated using the following equations:

$$\text{Projected T-W age } ^{206}\text{Pb}/^{238}\text{U} \left[\frac{\left(\frac{^{207}\text{Pb}}{^{206}\text{Pb}} \text{ predicted} - \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \text{ S.K.} \right)}{\left(\frac{^{207}\text{Pb}}{^{206}\text{Pb}} \text{ S.K.} - \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \text{ total} \right) / \frac{^{238}\text{U}}{^{206}\text{Pb}} \text{ total}} \right]$$

$$\frac{^{207}\text{Pb}}{^{206}\text{Pb}} \text{ predicted} = \frac{^{235}\text{U}}{^{238}\text{U}} \times \frac{[(\exp \lambda_{235} \times t \times 10^9) - 1]}{[(\exp \lambda_{238} \times t \times 10^9) - 1]}$$

(Equation 2.1)

$$t = \text{T-W age } ^{206}\text{Pb}/^{238}\text{U} \frac{\frac{^{207}\text{Pb}}{^{206}\text{Pb}} \text{ S.K.} - \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \text{ total}}{\frac{^{207}\text{Pb}}{^{206}\text{Pb}} \text{ S.K.} \times \frac{^{238}\text{U}}{^{206}\text{Pb}} \text{ total}}$$

(Equation 2.2)

S.K refers to the Stacey-Kramers model composition for common Pb of approximately 100 Ma old (Appendix 2.1).

The uncertainty is calculated by the following equation:

$$2\sigma (\text{Projected T-W age } ^{206}\text{Pb}/^{238}\text{U}) = 0.9 \times 0.5 \times 1 \div \left\{ \left(\text{Pb}_r \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \text{ S.K.} \right) \div \left\{ \frac{\frac{^{207}\text{Pb}}{^{206}\text{Pb}} \text{ S.K.} - \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \text{ total} \times 1 - \left[\frac{2\sigma \left(\frac{^{207}\text{Pb}}{^{206}\text{Pb}} \text{ total} \right)}{\frac{^{207}\text{Pb}}{^{206}\text{Pb}} \text{ total}} \right]}{0 - \frac{^{238}\text{U}}{^{206}\text{Pb}} \text{ total} \times \left[1 - \frac{^{238}\text{U}}{^{206}\text{Pb}} \text{ total} \left(\frac{\sqrt{2\sigma \left(\frac{^{206}\text{Pb}}{^{238}\text{U}} \right)^2 + \left(\frac{^{206}\text{Pb}}{^{238}\text{U}} \text{ total} \times \frac{\text{prop. } 2\sigma (WC-1)}{251}} \right)^2}{\frac{^{238}\text{U}}{^{206}\text{Pb}} \text{ total}} \right)} \right]} \right\} \right\} \quad (\text{Equation 2.3})$$

λ^{238} and λ^{235} are decay constants of ^{238}U and ^{235}U . λ^{238} equals 1.55×10^{-10} . λ^{235} equals 9.95×10^{-10} . The ratio $^{207}\text{Pb}/^{206}\text{Pb}_{\text{S.K}}$ is the lead ratio predicted by Stacey and Kramers' (1975) model equals 0.848 (Appendix 2.1. Table 1). The ratio $^{207}\text{Pb}/^{206}\text{Pb}_{\text{total}}$ is used directly from the Iolite spreadsheet with prior correction of ^{207}Pb signal for mass-bias effect. ^{207}Pb is adjusted for mass-bias using NIST612 standard. ^{206}Pb is used directly from the Iolite spreadsheet. No correction is applied. Error is taken directly from the Iolite program and equals 2SE for final counts of $^{207}\text{Pb}/^{206}\text{Pb}$ ratio. The ratio of $^{238}\text{U}/^{206}\text{Pb}_{\text{total}}$ is taken from the Iolite programme and corrected for Pb isotope fractionation correction factor using NIST612 standard measured along with the sample measurements. The uncertainty is presented as 2SE of the measured ratio of $^{238}\text{U}/^{206}\text{Pb}_{\text{total}}$, including uncertainties of NIST612 and WC-1 measurements.

Chapter 3

APPENDIX 3.1. Detailed results of clumped isotope and U-Pb measurements for dolomite samples, Resolution Guyot.

Table.1. Results of U-Pb measurements for dolomite samples

Sample Information	Counts sec ⁻¹ concentrations								Corrected ratios							Comm on Pb	Common Pb- corrected ratios and ages					
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ Pb _C / ²⁰⁶ Pb	2s	Projected T-W age corrected via 207 for Pbc		²⁰⁸ Pb _C -cor ²⁰⁶ Pb- ²³⁸ U		²⁰⁸ Pb _C -cor Age			
						ppm									(Ma)		2s	ratio	2s	(Ma)	2s	
DRT1 dolomite																						
Sample 168-4-125-130																						
168-4-125-130-spot-1	3310	1013	2196	132373	754	0.170	5.13	0.032	40.0	2.4	0.256	0.019	0.662	0.153	0.320	118	9.9	0.0170	0.0019	108.7	12.1	
168-4-125-130-spot-2	911	59	38	49047	239	0.003	1.95	0.010	53.8	2.7	0.066	0.010	0.040	-0.061	0.019	116	6.5	0.0182	0.0009	116.4	5.9	
168-4-125-130-spot-3	1051	126	186	54949	186	0.015	2.19	0.008	52.3	3.5	0.130	0.018	0.176	0.088	0.085	110	9.1	0.0175	0.0013	111.9	8.5	
168-4-125-130-spot-4	941	108	154	47880	167	0.012	1.93	0.007	50.9	3.4	0.117	0.020	0.162	0.082	0.078	115	9.6	0.0181	0.0013	115.7	8.5	
168-4-125-130-spot-5	883	140	239	47294	229	0.019	1.90	0.010	53.6	2.7	0.169	0.016	0.269	0.058	0.130	101	6.8	0.0162	0.0010	103.9	6.3	
168-4-125-130-spot-6	1076	100	129	62033	218	0.010	2.49	0.009	57.7	2.8	0.100	0.011	0.119	0.069	0.057	104	5.9	0.0164	0.0009	104.6	5.5	
168-4-125-130-spot-7	1205	114	124	68808	229	0.010	2.79	0.010	57.1	2.7	0.097	0.011	0.102	0.099	0.049	105	5.9	0.0167	0.0009	106.5	5.4	
DRT2 dolomite																						
Sample 161-1 (a-b)																						
161-1-a-sport-1-dark brown	787	81	95	40757	165	0.007	1.62	0.007	51.8	3.0	0.106	0.015	0.087	0.282	0.058	114	7.9	0.0182	0.0011	116.3	7.1	
161-1-a-sport-2-dark brown	600	42	23	31810	90	0.002	1.24	0.004	53.0	3.0	0.080	0.016	-0.041	0.208	0.018	116	7.9	0.0185	0.0011	118.3	6.7	
161-1-a-sport-3-dark brown	651	36	1	34125	100	0.000	1.33	0.004	52.4	2.9	0.058	0.011	-0.001	0.152	0.000	120	7.4	0.0191	0.0011	121.8	6.7	
161-1-b-sport-1-dark brown	775	39	35	40575	159	0.003	1.61	0.007	52.4	2.6	0.051	0.012	0.044	-0.063	0.021	122	7.1	0.0187	0.0010	119.4	6.2	
161-1-b-sport-2-dark brown	753	82	101	36898	175	0.008	1.45	0.007	49.0	2.6	0.109	0.015	0.132	0.099	0.064	120	7.8	0.0191	0.0011	122.0	6.9	
161-1-b-sport-1-light brown	1431	168	216	70302	98	0.016	2.75	0.004	49.1	2.7	0.121	0.014	0.150	0.035	0.073	118	7.8	0.0189	0.0011	120.6	7.2	
161-1-b-sport-2-light brown	687	51	56	37992	108	0.004	1.50	0.004	55.3	3.0	0.076	0.013	0.081	0.154	0.039	112	7.0	0.0174	0.0010	111.1	6.2	
161-1-b-sport-3-light brown	958	122	231	44989	162	0.018	1.77	0.007	47.0	2.5	0.129	0.016	0.240	0.256	0.116	122	8.2	0.0188	0.0012	120.2	7.7	
161-1-b-sport-4-light brown	908	102	159	45833	134	0.012	1.81	0.005	50.5	2.5	0.116	0.014	0.174	0.078	0.084	116	7.1	0.0181	0.0010	115.9	6.4	
Sample 162-2-(a-b)																						

Sample Information	Counts sec ⁻¹ concentrations								Corrected ratios						Comm on Pb	Common Pb- corrected ratios and ages						
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ PbC/ ²⁰⁶ Pb	2s		f ²⁰⁶ c via ²⁰⁸	Projected T-W age corrected via ²⁰⁷ for PbC		²⁰⁸ PbC-cor ²⁰⁶ Pb- ²³⁸ U		²⁰⁸ PbC-cor Age	
						ppm											(Ma)	2s	ratio	2s	(Ma)	2s
162-2-a-spot-1-dark brown	6310	29 41	6966	13284 3	2915	0.325	3.30	0.076	21.1	1.3	0.453	0.017	1.101	0.050	0.532	148	13.8	0.0222	0.0037	141.8	23.4	
162-2-a-spot-2-dark brown	2266	19 9	262	11932 1	3881	0.012	3.04	0.105	52.7	2.0	0.091	0.005	0.106	0.012	0.051	115	4.6	0.0180	0.0007	115.1	4.7	
162-2-a-spot-3-dark brown	6600	27 74	6280	12835 5	2075	0.303	3.32	0.058	19.4	1.3	0.409	0.015	0.949	0.043	0.458	178	15.9	0.0279	0.0039	177.1	24.5	
162-2-a-spot-4-dark brown	3200	26 3	303	19499 6	2866	0.015	5.06	0.080	60.9	2.6	0.089	0.007	0.090	0.028	0.044	100	4.5	0.0157	0.0007	100.4	4.4	
162-2-a-spot-1- light brown	1923	11 6	81	10962 8	2360	0.004	2.97	0.068	57.0	2.7	0.062	0.006	0.036	-0.025	0.017	110	5.3	0.0172	0.0008	110.2	5.2	
162-2-a-spot-2- light brown	4580	11 12	2400	18005 6	4207	0.122	4.80	0.119	39.3	2.6	0.218	0.020	0.518	0.066	0.250	128	11.2	0.0191	0.0020	121.8	12.4	
162-2-a-spot-3- light brown	3750	13 18	3135	11269 0	3809	0.159	3.09	0.111	30.1	2.3	0.320	0.026	0.829	0.098	0.400	140	15.9	0.0200	0.0033	127.4	20.6	
162-2-b-spot-1- dark_ brown	1715	96	27	92437	1406	0.005	2.35	0.050	53.9	2.1	0.058	0.006	0.011	-0.005	0.005	117	4.9	0.0185	0.0007	117.9	4.6	
162-2-b-spot-2- dark_ brown	3940	24 3	179	24694 8	3272	0.009	6.65	0.095	62.7	6.0	0.064	0.007	0.041	0.091	0.020	100	9.4	0.0156	0.0015	100.0	9.8	
162-2-b-spot-3- dark_ brown	597	32	21	43194	297	0.001	1.11	0.008	72.4	3.6	0.057	0.010	0.033	-0.007	0.016	88	4.9	0.0136	0.0007	87.1	4.4	
162-2-b-spot-1- light brown	2660	13 7	28	14295 1	1901	0.001	3.88	0.054	53.7	2.4	0.053	0.004	0.006	-0.003	0.003	118	5.2	0.0186	0.0008	118.5	5.2	
162-2-b-spot-2-light brown	2909	39 5	722	14118 3	1294	0.037	3.83	0.036	48.5	2.3	0.135	0.010	0.246	0.042	0.119	117	6.5	0.0182	0.0010	116.0	6.5	
162-2-b-spot-3- light brown	1431	11 1	97	87394	1785	0.001	2.44	0.040	61.1	3.0	0.084	0.011	0.061	-0.024	0.030	100	5.7	0.0159	0.0008	101.6	5.3	
DRT3 dolomite																						
Sample 165-2																						
165-2-spot-1- light brown	1559	11 9	116	82187	902	0.009	3.28	0.039	52.7	2.2	0.080	0.008	0.071	0.030	0.034	116	5.3	0.0183	0.0008	117.0	5.0	
165-2-spot-2- light brown	1135	61	43	64520	412	0.003	2.53	0.017	56.8	2.5	0.056	0.008	0.036	0.525	0.017	111	5.3	0.0173	0.0008	110.5	4.9	
165-2-spot-3-dark brown	1760	23 5	437	86390	454	0.033	3.28	0.018	49.1	2.3	0.132	0.011	0.247	0.144	0.119	116	6.5	0.0179	0.0010	114.6	6.4	
165-2-spot-4-dark brown	2770	93 4	2167	87214	643	0.166	3.44	0.027	31.5	1.6	0.345	0.020	0.781	0.053	0.377	127	10.3	0.0198	0.0019	126.3	11.9	
165-2-spot-5- light brown	2858	69 8	1425	12650 3	786	0.109	5.02	0.034	44.3	1.6	0.245	0.010	0.497	0.027	0.240	109	5.2	0.0172	0.0009	109.7	5.6	
165-2-spot-6-light brown	2092	39 3	781	84403	665	0.060	3.35	0.029	40.3	1.7	0.189	0.012	0.371	0.040	0.179	130	6.9	0.0203	0.0011	129.8	6.8	
165-2-spot-7-light brown	1493	11 6	89	81264	545	0.007	3.19	0.023	54.4	2.1	0.077	0.008	0.058	0.044	0.028	113	4.9	0.0179	0.0007	114.1	4.5	
DRT4 dolomite																						
Sample 133-2-136-137																						
Values are calculated using assumed values of common Pb for ²⁰⁸ Pb/ ²⁰⁶ Pb ratio equals 2.06 +/- 0.02																						

Sample Information	Counts sec ⁻¹ concentrations								Corrected ratios						Comm on Pb	Common Pb- corrected ratios and ages						
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ PbC/ ²⁰⁶ Pb	2s		f206c via208	Projected T-W age corrected via 207 for Pbc		²⁰⁸ PbC-cor ²⁰⁶ Pb- ²³⁸ U		²⁰⁸ PbC-cor Age	
						ppm											(Ma)	2s	ratio	2s	(Ma)	2s
133-2-136-137-spot-5-white	6710	10 23	1858	46346 8	131	0.101	13.32	0.004	69.1	2.5	0.145	0.012	0.277	0.055	0.134	81	3.8	0.0125	0.0006	80.4	3.7	
133-2-136-137-spot-8-white	4590	11 46	2516	24439 5	135	0.136	7.10	0.004	53.2	3.0	0.261	0.019	0.548	0.041	0.265	88	7.0	0.0138	0.0011	88.4	7.0	
133-2-136-137-spot-1-light brown	1202	27 3	531	54570	124	0.029	1.58	0.004	45.4	2.3	0.235	0.016	0.441	0.043	0.213	108	7.3	0.0173	0.0012	110.8	7.3	
133-2-136-137-spot-2-light brown	1234	22 6	392	61300	121	0.021	1.78	0.004	49.7	2.2	0.190	0.013	0.317	0.035	0.153	106	6.1	0.0170	0.0009	109.0	6.0	
133-2-136-137-spot-3-light brown	2669	25 5	331	14725 8	225	0.018	4.31	0.007	55.2	2.2	0.099	0.007	0.124	0.038	0.060	109	4.8	0.0170	0.0007	108.9	4.7	
133-2-136-137-spot-4-light brown	1479	16 2	212	85652	122	0.012	2.52	0.004	57.9	2.8	0.114	0.011	0.143	0.096	0.069	101	5.8	0.0161	0.0009	102.8	5.5	
133-2-136-137-spot-1-white*	903	402	887	2059	179	0.048	0.06	0.006	2.3	0.1	0.478	0.025	0.970	0.057	0.469	1220	123.6	0.2330	0.0277	1350.3	145.1	
133-2-136-137-spot-2-white*	986	427	1012	2539	375	0.054	0.08	0.012	2.6	0.1	0.460	0.025	1.004	0.060	0.485	1138	110.5	0.2000	0.0238	1175.1	127.8	
133-2-136-137-spot-3-white*	1075	477	1119	2963	107	0.061	0.13	0.005	2.8	0.2	0.466	0.022	1.036	0.052	0.500	1050	122.7	0.1813	0.0319	1073.9	174.2	
133-2-136-137-spot-4-white*	1147	524	1208	2912	152	0.066	0.14	0.008	2.5	0.3	0.479	0.022	1.046	0.065	0.505	1098	141.7	0.1948	0.0402	1147.5	216.9	
133-2-136-137-spot-6-white*	979	408	945	7121	228	0.051	0.21	0.008	7.3	0.4	0.440	0.022	0.961	0.065	0.464	437	39.4	0.0737	0.0076	458.4	45.5	
133-2-136-137-spot-7-white*	933	374	845	3967	87	0.046	0.12	0.003	4.3	0.3	0.424	0.034	0.902	0.074	0.436	766	95.0	0.1328	0.0176	803.6	100.0	
133-2-136-137-spot-9-white*	730	288	659	4042	246	0.036	0.12	0.008	5.5	0.3	0.416	0.026	0.892	0.067	0.431	603	59.2	0.1028	0.0108	630.5	63.3	
133-2-136-137-spot-10-white*	995	416	1005	1807	7	0.054	0.05	0.000	1.8	0.1	0.444	0.023	1.010	0.072	0.488	1655	152.2	0.2821	0.0381	1601.9	191.8	
133-2-136-137-spot-11-white*	806	313	735	3938	395	0.039	0.12	0.012	4.9	0.3	0.411	0.024	0.895	0.058	0.432	689	63.1	0.1162	0.0120	708.4	69.1	
133-2-136-137-spot-5-light brown*	809	307	703	5171	128	0.038	0.15	0.004	6.4	0.3	0.404	0.021	0.865	0.050	0.418	539	45.9	0.0911	0.0088	561.9	51.8	
Values are calculated using assumed values of common Pb for ²⁰⁸ Pb/ ²⁰⁶ Pb ratio equals 0.96 +/- 0.05																						
133-2-136-137-spot-5-white	6710	10 23	1858	46346 8	131	0.101	13.32	0.004	69.1	2.5	0.145	0.012	0.277	0.055	0.288	81	3.8	0.0783	0.0115	66.1	5.1	
133-2-136-137-spot-8-white	4590	11 46	2516	24439 5	135	0.136	7.10	0.004	53.2	3.0	0.261	0.019	0.548	0.041	0.570	88	7.0	0.0661	0.0100	51.9	8.8	
133-2-136-137-spot-1-light brown	1202	27 3	531	54570	124	0.029	1.58	0.004	45.4	2.3	0.235	0.016	0.441	0.043	0.459	108	7.3	0.1426	0.0196	76.4	9.0	
133-2-136-137-spot-2-light brown	1234	22 6	392	61300	121	0.021	1.78	0.004	49.7	2.2	0.190	0.013	0.317	0.035	0.330	106	6.1	0.1489	0.0190	86.4	7.0	
133-2-136-137-spot-3-light brown	2669	25 5	331	14725 8	225	0.018	4.31	0.007	55.2	2.2	0.099	0.007	0.124	0.038	0.128	109	4.8	0.1122	0.0128	101.0	5.0	
133-2-136-137-spot-4-light brown	1479	16 2	212	85652	122	0.012	2.52	0.004	57.9	2.8	0.114	0.011	0.143	0.096	0.149	101	5.8	0.1221	0.0166	94.1	6.0	
133-2-136-137-spot-1-white*	903	402	887	2059	179	0.048	0.06	0.006	2.3	0.1	0.478	0.025	0.970	0.057	1.009	1220	123.6	-0.0040	0.0685	-25.6	444.1	

Sample Information	Counts sec ⁻¹ concentrations								Corrected ratios						Comm on Pb	Common Pb- corrected ratios and ages						
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ Pb _C / ²⁰⁶ Pb	2s		f ²⁰⁶ c via ²⁰⁸	Projected T-W age corrected via ²⁰⁷ for Pb _C		²⁰⁸ Pb _C -cor ²⁰⁶ Pb- ²³⁸ U		²⁰⁸ Pb _C -cor Age	
						ppm											(Ma)	2s	ratio	2s	(Ma)	2s
133-2-136-137-spot-2-white*	986	427	1012	2539	375	0.054	0.08	0.012	2.6	0.1	0.460	0.025	1.004	0.060	1.045	1138	110.5	-0.0173	0.0398	-112.7	261.5	
133-2-136-137-spot-3-white*	1075	477	1119	2963	107	0.061	0.13	0.005	2.8	0.2	0.466	0.022	1.036	0.052	1.078	1050	122.7	-0.0281	0.0393	-184.0	260.6	
133-2-136-137-spot-4-white*	1147	524	1208	2912	152	0.066	0.14	0.008	2.5	0.3	0.479	0.022	1.046	0.065	1.088	1098	141.7	-0.0347	0.0485	-227.6	324.2	
133-2-136-137-spot-6-white*	979	408	945	7121	228	0.051	0.21	0.008	7.3	0.4	0.440	0.022	0.961	0.065	0.999	437	39.4	0.0001	0.1706	1.0	1110.2	
133-2-136-137-spot-7-white*	933	374	845	3967	87	0.046	0.12	0.003	4.3	0.3	0.424	0.034	0.902	0.074	0.938	766	95.0	0.0146	0.0250	93.6	158.9	
133-2-136-137-spot-9-white*	730	288	659	4042	246	0.036	0.12	0.008	5.5	0.3	0.416	0.026	0.892	0.067	0.928	603	59.2	0.0130	0.0163	83.1	104.0	
133-2-136-137-spot-10-white*	995	416	1005	1807	7	0.054	0.05	0.000	1.8	0.1	0.444	0.023	1.010	0.072	1.050	1655	152.2	-0.0276	0.0543	-180.6	360.2	
133-2-136-137-spot-11-white*	806	313	735	3938	395	0.039	0.12	0.012	4.9	0.3	0.411	0.024	0.895	0.058	0.931	689	63.1	0.0141	0.0192	90.1	121.8	
133-2-136-137-spot-5-light brown*	809	307	703	5171	128	0.038	0.15	0.004	6.4	0.3	0.404	0.021	0.865	0.050	0.900	539	45.9	0.0157	0.0126	100.2	80.0	
Sample 134-1-123-124																						
Values are calculated using assumed values of common Pb for ²⁰⁸ Pb/ ²⁰⁶ Pb ratio equals 2.06 +/- 0.02																						
134-1-123-124-spot-1	11290	5341	12540	466069	244	0.654	13.67	0.007	41.3	1.8	0.487	0.010	1.111	0.032	0.536	69	4.5	0.0112	0.0012	72.0	7.4	
134-1-124-124-spot-2	5980	1171	2361	496530	278	0.123	13.82	0.008	83.0	2.9	0.172	0.010	0.395	0.044	0.191	65	2.9	0.0097	0.0005	62.5	3.3	
134-1-123-124-spot-3	7500	1102	1906	697742	239	0.100	19.50	0.007	93.0	3.0	0.146	0.006	0.254	0.016	0.123	60	2.2	0.0094	0.0004	60.5	2.4	
134-1-123-124-spot-4	919	268	620	51272	242	0.032	1.42	0.007	55.8	2.5	0.298	0.019	0.674	0.058	0.325	79	5.7	0.0121	0.0009	77.5	5.8	
134-1-123-124-spot-6	10650	2489	5147	875015	312	0.269	24.12	0.009	82.2	2.3	0.232	0.008	0.483	0.026	0.233	60	2.2	0.0093	0.0004	59.9	2.5	
134-1-123-124-spot-7	1056	198	350	81225	284	0.018	2.40	0.009	76.9	3.7	0.211	0.018	0.331	0.047	0.160	66	4.5	0.0109	0.0006	70.0	4.1	
134-1-123-124-spot-8	975	279	654	58248	269	0.034	1.63	0.008	59.7	2.8	0.300	0.021	0.670	0.064	0.324	73	5.6	0.0113	0.0009	72.6	5.6	
134-1-123-124-spot-10	5546	507	621	579898	116	0.033	16.28	0.003	104.6	3.1	0.093	0.004	0.112	0.015	0.054	58	1.9	0.0090	0.0003	58.1	1.9	
134-1-123-124-spot-11	14160	6354	14639	713104	155	0.774	20.11	0.004	50.4	1.4	0.458	0.009	1.034	0.019	0.499	61	2.9	0.0099	0.0006	63.8	4.1	
134-1-123-124-spot-14	1020	196	393	78567	193	0.021	2.25	0.006	77.0	3.5	0.204	0.014	0.385	0.055	0.186	67	4.1	0.0106	0.0006	67.8	4.0	
134-1-123-124-spot-15	1527	224	398	131056	199	0.021	3.74	0.006	85.8	3.2	0.160	0.010	0.260	0.031	0.126	64	3.0	0.0102	0.0005	65.3	2.9	
134-1-123-124-spot-16	6102	2868	6405	265174	205	0.340	7.48	0.006	43.5	1.5	0.480	0.011	1.050	0.025	0.507	67	3.9	0.0113	0.0009	72.7	5.4	
134-1-123-124-spot-17	8020	3289	7373	415725	162	0.391	11.74	0.005	51.8	1.6	0.421	0.010	0.919	0.024	0.444	65	3.2	0.0107	0.0007	68.8	4.2	

Sample Information	Counts sec ⁻¹ concentrations								Corrected ratios						Comm on Pb	Common Pb- corrected ratios and ages						
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ Pb/ ²⁰⁶ Pb	2s		f ²⁰⁶ c via ²⁰⁸	Projected T-W age corrected via ²⁰⁷ for Pbc		²⁰⁸ Pb _C -cor ²⁰⁶ Pb- ²³⁸ U		²⁰⁸ Pb _C -cor Age	
						ppm											(Ma)	2s	ratio	2s	(Ma)	2s
134-1-123-124-spot-18	6350	16 16	3290	54499 2	274	0.174	15.07	0.008	85.8	3.2	0.257	0.011	0.518	0.027	0.250	55	2.8	0.0087	0.0005	56.1	3.1	
134-1 (123-124)-spot-1-fossil*	855	549	1365	3349	23	0.071	0.09	0.001	3.9	0.3	0.675	0.046	1.596	0.135	0.771	336	101.1	0.0585	0.0222	366.2	135.4	
134-1 (123-124)-spot-2-fossil*	638	427	1037	658	8	0.054	0.02	0.000	1.0	0.1	0.715	0.041	1.625	0.099	0.785	942	317.8	0.2086	0.0901	1221.4	481.5	
134-1 (123-124)-spot-3-fossil*	999	673	1639	2994	48	0.085	0.09	0.001	3.0	0.2	0.718	0.040	1.640	0.097	0.792	325	116.2	0.0694	0.0306	432.4	184.4	
134-1 (123-124)-spot-4-fossil*	2802	1723	4025	3654	146	0.213	0.11	0.004	1.3	0.1	0.628	0.021	1.433	0.059	0.692	1248	142.6	0.2360	0.0450	1365.8	234.8	
134-1 (123-124)-spot-5-fossil*	2038	1173	2738	46962	9	0.145	1.53	0.000	23.0	1.4	0.595	0.020	1.344	0.046	0.649	86	10.8	0.0152	0.0027	97.5	17.4	
134-1 (123-124)-spot-6-fossil*	801	604	1458	909	56	0.077	0.03	0.002	1.1	0.1	0.813	0.074	1.820	0.181	0.879	191	481.3	0.1067	0.1020	653.8	595.7	
134-1 (123-124)-spot-7-fossil*	1106	814	1973	3408	37	0.104	0.10	0.001	3.1	0.2	0.763	0.029	1.783	0.070	0.861	201	76.8	0.0450	0.0211	283.6	130.4	
134-1 (123-124)-spot-8-fossil*	2131	1174	2796	27793	126	0.148	0.84	0.004	13.0	0.8	0.569	0.022	1.312	0.061	0.634	167	21.3	0.0281	0.0053	178.6	33.2	
134-1 (123-124)-spot-9-fossil*	1177	588	1387	7545	99	0.073	0.21	0.003	6.4	0.3	0.518	0.031	1.176	0.083	0.568	400	51.6	0.0674	0.0100	420.2	60.2	
134-1 (123-124)-spot-10-fossil*	781	522	1215	3677	36	0.064	0.11	0.001	4.7	0.3	0.723	0.040	1.556	0.084	0.751	200	73.5	0.0528	0.0173	331.8	106.0	
134-1 (123-124)-spot-5*	7540	5459	13188	6533	225	0.690	0.18	0.007	0.9	0.0	0.739	0.012	1.748	0.031	0.844	907	112.4	0.1799	0.0514	1066.4	281.1	
134-1 (123-124)-spot-9*	9640	7161	17416	5725	188	0.915	0.16	0.005	0.6	0.0	0.761	0.013	1.806	0.034	0.872	1030	169.3	0.2153	0.0764	1257.1	405.8	
134-1 (123-124)-spot-12*	2542	1595	3821	4029	158	0.202	0.12	0.005	1.6	0.1	0.646	0.018	1.500	0.046	0.725	950	105.5	0.1738	0.0310	1032.9	170.5	
134-1 (123-124)-spot-13*	7150	5160	12298	4646	96	0.651	0.13	0.003	0.6	0.0	0.736	0.014	1.719	0.040	0.830	1230	171.3	0.2611	0.0719	1495.5	367.7	
134-1 (123-124)-spot-19*	2165	1256	2970	4087	126	0.155	0.12	0.004	1.9	0.1	0.608	0.030	1.369	0.072	0.661	954	145.0	0.1794	0.0340	1063.7	185.8	
134-1 (123-124)-spot-20*	2887	1731	4054	3522	147	0.212	0.10	0.004	1.2	0.1	0.617	0.025	1.401	0.066	0.677	1397	180.7	0.2651	0.0514	1516.1	261.8	
134-1 (123-124)-spot-21*	1672	951	2263	35749	14	0.118	1.20	0.000	21.4	1.7	0.596	0.027	1.354	0.068	0.654	92	15.7	0.0162	0.0040	103.6	25.1	
Values are calculated using assumed values of common Pb for ²⁰⁸ Pb/ ²⁰⁶ Pb ratio equals 1.647 ± 0.091																						
134-1 -123-124-spot-1	11290	53 41	12540	46606 9	244	0.654	13.67	0.007	41.3	1.8	0.487	0.010	1.111	0.032	0.674	69	4.5	0.0112	0.0012	50.7	11.4	
134-1-124-124-spot-2	5980	11 71	2361	49653 0	278	0.123	13.82	0.008	83.0	2.9	0.172	0.010	0.395	0.044	0.240	65	2.9	0.0097	0.0005	58.8	3.9	
134-1-123-124-spot-3	7500	11 02	1906	69774 2	239	0.100	19.50	0.007	93.0	3.0	0.146	0.006	0.254	0.016	0.154	60	2.2	0.0094	0.0004	58.3	2.6	
134-1-123-124-spot-4	919	26 8	620	51272	242	0.032	1.42	0.007	55.8	2.5	0.298	0.019	0.674	0.058	0.409	79	5.7	0.0121	0.0009	67.9	7.2	
134-1-123-124-spot-6	10650	24 89	5147	87501 5	312	0.269	24.12	0.009	82.2	2.3	0.232	0.008	0.483	0.026	0.293	60	2.2	0.0093	0.0004	55.2	3.2	

Sample Information	Counts sec ⁻¹ concentrations								Corrected ratios							Comm on Pb	Common Pb- corrected ratios and ages					
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ Pb/ ²⁰⁶ Pb	2s	f206c via208		Projected T-W age corrected via 207 for Pbc		²⁰⁸ Pb _C -cor ²⁰⁶ Pb- ²³⁸ U		²⁰⁸ Pb _C -cor Age	
						ppm											(Ma)	2s	ratio	2s	(Ma)	2s
134-1-123-124-spot-7	1056	198	350	81225	284	0.018	2.40	0.009	76.9	3.7	0.211	0.018	0.331	0.047	0.201	66	4.5	0.0109	0.0006	66.6	4.5	
134-1-123-124-spot-8	975	279	654	58248	269	0.034	1.63	0.008	59.7	2.8	0.300	0.021	0.670	0.064	0.407	73	5.6	0.0113	0.0009	63.7	6.9	
134-1-123-124-spot-10	5546	507	621	579898	116	0.033	16.28	0.003	104.6	3.1	0.093	0.004	0.112	0.015	0.068	58	1.9	0.0090	0.0003	57.2	1.9	
134-1-123-124-spot-11	14160	6354	14639	713104	155	0.774	20.11	0.004	50.4	1.4	0.458	0.009	1.034	0.019	0.628	61	2.9	0.0099	0.0006	47.5	7.7	
134-1-123-124-spot-14	1020	196	393	78567	193	0.021	2.25	0.006	77.0	3.5	0.204	0.014	0.385	0.055	0.233	67	4.1	0.0106	0.0006	63.8	4.5	
134-1-123-124-spot-15	1527	224	398	131056	199	0.021	3.74	0.006	85.8	3.2	0.160	0.010	0.260	0.031	0.158	64	3.0	0.0102	0.0005	62.9	3.1	
134-1-123-124-spot-16	6102	2868	6405	265174	205	0.340	7.48	0.006	43.5	1.5	0.480	0.011	1.050	0.025	0.637	67	3.9	0.0113	0.0009	53.6	9.4	
134-1-123-124-spot-17	8020	3289	7373	415725	162	0.391	11.74	0.005	51.8	1.6	0.421	0.010	0.919	0.024	0.558	65	3.2	0.0107	0.0007	54.7	7.0	
134-1-123-124-spot-18	6350	1616	3290	544992	274	0.174	15.07	0.008	85.8	3.2	0.257	0.011	0.518	0.027	0.314	55	2.8	0.0087	0.0005	51.3	3.7	
134-1 (123-124)-spot-1-fossil*	855	549	1365	3349	23	0.071	0.09	0.001	3.9	0.3	0.675	0.046	1.596	0.135	0.969	336	101.1	-0.3846	-0.0654	-493.0	-108.3	
134-1 (123-124)-spot-2-fossil*	638	427	1037	658	8	0.054	0.02	0.000	1.0	0.1	0.715	0.041	1.625	0.099	0.986	942	317.8	0.5933	0.0976	473.0	62.3	
134-1 (123-124)-spot-3-fossil*	999	673	1639	2994	48	0.085	0.09	0.001	3.0	0.2	0.718	0.040	1.640	0.097	0.995	325	116.2	0.1271	0.0214	121.5	19.3	
134-1 (123-124)-spot-4-fossil*	2802	1723	4025	3654	146	0.213	0.11	0.004	1.3	0.1	0.628	0.021	1.433	0.059	0.870	1248	142.6	3.0508	0.4168	1420.4	104.9	
134-1 (123-124)-spot-5-fossil*	2038	1173	2738	46962	9	0.145	1.53	0.000	23.0	1.4	0.595	0.020	1.344	0.046	0.816	86	10.8	0.1544	0.0212	145.7	18.7	
134-1 (123-124)-spot-6-fossil*	801	604	1458	909	56	0.077	0.03	0.002	1.1	0.1	0.813	0.074	1.820	0.181	1.105	191	481.3	1.1839	0.2257	793.1	105.3	
134-1 (123-124)-spot-7-fossil*	1106	814	1973	3408	37	0.104	0.10	0.001	3.1	0.2	0.763	0.029	1.783	0.070	1.083	201	76.8	0.3118	0.0447	275.6	34.6	
134-1 (123-124)-spot-8-fossil*	2131	1174	2796	27793	126	0.148	0.84	0.004	13.0	0.8	0.569	0.022	1.312	0.061	0.796	167	21.3	0.1549	0.0223	146.2	19.6	
134-1 (123-124)-spot-9-fossil*	1177	588	1387	7545	99	0.073	0.21	0.003	6.4	0.3	0.518	0.031	1.176	0.083	0.714	400	51.6	0.4008	0.0609	342.2	44.1	
134-1 (123-124)-spot-10-fossil*	781	522	1215	3677	36	0.064	0.11	0.001	4.7	0.3	0.723	0.040	1.556	0.084	0.944	200	73.5	0.9529	0.1459	679.6	76.0	
134-1 (123-124)-spot-5*	7540	5459	13188	6533	225	0.690	0.18	0.007	0.9	0.0	0.739	0.012	1.748	0.031	1.061	907	112.4	1.4685	0.1896	917.5	78.1	
134-1 (123-124)-spot-9*	9640	7161	17416	5725	188	0.915	0.16	0.005	0.6	0.0	0.761	0.013	1.806	0.034	1.096	1030	169.3	1.0050	0.1310	706.3	66.4	
134-1 (123-124)-spot-12*	2542	1595	3821	4029	158	0.202	0.12	0.005	1.6	0.1	0.646	0.018	1.500	0.046	0.911	950	105.5	1.2253	0.1624	812.2	74.2	
134-1 (123-124)-spot-13*	7150	5160	12298	4646	96	0.651	0.13	0.003	0.6	0.0	0.736	0.014	1.719	0.040	1.044	1230	171.3	3.9418	0.5049	1622.3	104.1	
134-1 (123-124)-spot-19*	2165	1256	2970	4087	126	0.155	0.12	0.004	1.9	0.1	0.608	0.030	1.369	0.072	0.831	954	145.0	1.4737	0.2118	919.7	87.2	
134-1 (123-124)-spot-20*	2887	1731	4054	3522	147	0.212	0.10	0.004	1.2	0.1	0.617	0.025	1.401	0.066	0.850	1397	180.7	3.0275	0.4233	1414.6	107.1	
134-1 (123-124)-spot-21*	1672	951	2263	35749	14	0.118	1.20	0.000	21.4	1.7	0.596	0.027	1.354	0.068	0.822	92	15.7	0.0987	0.0151	95.5	14.0	

Sample Information	Counts sec ⁻¹ concentrations								Corrected ratios						Comm on Pb	Common Pb- corrected ratios and ages					
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ Pb/ ²⁰⁶ Pb	2s		f206c via208	Projected T-W age corrected via 207 for Pbc		²⁰⁸ Pb _C -cor ²⁰⁶ Pb- ²³⁸ U		²⁰⁸ Pb _C -cor Age
						ppm									(Ma)		2s	ratio	2s	(Ma)	2s
DRT5 dolomite																					
161-1-a-sport-1-white	768	36	0	44224	59	0.000	1.75	0.002	57.6	3.0	0.049	0.010	0.000	0.117	0.000	111	6.4	0.0174	0.0009	111.0	5.8
161-1-a-sport-2-white	1587	72	1	85975	22	0.000	3.39	0.001	54.2	2.3	0.048	0.006	0.000	0.122	0.000	118	5.2	0.0185	0.0008	117.9	4.9
161-1-a-sport-3-white	731	42	22	43928	45	0.002	1.74	0.002	60.1	3.2	0.061	0.013	-0.026	0.140	0.015	105	6.6	0.0164	0.0009	104.9	5.7
161-1-a-sport-4-white	633	31	1	40134	27	0.000	1.58	0.001	63.4	3.4	0.053	0.013	-0.001	0.115	0.001	100	6.3	0.0158	0.0009	100.8	5.4
161-1-b-sport-1-white	806	40	10	48797	47	0.004	0.93	0.000	60.5	3.0	0.052	0.011	0.012	-0.016	0.006	105	6.0	0.0164	0.0008	105.0	5.3
161-1-b-sport-2-white	697	49	35	40082	27	0.003	1.57	0.001	57.5	2.9	0.074	0.012	0.050	-0.047	0.024	108	6.3	0.0170	0.0009	108.5	5.5
161-1-b-sport-3-white	293	17	25	19083	11	0.002	0.76	0.000	65.1	4.5	0.042	0.035	0.086	-0.098	0.041	99	10.1	0.0147	0.0011	94.2	7.0
161-1-b-sport-4-white	418	24	16	26062	14	0.001	1.04	0.000	62.4	3.9	0.065	0.019	0.039	-0.033	0.019	100	7.9	0.0157	0.0010	100.6	6.5
161-1-b-sport-5-white	326	21	17	20416	16	0.001	0.81	0.000	62.6	4.6	0.074	0.025	0.053	-0.044	0.026	99	9.4	0.0156	0.0012	99.5	7.5

Counts for ²⁰⁶Pb are taken from Iolite; Counts for ²⁰⁷Pb adjusted using mass-bias using one mass unit and power law; Counts for ²⁰⁸Pb adjusted using final 206 counts and mass bias power law and two mass units; ²³⁸U counts are derived by multiplying the ²⁰⁶Pb counts by the ²³⁸U/²⁰⁶Pb ratio; Ppm values are derived from Iolite where they are adjusted to accepted values; F206c via 208 is the common lead proportion and is derived by subtraction of ²⁰⁸Pb_{rad} from ²⁰⁸Pb_{total} using T-W age; ²⁰⁸Pb_{com} – corrected ratios

Table 1 (continued)

ID	Analysis	d ¹³ C VPDB (Final)	d ¹⁸ O VPDB (Final)	d ¹⁸ O VSMOW (Final)	d ¹⁸ O VSMOW (Final) SE	D ₄₈ Offset	49 Param	D ₄₇ CDES (Final)	D ₄₇ CDES (Final) SE	d ¹³ C VPDB (Final) SE	d ¹¹⁸ O VPDB (Final) SE	d ¹¹⁸ O VSMOW (Final) SE
S1	133-2-136-137	CO2 clumped	3.14	1.69	0.074	32.66			0.006	0.708	0.02	0.07
R1	2016-11-06 20:01 GMT	CO2 clumped	3.13	1.85		32.82	0.297	0.172		0.703		
R2	2016-11-24 18:28 GMT	CO2 clumped	3.15	1.75		32.73	0.078	0.154		0.709		
R3	2016-12-03 17:45 GMT	CO2 clumped	3.19	1.51		32.48	-0.063	0.088		0.695		
R4	2017-03-02 17:13 GMT	CO2 clumped	3.09	1.64		32.61	0.063	0.019		0.725		
S2	134-2-27-28	CO2 clumped	3.39	0.17	0.083	31.09			0.011	0.699	0.04	0.08
R1	2016-11-11 12:37 GMT	CO2 clumped	3.3	0.14		31.06	-0.026	0.134		0.698		
R2	2016-11-11 20:31 GMT	CO2 clumped	3.46	-0.04		30.87	0.133	0.124		0.687		
R3	2016-12-03 20:02 GMT	CO2 clumped	3.36	0.27		31.19	0.123	0.167		0.731		
R4	2016-12-09 17:43 GMT	CO2 clumped	3.44	0.31		31.24	0.068	0.061		0.679		
S3	134-2-40-42	CO2 clumped	3.31	1.19	0.256	32.15			0.006	0.697	0.02	0.25
R1	2016-08-09 12:31 BST	CO2 clumped	3.3	1.07		32.02	0.149	0.094		0.712		
R2	2016-08-24 23:14 BST	CO2 clumped	3.28	1.91		32.89	-0.037	0.087		0.697		
R3	2016-12-03 22:24 GMT	CO2 clumped	3.35	0.77		31.72	0.15	0.131		0.694		
R4	2017-02-24 18:19 GMT	CO2 clumped	3.29	1.01		31.96	0.025	0.023		0.684		

ID	Analysis	d ¹³ C VPDB (Final)	d ¹⁸ O VPDB (Final)	d ¹⁸ O VSMOW (Final)	d ¹⁸ O VSMOW (Final) SE	D ₄₈ Offset	49 Param	D ₄₇ CDES (Final)	D ₄₇ CDES (Final) SE	d ¹³ C VPDB (Final) SE	d ¹¹⁸ O VPDB (Final) SE	d ¹¹⁸ O VSMOW (Final) SE
S4	137-1-43-44	CO2 clumped	2.7	2.11	0.068	33.09			0.005	0.708	0.04	0.07
R1	2016-11-08 18:36 GMT	CO2 clumped	2.69	2.28		33.27	-0.263	-0.051		0.693		
R2	2016-11-25 21:07 GMT	CO2 clumped	2.77	1.97		32.96	0.09	0.145		0.71		
R3	2016-12-03 12:54 GMT	CO2 clumped	2.75	2.04		33.02	-0.147	0.056		0.708		
R4	2017-02-24 11:14 GMT	CO2 clumped	2.6	2.14		33.13	-0.136	-0.018		0.719		
S5	137-2-73-74	CO2 clumped	3.27	-0.69	0.131	30.21			0.003	0.692	0.03	0.13
R1	2016-11-11 14:56 GMT	CO2 clumped	3.29	-0.92		29.97	0.03	0.08		0.695		
R2	2016-11-25 23:44 GMT	CO2 clumped	3.3	-0.65		30.25	0.051	0.101		0.686		
R3	2017-02-24 16:08 GMT	CO2 clumped	3.22	-0.49		30.42	0.133	0.071		0.696		
S6	161-1	CO2 clumped	1.82	-1.23	0.826	29.66			0.015	0.677	0.07	0.8
R1	2016-08-04 19:37 BST	CO2 clumped	1.88	-2.17		28.69	-0.094	0.045		0.655		
R2	2016-08-25 18:32 BST	CO2 clumped	1.9	-1.88		28.98	0.174	0.093		0.67		
R3	2017-03-04 17:38 GMT	CO2 clumped	1.69	0.37		31.3	-0.321	-0.025		0.706		
S7	162-2	CO2 clumped	2.55	-3.14	0.174	27.69			0.005	0.639	0.02	0.17
R1	2016-08-09 15:07 BST	CO2 clumped	2.53	-3.16		27.66	0.135	0.057		0.65		
R2	2016-08-25 16:07 BST	CO2 clumped	2.52	-2.65		28.18	0.071	0.06		0.642		
R3	2016-11-25 18:46 GMT	CO2 clumped	2.54	-3.42		27.39	0.178	0.109		0.624		
R4	2016-12-06 18:46 GMT	CO2 clumped	2.59	-3.31		27.51	0.032	0.108		0.64		
S8	164-1-114-118	CO2 clumped	2.34	-3.66	0.089	27.15			0.011	0.655	0.11	0.09
R1	2016-05-08 14:04 BST	CO2 clumped	2.46	-3.71		27.1	0.246	0.142		0.686		
R2	2016-08-25 23:16 BST	CO2 clumped	1.88	-3.54		27.27	0.34	0.106		0.669		
R3	2016-11-25 16:36 GMT	CO2 clumped	2.44	-3.93		26.87	0.063	0.098		0.634		
R4	2017-03-02 12:57 GMT	CO2 clumped	2.43	-3.41		27.4	-0.342	-0.05		0.627		
R5	2017-05-16 18:03 BST	CO2 clumped	2.47	-3.69		27.12	0.13	0.043		0.656		
S9	165-2-79-81	CO2 clumped	2.37	-3.85	0.229	26.95			0.005	0.625	0.02	0.22
R1	2016-08-09 17:27 BST	CO2 clumped	2.34	-4.07		26.73	1.043	0.081		0.622		
R2	2016-08-12 22:20 BST	CO2 clumped	2.39	-3.12		27.7	0.12	0.085		0.638		
R3	2016-11-25 14:29 GMT	CO2 clumped	2.42	-4.1		26.69	0.033	0.079		0.613		
R4	2017-03-02 15:04 GMT	CO2 clumped	2.37	-3.6		27.21	-0.119	-0.022		0.634		
R5	2017-09-28 09:54 BST	CO2 clumped	2.33	-4.38		26.4	0.121	0.13		0.617		
S10	168-4-125-130	CO2 clumped	2.46	-3.61	0.187	27.2			0.009	0.649	0.02	0.18
R1	2016-08-04 22:27 BST	CO2 clumped	2.48	-3.53		27.28	0.166	0.111		0.691		
R2	2016-08-12 19:56 BST	CO2 clumped	2.44	-2.8		28.04	0.071	0.066		0.63		
R3	2016-11-24 23:14 GMT	CO2 clumped	2.44	-4.05		26.75	0.167	0.117		0.644		
R4	2016-12-09 15:23 GMT	CO2 clumped	2.55	-3.74		27.07	0.17	0.07		0.646		
R5	2017-05-04 18:23 BST	CO2 clumped	2.46	-3.59		27.22	0.287	0.107		0.651		
R6	2017-05-16 15:29 BST	CO2 clumped	2.37	-3.94		26.86	-0.094	0.102		0.629		

Table 2. Results of U-Pb measurements of white dolomite samples. Samples were excluded from data analyses due to low concentration of uranium.

Sample Information	Counts sec ⁻¹ concentrations								Corrected ratios						Comm on Pb	Common Pb- corrected ratios and ages						
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ Pb _C / ²⁰⁶ Pb	2s		f206c via208	Projected T-W age		²⁰⁸ Pb _C -cor ²⁰⁶ Pb- ²³⁸ U			
						ppm											(Ma)	2s	ratio	2s	(Ma)	2s
Sample: 134-1-25-30																						
134-1-25-30-spot-1	1206	347	743	4810	93	0.040	0.14	0.003	4.0	0.2	0.303	0.015	0.612	0.042	0.296	1042	64.4	0.1766	0.0129	1048.3	70.5	
134-1-25-30-spot-2	1604	503	1068	5675	109	0.058	0.17	0.003	3.5	0.2	0.322	0.015	0.662	0.034	0.320	1129	68.9	0.1922	0.0141	1133.5	76.0	
134-1-25-30-spot-3	1322	359	735	5812	161	0.039	0.17	0.005	4.4	0.2	0.282	0.014	0.550	0.037	0.266	984	55.8	0.1670	0.0106	995.7	58.8	
134-1-25-30-spot-4	1819	684	1459	2943	125	0.078	0.09	0.004	1.6	0.1	0.391	0.017	0.795	0.037	0.384	2090	129.7	0.3809	0.0315	2080.4	147.3	
134-1-25-30-spot-5	1410	394	842	4180	153	0.045	0.12	0.005	3.0	0.2	0.297	0.016	0.589	0.042	0.285	1400	88.5	0.2413	0.0183	1393.6	95.0	
134-1-25-30-spot-6	1613	520	1124	2840	95	0.061	0.08	0.003	1.8	0.1	0.332	0.015	0.690	0.043	0.333	2171	123.5	0.3786	0.0303	2069.7	141.8	
134-1-25-30-spot-7	1785	695	1584	4718	110	0.086	0.14	0.003	2.6	0.1	0.401	0.014	0.883	0.041	0.427	1274	77.0	0.2169	0.0182	1265.6	96.7	
Sample: 134-2-27-28																						
134-2-27-28-spot-1	1780	992	2371	6675	72	0.127	0.19	0.002	3.7	0.2	0.564	0.020	1.331	0.059	0.643	581	56.8	0.0953	0.0156	586.7	92.1	
134-2-27-28-spot-2	1734	1064	2620	6602	15	0.140	0.19	0.000	3.8	0.2	0.641	0.024	1.511	0.059	0.730	416	58.8	0.0710	0.0137	442.1	82.2	
134-2-27-28-spot-3	1759	853	1980	7569	303	0.106	0.22	0.009	4.3	0.2	0.508	0.019	1.120	0.043	0.541	608	54.0	0.1067	0.0122	653.3	71.1	
134-2-27-28-spot-4	271	90	184	6406	2	0.010	0.19	0.000	23.6	1.7	0.437	0.063	0.678	0.678	0.328	137	27.9	0.0284	0.0033	180.8	21.0	
134-2-27-28-spot-5	1397	544	1173	6662	320	0.063	0.20	0.010	4.8	0.3	0.402	0.018	0.831	0.055	0.401	720	58.8	0.1255	0.0131	762.2	74.8	
134-2-27-28-spot-6	1458	916	2264	4676	0	0.122	0.14	0.000	3.2	0.2	0.654	0.034	1.553	0.087	0.750	460	96.7	0.0779	0.0233	483.8	139.2	
134-2-27-28-spot-7	832	487	1191	7036	0	0.064	0.21	0.000	8.5	0.4	0.621	0.033	1.432	0.073	0.691	208	37.5	0.0365	0.0073	231.0	45.6	
134-2-27-28-spot-8	557	167	386	6966	0	0.021	0.21	0.000	12.5	0.9	0.353	0.030	0.693	0.080	0.335	311	36.4	0.0532	0.0061	334.1	37.6	
134-2-27-28-spot-9	1173	483	1131	6130	72	0.061	0.18	0.002	5.2	0.2	0.437	0.021	0.962	0.040	0.465	608	51.0	0.1024	0.0098	628.5	57.1	
134-2-27-28-spot-10	864	390	860	5575	13	0.047	0.17	0.000	6.5	0.5	0.452	0.031	0.995	0.119	0.481	477	65.7	0.0805	0.0150	499.0	89.5	
134-2-27-28-spot-11	307	78	205	5205	0	0.011	0.16	0.000	17.0	1.5	0.311	0.037	0.668	0.310	0.323	250	34.4	0.0400	0.0055	252.5	33.9	
134-2-27-28-spot-12	792	390	929	7337	11	0.050	0.21	0.000	9.3	0.7	0.510	0.041	1.173	0.147	0.566	285	48.8	0.0468	0.0101	294.9	61.9	
134-2-27-28-spot-13	576	314	750	6170	8	0.041	0.19	0.000	10.7	0.8	0.578	0.035	1.302	0.087	0.629	197	36.7	0.0347	0.0084	219.7	52.0	
Sample: 134-2-40-42																						
134-2-40-42-spot-1	1525	646	1452	2987	248	0.076	0.09	0.007	2.0	0.1	0.441	0.019	0.939	0.052	0.454	1550	115.3	0.2789	0.0277	1585.8	139.9	
134-2-40-42-spot-2	2770	1499	3648	8256	352	0.187	0.23	0.011	3.0	0.1	0.556	0.014	1.312	0.042	0.634	746	56.4	0.1229	0.0159	747.1	91.2	
134-2-40-42-spot-3	1568	577	1347	7610	483	0.069	0.21	0.015	4.9	0.2	0.391	0.017	0.848	0.042	0.409	725	52.5	0.1217	0.0109	740.2	62.4	
134-2-40-42-spot-4	1957	965	2205	6408	313	0.113	0.18	0.009	3.3	0.1	0.509	0.019	1.120	0.045	0.541	790	66.8	0.1401	0.0156	845.5	88.1	
134-2-40-42-spot-5	3610	2361	5651	3948	279	0.289	0.11	0.008	1.1	0.0	0.659	0.019	1.560	0.042	0.754	1270	147.7	0.2253	0.0569	1309.9	299.5	

Sample Information	Counts sec ⁻¹ concentrations								Corrected ratios						Comm on Pb	Common Pb- corrected ratios and ages						
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ Pb _C / ²⁰⁶ Pb	2s		f206c via208	Projected T-W age		²⁰⁸ Pb _C -cor ²⁰⁶ Pb- ²³⁸ U			
						ppm											(Ma)	2s	ratio	2s	(Ma)	2s
134-2-40-42-spot-6	2113	1227	2941	3876	221	0.151	0.11	0.007	1.8	0.1	0.596	0.022	1.387	0.060	0.670	1030	112.9	0.1801	0.0318	1067.3	173.9	
134-2-40-42-spot-7	2557	1463	3328	6389	314	0.171	0.18	0.009	2.5	0.1	0.583	0.019	1.297	0.045	0.626	803	77.8	0.1496	0.0208	898.5	116.4	
134-2-40-42-spot-8	836	276	584	4305	23	0.030	0.12	0.001	5.1	0.3	0.345	0.022	0.698	0.056	0.337	752	62.8	0.1287	0.0116	780.6	66.1	
134-2-40-42-spot-9	5580	3915	9192	8001	366	0.474	0.22	0.011	1.4	0.1	0.709	0.015	1.645	0.036	0.794	716	93.4	0.1433	0.0386	863.4	217.6	
134-2-40-42-spot-10	2687	1567	3696	4116	282	0.191	0.12	0.009	1.5	0.1	0.598	0.025	1.369	0.064	0.661	1214	148.2	0.2211	0.0400	1287.8	211.4	
134-2-40-42-spot-11	818	367	809	5402	0	0.042	0.15	0.000	6.6	0.4	0.483	0.031	0.989	0.082	0.478	430	52.3	0.0791	0.0093	490.8	55.8	
134-2-40-42-spot-12	2670	1606	3735	2816	259	0.195	0.08	0.008	1.1	0.1	0.618	0.018	1.391	0.046	0.672	1600	165.3	0.3112	0.0593	1746.7	291.6	
Sample: 134-2-128-129																						
134-2-128-129_spot-1	1033	413	923	3608	19	0.050	0.11	0.001	3.5	0.2	0.423	0.021	0.893	0.051	0.431	928	78.6	0.1628	0.0164	972.5	90.9	
134-2-128-129_spot-2	1015	394	927	5284	8	0.050	0.16	0.000	5.2	0.3	0.414	0.021	0.913	0.056	0.441	644	53.3	0.1074	0.0103	657.6	59.8	
134-2-128-129_spot-3	1303	471	1081	4686	62	0.059	0.14	0.002	3.6	0.2	0.374	0.018	0.827	0.048	0.399	1004	70.5	0.1670	0.0144	995.5	79.3	
Sample: 136-2-136-137																						
136-2-136-137-spot-1	2213	1016	2399	5542	217	0.130	0.16	0.007	2.5	0.1	0.474	0.017	1.078	0.042	0.521	1127	78.7	0.1914	0.0186	1128.7	100.8	
136-2-136-137-spot-2	1985	833	1906	6048	236	0.104	0.18	0.008	3.0	0.1	0.429	0.016	0.954	0.038	0.461	1043	72.8	0.1770	0.0173	1050.5	94.7	
136-2-136-137-spot-3	1602	702	1651	5390	39	0.090	0.16	0.001	3.4	0.2	0.460	0.020	1.029	0.047	0.497	879	75.3	0.1495	0.0167	897.9	93.8	
136-2-136-137-spot-4	1050	516	1225	6062	0	0.067	0.18	0.000	5.8	0.4	0.523	0.026	1.167	0.063	0.563	436	54.0	0.0756	0.0115	469.9	69.0	
136-2-136-137-spot-5	1424	624	1422	4958	18	0.076	0.15	0.000	3.5	0.2	0.459	0.021	0.998	0.049	0.482	853	73.8	0.1487	0.0156	893.7	87.6	
136-2-136-137-spot-6	1774	686	1610	3830	292	0.086	0.12	0.009	2.2	0.1	0.403	0.014	0.895	0.037	0.432	1540	96.6	0.2630	0.0245	1505.4	125.0	
136-2-136-137-spot-7	1782	728	1665	3878	255	0.090	0.11	0.008	2.2	0.1	0.429	0.017	0.924	0.037	0.446	1441	100.0	0.2545	0.0235	1461.4	120.9	
136-2-136-137-spot-8	1798	675	1570	5976	180	0.086	0.18	0.006	3.3	0.1	0.385	0.016	0.868	0.043	0.419	1058	68.4	0.1747	0.0145	1038.1	79.8	
136-2-136-137-spot-9	1894	744	1682	5079	357	0.090	0.15	0.011	2.7	0.1	0.405	0.015	0.876	0.038	0.423	1246	76.2	0.2151	0.0172	1256.1	91.5	
Sample: 137-1-43-44																						
137-1-43-44-spot-1	1465	553	1235	4464	177	0.067	0.13	0.006	3.0	0.2	0.395	0.018	0.836	0.044	0.404	1126	81.8	0.1957	0.0177	1152.2	95.4	
137-1-43-44-spot-2	1428	476	1107	4037	152	0.060	0.12	0.005	2.8	0.1	0.349	0.015	0.768	0.040	0.371	1330	83.7	0.2225	0.0187	1295.3	98.7	
137-1-43-44-spot-3	1415	543	1183	6135	167	0.064	0.20	0.006	4.3	0.2	0.401	0.016	0.832	0.038	0.402	791	60.8	0.1380	0.0135	833.4	76.7	
137-1-43-44-spot-4	2145	508	1052	7027	174	0.057	0.21	0.005	3.3	0.1	0.243	0.010	0.485	0.027	0.234	1393	62.8	0.2338	0.0132	1354.4	68.8	
137-1-43-44-spot-5	1346	442	997	6061	141	0.054	0.18	0.004	4.5	0.2	0.346	0.018	0.736	0.044	0.355	855	59.5	0.1432	0.0114	862.5	64.3	
137-1-43-44-spot-6	1543	626	1446	3426	95	0.078	0.10	0.003	2.2	0.1	0.428	0.019	0.932	0.047	0.450	1417	102.4	0.2476	0.0228	1425.9	117.8	
137-1-43-44-spot-7	1379	537	1231	2865	113	0.066	0.09	0.004	2.1	0.1	0.410	0.020	0.886	0.046	0.428	1574	123.1	0.2754	0.0285	1568.2	144.0	

Sample Information	Counts sec ⁻¹ concentrations								Corrected ratios						Comm on Pb	Common Pb- corrected ratios and ages						
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ Pb/ _C / ²⁰⁶ Pb	2s		f _{206c} via ₂₀₈	Projected T-W age		²⁰⁸ Pb _C -cor ²⁰⁶ Pb- ²³⁸ U			
						ppm											(Ma)	2s	ratio	2s	(Ma)	2s
137-1-43-44-spot-8	1510	512	1132	5292	123	0.061	0.16	0.004	3.5	0.2	0.352	0.015	0.745	0.036	0.360	1076	72.8	0.1826	0.0159	1081.4	86.7	
137-1-43-44-spot-9	1483	498	1119	4544	145	0.060	0.13	0.005	3.1	0.2	0.351	0.016	0.748	0.040	0.361	1226	80.8	0.2084	0.0175	1220.6	93.2	
Sample: 137-2-27-28																						
137-2-27-28- fine-graines-spot-1	2127	889	2007	9660	92	0.105	0.27	0.003	4.5	0.2	0.437	0.015	0.942	0.038	0.455	696	44.5	0.1200	0.0096	730.6	55.2	
137-2-27-28- fine-graines-spot-2	3940	2567	6076	8048	46	0.318	0.23	0.001	2.0	0.1	0.654	0.018	1.542	0.040	0.745	714	95.5	0.1250	0.0383	759.3	219.5	
137-2-27-28- fine-graines-spot-3	1824	835	1944	7911	49	0.102	0.23	0.001	4.3	0.2	0.478	0.018	1.065	0.044	0.514	656	48.8	0.1120	0.0101	684.3	58.5	
137-2-27-28- fine-graines-spot-4	1897	752	1726	9289	55	0.091	0.27	0.002	4.9	0.2	0.415	0.016	0.909	0.035	0.439	682	43.7	0.1146	0.0087	699.2	50.2	
137-2-27-28- fine-graines-spot-5	2149	997	2301	9073	36	0.122	0.26	0.001	4.2	0.2	0.476	0.016	1.070	0.040	0.517	677	49.2	0.1144	0.0116	698.5	66.9	
137-2-27-28- fine-graines-spot-6	2532	1485	3474	8192	32	0.184	0.23	0.001	3.2	0.1	0.605	0.020	1.372	0.050	0.662	573	61.5	0.1043	0.0151	639.7	88.4	
137-2-27-28- spot-1	1927	863	2097	5069	230	0.109	0.14	0.007	2.6	0.1	0.469	0.020	1.081	0.042	0.522	1089	84.2	0.1816	0.0176	1075.7	96.2	
137-2-27-28- spot-2	2384	1044	2362	4678	216	0.122	0.13	0.006	2.0	0.1	0.449	0.014	0.984	0.037	0.475	1518	91.4	0.2675	0.0238	1528.1	120.9	
137-2-27-28- spot-3	1588	706	1613	6373	180	0.084	0.18	0.005	4.0	0.2	0.466	0.017	1.012	0.041	0.489	730	52.5	0.1274	0.0113	773.2	64.9	
137-2-27-28- spot-4	2689	1218	2833	5248	214	0.148	0.16	0.007	2.0	0.1	0.475	0.017	1.048	0.038	0.506	1428	110.3	0.2531	0.0290	1454.3	149.1	
137-2-27-28- spot-5	2179	1023	2362	9704	259	0.124	0.28	0.008	4.5	0.2	0.490	0.017	1.080	0.042	0.522	619	48.8	0.1074	0.0110	657.6	63.8	
137-2-27-28- spot-6	2444	1061	2470	4395	204	0.129	0.12	0.006	1.8	0.1	0.450	0.014	1.004	0.037	0.485	1646	94.4	0.2865	0.0242	1624.2	121.2	
137-2-27-28- spot-7	2521	1173	2699	4171	262	0.142	0.12	0.008	1.7	0.1	0.480	0.014	1.062	0.036	0.513	1651	100.8	0.2945	0.0276	1664.1	137.5	
137-2-27-28- spot-8	2076	903	2079	5083	294	0.110	0.15	0.009	2.4	0.1	0.452	0.015	0.993	0.035	0.480	1218	82.3	0.2126	0.0201	1242.6	107.0	
137-2-27-28- spot-9	2540	1093	2402	5744	122	0.127	0.17	0.004	2.3	0.1	0.442	0.014	0.943	0.034	0.455	1347	91.7	0.2409	0.0240	1391.3	124.8	
137-2-27-28- spot-10	2230	977	2137	6420	131	0.113	0.18	0.004	2.9	0.1	0.454	0.014	0.955	0.039	0.461	1037	64.2	0.1871	0.0154	1105.5	83.4	
137-2-27-28- spot-11	2557	1213	2835	7082	127	0.151	0.20	0.004	2.8	0.1	0.487	0.015	1.106	0.038	0.534	988	65.6	0.1681	0.0165	1001.8	90.9	
137-2-27-28- spot-12	2375	993	2312	5975	176	0.123	0.17	0.005	2.5	0.1	0.432	0.019	0.969	0.056	0.468	1245	97.2	0.2115	0.0225	1236.6	119.9	
137-2-27-28- spot-13	2601	1421	3241	6697	172	0.171	0.19	0.005	2.6	0.1	0.568	0.024	1.243	0.055	0.601	824	90.1	0.1551	0.0194	929.6	108.1	
137-2-27-28- spot-14	2900	1374	3119	9143	203	0.164	0.26	0.006	3.2	0.1	0.489	0.015	1.073	0.034	0.518	867	56.1	0.1529	0.0129	917.0	72.2	
137-2-27-28- spot-15	2423	1013	2262	8936	146	0.117	0.25	0.004	3.7	0.1	0.430	0.014	0.931	0.036	0.450	866	50.9	0.1492	0.0114	896.6	63.8	
137-2-27-28- spot-16	2298	1007	2329	5001	156	0.121	0.14	0.005	2.2	0.1	0.460	0.017	1.009	0.036	0.487	1337	89.2	0.2356	0.0205	1363.8	106.8	
137-2-27-28- spot-17	2825	1247	2973	5504	177	0.155	0.15	0.005	1.9	0.1	0.455	0.014	1.048	0.039	0.506	1505	87.2	0.2535	0.0224	1456.8	115.3	
137-2-27-28- spot-18	2129	875	2014	9020	210	0.105	0.25	0.006	4.2	0.2	0.428	0.016	0.942	0.035	0.455	761	49.3	0.1286	0.0102	780.2	58.2	
137-2-27-28- spot-19	2133	972	2231	3577	173	0.117	0.10	0.005	1.7	0.1	0.470	0.015	1.039	0.036	0.502	1673	104.6	0.2970	0.0274	1676.5	136.3	
137-2-27-28- spot-20	1956	879	2088	5487	206	0.109	0.16	0.006	2.8	0.1	0.464	0.017	1.062	0.042	0.513	1037	73.1	0.1736	0.0166	1032.1	91.4	

Sample Information	Counts sec ⁻¹ concentrations								Corrected ratios							Comm on Pb	Common Pb- corrected ratios and ages					
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ Pb/ _C / ²⁰⁶ Pb	2s	f206c via208		Projected T-W age		²⁰⁸ Pb _C -cor ²⁰⁶ Pb- ²³⁸ U			
						ppm											(Ma)	2s	ratio	2s	(Ma)	2s
137-2-27-28- spot-21	2525	1096	2489	2988	141	0.130	0.08	0.004	1.2	0.0	0.447	0.014	0.978	0.039	0.472	2495	133.1	0.4458	0.0391	2376.7	174.3	
Sample: 137-2-73-74																						
137-2-73-74-spot-1	2840	1692	4073	3978	235	0.218	0.12	0.007	1.4	0.1	0.589	0.019	1.429	0.056	0.690	1370	135.1	0.2213	0.0522	1288.8	275.6	
137-2-73-74-spot-2	1062	421	980	3236	90	0.053	0.10	0.003	3.0	0.2	0.412	0.020	0.918	0.054	0.444	1085	87.1	0.1826	0.0191	1081.4	103.9	
137-2-73-74-spot-3	1229	502	1163	4920	125	0.063	0.19	0.005	4.0	0.3	0.428	0.022	0.942	0.052	0.455	804	88.5	0.1361	0.0205	822.7	116.3	
137-2-73-74-spot-4	1443	602	1426	2986	128	0.077	0.09	0.004	2.1	0.1	0.429	0.018	0.981	0.047	0.474	1513	118.0	0.2541	0.0296	1459.8	152.3	
137-2-73-74-spot-5	1537	640	1510	2922	148	0.081	0.09	0.005	1.9	0.1	0.431	0.019	0.975	0.046	0.471	1634	121.7	0.2784	0.0295	1583.4	148.9	
137-2-73-74-spot-6	1216	523	1158	5592	198	0.062	0.17	0.006	4.6	0.2	0.450	0.021	0.947	0.053	0.457	666	56.8	0.1180	0.0114	718.9	65.9	

Counts for ²⁰⁶Pb are taken from Iolite; Counts for ²⁰⁷Pb are adjusted using mass bias of one mass unit and power law); Counts for ²⁰⁸Pb are adjusted using the final ²⁰⁶ counts and mass bias power law and two mass units; ²³⁸U counts are derived by multiplying the ²⁰⁶Pb counts by the ²³⁸U/²⁰⁶Pb ratio; Ppm values are derived from Iolite where they are adjusted to accepted values; F_{206c} via 208 is the common lead proportion and is derived by subtraction of ²⁰⁸Pb_{rad} from ²⁰⁸Pb_{total} using T-W age; ²⁰⁸Pb_{com} – corrected ratios and ages are derived by 8-6 TW regressions with the x-axis . *- results of these measurements were considered unreliable due to the low concentration of radiogenic material and high common lead concentrations. Mean value of ²⁰⁸Pb_c/²⁰⁶Pb ratios for these data points were used as an anchor to calculate the single data point ages. **- measurements were considered unreliable and were excluded from data analyses.

APPENDIX 3.2. Results of U-Pb measurements of standards (WC-1, Mud Tank zircon, NIST 614) for dolomite and calcite samples from Resolution Guyot

U-Pb measurements for Resolution Guyot were done in time period between 29/09/2016-28/09/2016; 03/10/2016-04/10/2016; 09/03/2017-10/03/2017. Calcite and dolomite samples were measured together. Due to lack of dolomite standard, it was decided to measured dolomite samples using WC-1 calcite standard.

Table 1. Detailed information for U-Pb measurements of standard material, Resolution Guyot

Sample Information (date- time of taken measurement)	Counts sec ⁻¹ . concentrations								Corrected ratios						Commo n Pb	Common Pb- corrected ratios and ages						
																Projected T-W age corrected via 207 for Pbc		208PbC-cor 206Pb-238U		208PbC-cor Age		
	206pb	207pb	208pb	238U	232Th	Pb	U	Th	238U/206Pb	2s	207pb/206pb	2s	208PbC/206Pb	2s				f206c via208	(Ma)	2s	ratio	2s
	ppm																					
WC-1																						
09/03/2017 (5) 14:30:15.02+D6: D83	7670	662	697	174396	10	0.034	4.64	0.000	22.7	0.9	0.088	0.003	0.091	0.006	0.044	265	10.2	0.0421	0.0018	264.9	12.8	
09/03/2017 (5) 14:34:51.69	7485	689	840	173351	40	0.042	4.54	0.001	23.2	0.9	0.094	0.003	0.112	0.007	0.054	258	10.1	0.0408	0.0017	246.3	12.3	
09/03/2017 (5) 14:44:07.19	9070	680	616	217357	32	0.031	5.81	0.001	24.0	0.9	0.077	0.003	0.068	0.006	0.033	255	9.6	0.0404	0.0016	243.7	11.9	
09/03/2017 (5) 14:54:48.83	8430	762	853	195114	46	0.043	5.25	0.001	23.1	0.9	0.093	0.003	0.101	0.006	0.049	259	10.0	0.0411	0.0017	260.2	12.1	
09/03/2017 (5) 15:22:17.06	7890	570	420	183040	9	0.022	5.06	0.000	23.2	0.9	0.074	0.003	0.053	0.006	0.026	265	10.2	0.0420	0.0017	266.0	13.3	
09/03/2017 (5) 15:42:06.40	8590	734	768	206169	50	0.039	5.49	0.001	24.0	0.9	0.087	0.003	0.089	0.005	0.043	251	9.5	0.0399	0.0016	251.2	11.8	
09/03/2017 (5) 16:33:59.65	8780	876	1080	203086	40	0.056	5.62	0.001	23.1	0.9	0.102	0.003	0.123	0.006	0.059	256	10.0	0.0407	0.0017	262.6	12.5	
09/03/2017 (5) 18:55:56.85	7080	629	670	174864	23	0.034	4.71	0.001	24.7	0.7	0.090	0.003	0.095	0.008	0.046	243	7.3	0.0386	0.0012	250.4	11.4	
09/03/2017 (5) 19:00:33.93	8130	707	757	193814	16	0.039	5.30	0.000	23.8	0.7	0.089	0.003	0.093	0.006	0.045	252	7.3	0.0401	0.0012	253.0	10.5	
09/03/2017 (5) 19:23:26.33	6730	632	718	167540	9	0.038	4.66	0.000	24.9	0.7	0.096	0.003	0.107	0.007	0.052	240	7.1	0.0381	0.0012	249.7	10.7	
09/03/2017 (5) 19:38:36.19	8220	611	494	194313	6	0.026	5.42	0.000	23.6	0.7	0.076	0.002	0.060	0.004	0.029	259	7.3	0.0411	0.0012	258.4	10.0	
09/03/2017 (5) 19:53:57.47	5255	485	489	124599	9	0.026	3.47	0.000	23.7	0.7	0.095	0.004	0.093	0.011	0.045	252	8.0	0.0403	0.0013	278.3	12.6	
09/03/2017 (5) 20:15:14.46	5157	433	472	121461	8	0.025	3.43	0.000	23.6	0.7	0.086	0.004	0.092	0.010	0.044	257	8.2	0.0406	0.0013	244.3	13.1	
09/03/2017 (5) 20:32:17.42	6780	762	1044	153333	27	0.055	4.32	0.001	22.6	0.8	0.114	0.006	0.154	0.010	0.074	257	9.4	0.0409	0.0015	267.6	15.6	
09/03/2017 (5) 20:50:23.17	7070	699	833	162097	10	0.044	4.53	0.000	22.9	0.7	0.101	0.005	0.118	0.009	0.057	258	8.3	0.0411	0.0013	270.3	14.7	
09/03/2017 (5) 21:26:55.54	7850	601	510	186814	10	0.026	5.17	0.000	23.8	0.7	0.078	0.003	0.065	0.006	0.031	257	7.3	0.0407	0.0012	258.2	10.8	
09/03/2017 (5) 21:58:58.55	6855	546	536	159977	13	0.028	4.53	0.000	23.3	0.7	0.081	0.003	0.078	0.010	0.038	261	7.6	0.0412	0.0013	251.8	11.0	

Sample Information (data- time of taken measurement)	Counts sec ⁻¹ . concentrations								Corrected ratios							Commo n Pb	Common Pb- corrected ratios and ages					
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ Pb _C / ²⁰⁶ Pb	2s	f206c via208		Projected T-W age corrected via 207 for Pbc		²⁰⁸ Pb _C -cor ²⁰⁶ Pb- ²³⁸ U		²⁰⁸ Pb _C -cor Age	
						ppm											(Ma)	2s	ratio	2s	(Ma)	2s
09/03/2017 (5) 22:26:25.49	9030	817	940	211862	44	0.050	5.98	0.001	23.5	0.7	0.093	0.003	0.104	0.006	0.050	255	7.3	0.0405	0.0012	252.0	11.1	
09/03/2017 (5) 22:53:54.05	6726	552	602	162821	10	0.031	4.49	0.000	24.2	0.7	0.084	0.003	0.089	0.009	0.043	251	7.4	0.0395	0.0012	233.7	10.3	
09/03/2017 (5) 23:21:20.75	7640	679	810	178448	41	0.042	4.92	0.001	23.4	0.7	0.091	0.003	0.106	0.007	0.051	257	7.5	0.0406	0.0013	241.5	10.6	
09/03/2017 (5) 23:44:12.25	5771	507	570	138208	7	0.030	3.87	0.000	23.9	0.7	0.090	0.003	0.099	0.006	0.048	251	7.5	0.0398	0.0012	244.9	11.1	
09/03/2017 (5) 23:45:43.47	5182	506	597	117242	0	0.031	3.29	0.000	22.6	0.7	0.100	0.004	0.115	0.010	0.056	262	8.2	0.0417	0.0013	272.1	13.4	
10/03/2017 (6) 12:05:29.28	5944	508	554	146312	11	0.030	4.15	0.000	24.6	0.8	0.087	0.004	0.093	0.010	0.045	245	8.1	0.0388	0.0013	238.3	13.2	
10/03/2017 (6) 12:10:06.77	4401	348	314	103478	0	0.017	2.94	0.000	23.5	0.8	0.082	0.004	0.071	0.008	0.035	258	8.6	0.0411	0.0014	260.5	13.6	
10/03/2017 (6) 12:28:22.32	7220	755	1003	167959	42	0.054	4.81	0.001	23.3	0.7	0.107	0.003	0.139	0.006	0.067	253	7.9	0.0401	0.0013	253.3	10.7	
10/03/2017 (6) 12:43:34.79	6832	546	546	170311	6	0.029	4.98	0.000	24.9	0.8	0.082	0.003	0.080	0.005	0.039	244	7.3	0.0386	0.0012	235.6	9.9	
10/03/2017 (6) 12:57:22.38	3628	364	415	83077	0	0.022	2.41	0.000	22.9	0.9	0.104	0.006	0.114	0.016	0.055	258	10.3	0.0413	0.0017	283.5	17.1	
10/03/2017 (6) 13:18:37.02	5756	461	426	145237	0	0.023	4.21	0.000	25.2	0.8	0.082	0.004	0.074	0.007	0.036	241	7.9	0.0382	0.0013	244.7	12.3	
10/03/2017 (6) 13:32:20.41	7585	859	1256	170170	39	0.068	4.97	0.001	22.4	0.7	0.116	0.004	0.166	0.008	0.080	259	8.6	0.0410	0.0014	250.4	11.8	
10/03/2017 (6) 13:53:39.02	5934	428	330	144542	0	0.018	4.23	0.000	24.4	0.8	0.074	0.003	0.056	0.006	0.027	252	8.4	0.0400	0.0014	250.1	12.9	
10/03/2017 (6) 14:07:21.86	6469	719	990	149948	30	0.053	4.32	0.001	23.2	0.7	0.114	0.004	0.153	0.008	0.074	251	8.0	0.0400	0.0013	257.7	11.5	
10/03/2017 (6) 14:28:41.12	7041	702	952	158516	28	0.052	4.60	0.001	22.5	0.7	0.102	0.004	0.135	0.007	0.065	263	8.5	0.0415	0.0014	244.4	11.6	
10/03/2017 (6) 14:46:53.77	7960	867	1175	180877	69	0.064	5.30	0.002	22.7	0.7	0.110	0.004	0.147	0.008	0.071	257	8.1	0.0409	0.0014	262.1	12.3	
10/03/2017 (6) 15:03:45.18	6042	493	446	144983	10	0.024	4.15	0.000	24.0	0.8	0.084	0.003	0.074	0.009	0.036	253	8.4	0.0402	0.0014	262.6	12.8	
10/03/2017 (6) 15:21:55.87	7750	817	1115	179375	29	0.061	5.26	0.001	23.1	0.8	0.107	0.004	0.144	0.008	0.069	254	8.4	0.0402	0.0014	249.0	11.5	
10/03/2017 (6) 15:38:50.95	6102	608	767	146199	0	0.042	4.32	0.000	24.0	0.8	0.102	0.004	0.126	0.009	0.061	247	8.0	0.0392	0.0013	248.4	12.3	
10/03/2017 (6) 16:06:15.26	7549	735	995	173515	25	0.054	5.08	0.001	23.0	0.7	0.099	0.003	0.132	0.007	0.064	258	8.3	0.0407	0.0014	235.2	10.4	
29/09/2016 (5) 14:36:39.79	4436	425	517	102102	17	0.038	3.99	0.000	23.0	0.8	0.098	0.004	0.116	0.008	0.056	258	9.4	0.0410	0.0016	257.3	13.8	
29/09/2016 (5) 14:47:41.36	4276	406	511	99548	16	0.038	3.88	0.000	23.3	0.8	0.097	0.005	0.119	0.012	0.058	256	9.8	0.0405	0.0016	245.3	16.1	
29/09/2016 (5) 15:10:53.71	4180	397	482	98546	64	0.036	3.93	0.003	23.6	0.9	0.097	0.005	0.115	0.010	0.056	253	9.5	0.0401	0.0016	251.1	14.6	
29/09/2016 (5) 15:35:45.10	4555	460	599	108347	19	0.045	4.31	0.001	23.8	0.8	0.102	0.004	0.131	0.009	0.063	249	9.0	0.0394	0.0015	246.0	13.2	
29/09/2016 (5) 15:46:32.87	4652	414	449	109882	12	0.034	4.34	0.000	23.6	0.8	0.090	0.005	0.096	0.009	0.047	254	9.4	0.0404	0.0015	257.9	15.4	
29/09/2016 (5) 16:19:07.95	4568	435	536	105335	48	0.040	4.17	0.002	23.1	0.8	0.096	0.004	0.117	0.010	0.057	259	9.5	0.0409	0.0016	252.5	14.1	
29/09/2016 (5) 16:33:05.95	4036	385	455	90726	12	0.034	3.62	0.000	22.5	0.8	0.097	0.005	0.113	0.013	0.054	265	10.3	0.0421	0.0017	267.8	17.0	
29/09/2016 (5) 16:50:22.13	4668	457	582	113083	23	0.044	4.48	0.001	24.2	0.9	0.099	0.004	0.125	0.008	0.060	245	8.8	0.0388	0.0015	240.5	12.9	

Sample Information (data- time of taken measurement)	Counts sec ⁻¹ . concentrations								Corrected ratios						Commo n Pb	Common Pb- corrected ratios and ages						
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ Pb/ ²⁰⁶ Pb	2s		f ²⁰⁶ c via ²⁰⁸	Projected T-W age corrected via ²⁰⁷ for Pbc		²⁰⁸ Pb _C -cor ²⁰⁶ Pb- ²³⁸ U		²⁰⁸ Pb _C -cor Age	
						ppm											(Ma)	2s	ratio	2s	(Ma)	2s
29/09/2016 (5) 17:01:17.96	5251	485	526	131722	39	0.040	5.22	0.001	25.1	0.9	0.093	0.004	0.100	0.008	0.048	239	8.7	0.0379	0.0014	252.5	13.6	
29/09/2016 (5) 17:05:58.56	4833	477	577	114715	18	0.044	4.55	0.001	23.7	0.8	0.099	0.004	0.119	0.009	0.058	250	9.1	0.0397	0.0015	258.5	13.8	
28/09/2016 (4) 15:05:16.18	4695	499	713	105893	24	0.054	4.24	0.001	22.6	0.8	0.108	0.005	0.152	0.011	0.073	260	9.3	0.0411	0.0015	242.4	13.8	
28/09/2016 (4) 15:11:36.54	4898	597	904	109756	45	0.068	4.44	0.002	22.4	0.7	0.124	0.004	0.184	0.010	0.089	256	8.6	0.0407	0.0015	255.3	12.6	
28/09/2016 (4) 15:13:06.86	5206	561	736	119614	42	0.056	4.80	0.002	23.0	0.7	0.109	0.004	0.141	0.010	0.068	255	8.5	0.0406	0.0014	265.8	12.8	
28/09/2016 (4) 15:14:39.16	5176	560	738	121834	50	0.056	4.89	0.002	23.5	0.8	0.110	0.004	0.143	0.010	0.069	249	8.3	0.0396	0.0014	260.0	12.7	
28/09/2016 (4) 15:35:21.09	4103	435	569	93034	28	0.043	3.75	0.001	22.7	0.8	0.107	0.005	0.139	0.010	0.067	259	9.2	0.0412	0.0015	266.1	14.6	
28/09/2016 (4) 15:41:41.65	4322	470	631	102430	45	0.048	4.14	0.002	23.7	0.8	0.111	0.005	0.146	0.012	0.070	247	8.3	0.0392	0.0014	255.2	13.3	
28/09/2016 (4) 15:43:15.33	4822	501	663	113502	21	0.051	4.58	0.001	23.5	0.8	0.106	0.004	0.137	0.011	0.066	250	8.6	0.0397	0.0014	249.8	13.0	
28/09/2016 (4) 15:44:45.59	5333	630	878	117809	35	0.067	4.79	0.001	22.1	0.7	0.119	0.005	0.164	0.012	0.079	261	8.8	0.0417	0.0015	279.4	13.6	
28/09/2016 (4) 16:13:27.60	4155	414	490	96548	22	0.038	3.94	0.001	23.2	0.8	0.101	0.005	0.118	0.009	0.057	255	9.5	0.0406	0.0016	270.7	14.9	
28/09/2016 (4) 16:19:46.83	3366	291	328	77418	7	0.025	3.17	0.000	23.0	0.8	0.087	0.004	0.097	0.014	0.047	262	9.2	0.0414	0.0015	250.3	13.9	
28/09/2016 (4) 16:21:19.40	5292	565	734	125580	49	0.057	5.15	0.002	23.7	0.8	0.107	0.004	0.139	0.010	0.067	248	8.2	0.0393	0.0014	258.8	12.3	
28/09/2016 (4) 16:22:53.21	5207	589	810	121915	45	0.063	5.01	0.002	23.4	0.8	0.115	0.004	0.155	0.009	0.075	248	8.2	0.0395	0.0014	260.0	12.2	
28/09/2016 (4) 16:27:43.99	5217	610	853	117023	35	0.066	4.82	0.001	22.4	0.7	0.118	0.004	0.163	0.008	0.079	258	8.7	0.0411	0.0015	272.2	13.3	
28/09/2016 (4) 16:34:06.32	5579	629	889	126684	56	0.069	5.22	0.002	22.7	0.7	0.114	0.004	0.159	0.008	0.077	256	8.4	0.0407	0.0014	257.4	12.0	
03/10/2016 (2) 17:16:43.54	4404	451	600	104492	17	0.043	4.08	0.000	23.7	0.8	0.104	0.004	0.136	0.009	0.066	249	8.3	0.0394	0.0014	243.3	12.3	
03/10/2016 (2) 17:39:53.08	5229	497	601	123689	25	0.044	4.86	0.001	23.7	0.7	0.098	0.004	0.115	0.009	0.055	252	8.0	0.0399	0.0013	250.5	11.9	
03/10/2016 (2) 17:44:52.26	5233	578	780	118069	30	0.057	4.69	0.001	22.6	0.7	0.113	0.005	0.149	0.011	0.072	258	8.7	0.0411	0.0014	268.7	13.4	
03/10/2016 (2) 18:11:07.29	5370	575	715	122942	40	0.053	4.90	0.002	22.9	0.7	0.110	0.004	0.133	0.009	0.064	256	8.3	0.0409	0.0014	279.9	12.6	
03/10/2016 (2) 18:29:18.29	3911	402	523	89539	13	0.039	3.64	0.000	22.9	0.8	0.105	0.004	0.134	0.012	0.065	257	9.1	0.0409	0.0015	258.4	13.7	
03/10/2016 (2) 19:04:03.09	4936	507	631	113819	19	0.046	4.55	0.001	23.1	0.7	0.105	0.004	0.128	0.012	0.062	256	8.4	0.0407	0.0014	267.3	13.4	
04/10/2016 (3) 11:03:32.06	4466	331	251	108032	25	0.018	4.13	0.001	24.2	0.9	0.075	0.004	0.056	0.010	0.027	253	9.1	0.0402	0.0015	259.4	14.9	
04/10/2016 (3) 11:25:29.32	4166	429	582	93657	23	0.043	3.74	0.001	22.5	0.8	0.105	0.004	0.140	0.010	0.067	262	9.3	0.0415	0.0015	251.2	13.4	
04/10/2016 (3) 11:30:15.68	4228	466	612	95377	17	0.046	3.78	0.001	22.6	0.8	0.111	0.005	0.145	0.011	0.070	259	9.2	0.0412	0.0015	275.6	14.1	
04/10/2016 (3) 11:52:05.28	4991	462	513	122289	14	0.039	4.85	0.000	24.5	0.8	0.094	0.004	0.103	0.009	0.050	244	8.4	0.0388	0.0014	254.4	12.9	
04/10/2016 (3) 12:09:22.71	4718	467	580	108239	17	0.044	4.33	0.001	22.9	0.8	0.100	0.004	0.123	0.010	0.059	259	9.2	0.0410	0.0015	261.1	14.0	

Sample Information (data- time of taken measurement)	Counts sec ⁻¹ . concentrations								Corrected ratios						Commo n Pb	Common Pb- corrected ratios and ages						
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ Pb/ ²⁰⁶ Pb	2s		f206c via208	Projected T-W age corrected via 207 for Pbc		²⁰⁸ Pb _C -cor ²⁰⁶ Pb- ²³⁸ U		²⁰⁸ Pb _C -cor Age	
						ppm											(Ma)	2s	ratio	2s	(Ma)	2s
04/10/2016 (3) 12:29:42.87	2445	238	299	58041	0	0.023	2.35	0.000	23.7	0.9	0.097	0.006	0.122	0.018	0.059	251	10.4	0.0396	0.0017	246.6	18.1	
04/10/2016 (3) 13:20:32.97	4332	430	519	102014	10	0.040	4.05	0.000	23.5	0.8	0.100	0.004	0.120	0.009	0.058	252	8.4	0.0400	0.0014	261.9	13.2	
04/10/2016 (3) 13:31:39.80	4205	320	296	99434	6	0.023	3.92	0.000	23.6	0.8	0.077	0.005	0.070	0.009	0.034	259	9.6	0.0409	0.0015	246.9	17.3	
04/10/2016 (3) 13:48:49.23	4247	335	324	101416	8	0.025	4.03	0.000	23.9	0.8	0.079	0.004	0.076	0.011	0.037	255	8.4	0.0403	0.0014	247.3	14.2	
04/10/2016 (3) 14:13:43.78	4940	412	422	118286	28	0.033	4.79	0.001	23.9	0.8	0.084	0.004	0.085	0.010	0.041	253	8.2	0.0400	0.0013	250.1	13.8	
04/10/2016 (3) 14:31:01.16	6900	607	674	168430	111	0.053	8.47	0.006	24.4	0.9	0.089	0.007	0.098	0.013	0.047	247	9.5	0.0390	0.0015	243.8	18.9	
04/10/2016 (3) 14:56:02.90	6570	650	781	150294	97	0.061	7.43	0.005	22.9	0.8	0.099	0.005	0.119	0.012	0.057	260	8.9	0.0412	0.0015	269.4	15.6	
Mud Tank Zircon																						
09/03/2017 (5) 14:36:19.85	49790	3068	7595	437247	205482	0.376	11.42	5.756	8.8	0.3	0.063	0.001	0.008	0.002	0.004	695	22.6	0.1134	0.0044	692.5	25.7	
09/03/2017 (5) 15:25:16.11	46230	2921	7083	384555	183013	0.370	10.69	5.386	8.3	0.3	0.064	0.001	0.008	0.002	0.004	731	23.8	0.1198	0.0047	729.2	27.0	
09/03/2017 (5) 15:45:05.60	48030	3032	7402	414165	195948	0.372	11.13	5.603	8.6	0.3	0.064	0.001	0.009	0.003	0.005	706	23.2	0.1154	0.0046	704.3	26.3	
09/03/2017 (5) 16:38:36.59	48650	3034	7460	413657	201215	0.375	11.08	5.610	8.5	0.3	0.064	0.001	0.004	0.002	0.002	716	23.3	0.1174	0.0046	715.3	26.4	
09/03/2017 (5) 19:02:01.81	45380	2827	6928	402418	193318	0.356	10.99	5.598	8.9	0.2	0.064	0.001	0.006	0.003	0.003	687	15.8	0.1125	0.0032	687.1	18.3	
09/03/2017 (5) 20:19:54.83	43330	2726	6589	380243	184141	0.349	10.63	5.367	8.8	0.2	0.064	0.001	0.004	0.003	0.002	694	15.9	0.1137	0.0032	694.4	18.4	
09/03/2017 (5) 20:53:26.87	43750	2742	6773	379286	184793	0.358	10.62	5.382	8.7	0.2	0.064	0.001	0.006	0.003	0.003	702	16.1	0.1150	0.0032	701.9	18.5	
09/03/2017 (5) 21:31:40.86	44590	2742	6763	380760	180889	0.351	10.51	5.388	8.5	0.2	0.062	0.001	0.006	0.003	0.003	714	16.5	0.1168	0.0033	711.9	18.9	
09/03/2017 (5) 22:01:59.97	44680	2765	6783	381261	181398	0.359	10.81	5.443	8.5	0.2	0.063	0.001	0.006	0.003	0.003	714	16.4	0.1168	0.0033	712.4	19.0	
09/03/2017 (5) 22:29:26.22	44320	2776	6802	385385	186136	0.360	10.90	5.506	8.7	0.2	0.064	0.001	0.006	0.003	0.003	701	15.9	0.1147	0.0032	699.9	18.5	
09/03/2017 (5) 22:56:55.91	45050	2812	7092	392666	186721	0.368	10.83	5.480	8.7	0.2	0.064	0.001	0.012	0.003	0.006	699	16.3	0.1141	0.0032	696.4	18.8	
09/03/2017 (5) 23:24:28.21	44160	2798	6870	382568	177709	0.352	10.49	5.318	8.7	0.2	0.064	0.001	0.013	0.003	0.007	702	16.0	0.1147	0.0032	699.9	18.5	
10/03/2017 (6) 12:11:36.33	42570	2671	6744	372055	174438	0.361	10.68	5.434	8.7	0.3	0.064	0.001	0.015	0.003	0.007	697	18.3	0.1136	0.0036	693.6	21.0	
10/03/2017 (6) 12:46:32.97	41460	2573	6405	373361	179794	0.343	10.85	5.454	9.0	0.3	0.063	0.001	0.007	0.003	0.003	677	17.7	0.1107	0.0035	676.7	20.4	
10/03/2017 (6) 13:21:38.40	40450	2565	6289	352600	169890	0.338	10.27	5.183	8.7	0.3	0.064	0.001	0.008	0.003	0.004	698	17.7	0.1143	0.0035	697.5	20.3	
10/03/2017 (6) 13:56:39.64	40510	2538	6212	355666	168238	0.335	10.35	5.184	8.8	0.3	0.064	0.001	0.009	0.003	0.004	694	17.6	0.1134	0.0035	692.6	20.2	
10/03/2017 (6) 14:31:52.87	39690	2481	6086	333594	153176	0.329	9.69	4.936	8.4	0.2	0.064	0.002	0.013	0.004	0.006	724	19.0	0.1182	0.0037	720.4	21.2	
10/03/2017 (6) 15:06:46.26	42470	2670	6589	368626	167978	0.357	10.58	5.408	8.7	0.2	0.064	0.001	0.016	0.003	0.008	702	17.7	0.1143	0.0035	697.9	20.2	
10/03/2017 (6) 15:41:49.31	40480	2538	6289	351687	160193	0.342	10.43	5.283	8.7	0.3	0.064	0.001	0.016	0.003	0.008	701	18.0	0.1142	0.0036	697.2	20.6	

Sample Information (data- time of taken measurement)	Counts sec ⁻¹ . concentrations								Corrected ratios						Commo n Pb	Common Pb- corrected ratios and ages						
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ Pb _C / ²⁰⁶ Pb	2s		f206c via208	Projected T-W age corrected via 207 for Pbc		²⁰⁸ Pb _C -cor ²⁰⁶ Pb, ²³⁸ U		²⁰⁸ Pb _C -cor Age	
						ppm											(Ma)	2s	ratio	2s	(Ma)	2s
10/03/2017 (6) 16:09:15.72	42040	2630	6483	362598	165778	0.353	10.62	5.391	8.6	0.3	0.064	0.001	0.014	0.003	0.007	706	18.1	0.1151	0.0036	702.6	20.6	
29/09/2016 (5) 14:35:08.60	34600	2166	5293	303140	140376	0.386	11.63	5.908	8.8	0.3	0.063	0.001	0.011	0.003	0.005	696	19.6	0.1135	0.0038	693.2	22.1	
29/09/2016 (5) 14:55:27.19	33230	2130	5089	297391	137790	0.377	11.58	5.876	8.9	0.3	0.064	0.001	0.011	0.003	0.005	681	19.1	0.1111	0.0037	679.3	21.6	
29/09/2016 (5) 15:14:05.05	32910	2130	5089	288718	135812	0.381	11.40	5.817	8.8	0.3	0.065	0.001	0.011	0.003	0.005	693	19.3	0.1134	0.0038	692.4	21.9	
29/09/2016 (5) 15:28:04.39	32920	2056	4935	290266	135662	0.371	11.52	5.802	8.8	0.3	0.063	0.001	0.007	0.003	0.003	692	19.2	0.1130	0.0038	690.4	21.8	
29/09/2016 (5) 15:43:29.87	33160	2099	5167	293587	138479	0.387	11.60	5.910	8.9	0.3	0.063	0.001	0.011	0.003	0.005	689	19.2	0.1123	0.0038	686.3	21.8	
29/09/2016 (5) 16:02:05.86	33060	2087	5080	292285	137914	0.380	11.48	5.869	8.8	0.3	0.063	0.001	0.009	0.003	0.004	690	19.2	0.1126	0.0038	687.9	21.8	
29/09/2016 (5) 16:16:01.77	33840	2159	5167	298354	141451	0.388	11.78	6.013	8.8	0.3	0.064	0.001	0.008	0.004	0.004	691	19.2	0.1130	0.0038	690.2	21.8	
29/09/2016 (5) 16:36:15.96	33520	2144	5070	294347	138236	0.382	11.69	5.866	8.8	0.3	0.064	0.001	0.008	0.003	0.004	693	19.4	0.1135	0.0038	692.8	21.9	
29/09/2016 (5) 16:58:14.85	28180	1780	4404	235544	112194	0.331	9.29	4.752	8.4	0.3	0.063	0.001	0.010	0.003	0.005	728	20.4	0.1190	0.0040	725.0	22.8	
29/09/2016 (5) 17:04:28.63	22750	1439	3507	180278	86314	0.264	7.12	3.657	7.9	0.3	0.064	0.002	0.008	0.004	0.004	767	21.7	0.1257	0.0042	763.4	24.1	
28/09/2016 (4) 14:55:23.74	34370	2207	5312	296318	138874	0.398	11.74	5.967	8.6	0.2	0.065	0.001	0.011	0.003	0.005	705	17.7	0.1154	0.0035	703.8	20.2	
28/09/2016 (4) 14:58:40.51	34600	2223	5215	296959	138474	0.391	11.83	6.018	8.6	0.2	0.065	0.001	0.008	0.003	0.004	709	18.2	0.1161	0.0036	707.8	20.5	
28/09/2016 (4) 15:01:56.45	34810	2182	5418	297446	138384	0.407	11.91	6.048	8.5	0.2	0.063	0.001	0.013	0.003	0.006	713	18.1	0.1163	0.0036	709.2	20.6	
28/09/2016 (4) 15:10:05.25	33450	2114	5138	291154	135347	0.387	11.72	5.958	8.7	0.3	0.064	0.001	0.011	0.003	0.005	700	18.0	0.1143	0.0035	697.5	20.4	
28/09/2016 (4) 15:17:57.93	33220	2104	5186	290547	135799	0.391	11.63	5.949	8.7	0.3	0.064	0.001	0.013	0.003	0.006	697	17.6	0.1136	0.0035	693.7	20.0	
28/09/2016 (4) 15:25:50.55	32400	2061	4848	280404	130750	0.367	11.21	5.738	8.7	0.2	0.064	0.001	0.007	0.003	0.003	703	17.8	0.1152	0.0035	702.6	20.1	
28/09/2016 (4) 15:33:49.25	31900	2030	4828	275818	128087	0.367	11.06	5.649	8.6	0.3	0.064	0.001	0.009	0.003	0.004	704	18.0	0.1151	0.0035	702.5	20.5	
28/09/2016 (4) 15:40:09.34	32380	2089	4973	280824	130634	0.379	11.33	5.782	8.7	0.3	0.065	0.001	0.011	0.003	0.006	701	18.0	0.1147	0.0035	699.8	20.4	
28/09/2016 (4) 15:48:03.75	32460	2044	5080	280902	131139	0.388	11.42	5.861	8.7	0.3	0.063	0.001	0.013	0.003	0.006	704	18.0	0.1148	0.0035	700.6	20.5	
28/09/2016 (4) 15:55:59.05	32830	2076	5051	283704	131775	0.386	11.58	5.881	8.6	0.2	0.063	0.001	0.012	0.003	0.006	705	17.7	0.1151	0.0035	702.1	20.2	
28/09/2016 (4) 16:04:01.38	32310	2012	4915	277822	129961	0.377	11.32	5.792	8.6	0.2	0.063	0.001	0.009	0.004	0.004	709	18.1	0.1158	0.0036	706.4	20.5	
28/09/2016 (4) 16:11:55.96	33090	2096	5157	287772	134137	0.397	11.71	5.950	8.7	0.2	0.064	0.001	0.013	0.003	0.006	701	17.7	0.1143	0.0035	697.4	20.1	
28/09/2016 (4) 16:18:16.84	31840	1993	5041	276401	129247	0.389	11.30	5.753	8.7	0.3	0.063	0.001	0.015	0.004	0.007	702	18.0	0.1144	0.0035	698.0	20.5	
28/09/2016 (4) 16:26:13.96	32680	2086	5004	282938	131779	0.387	11.63	5.910	8.7	0.2	0.064	0.001	0.011	0.003	0.005	703	17.7	0.1149	0.0035	701.2	20.1	
28/09/2016 (4) 16:32:35.36	31340	1970	4811	270111	126155	0.373	11.15	5.650	8.6	0.2	0.063	0.001	0.010	0.003	0.005	707	17.7	0.1154	0.0035	704.3	20.2	
28/09/2016 (4) 16:40:30.57	32620	2058	5012	282088	132156	0.389	11.66	5.946	8.6	0.2	0.063	0.001	0.010	0.003	0.005	705	17.8	0.1151	0.0035	702.1	20.2	

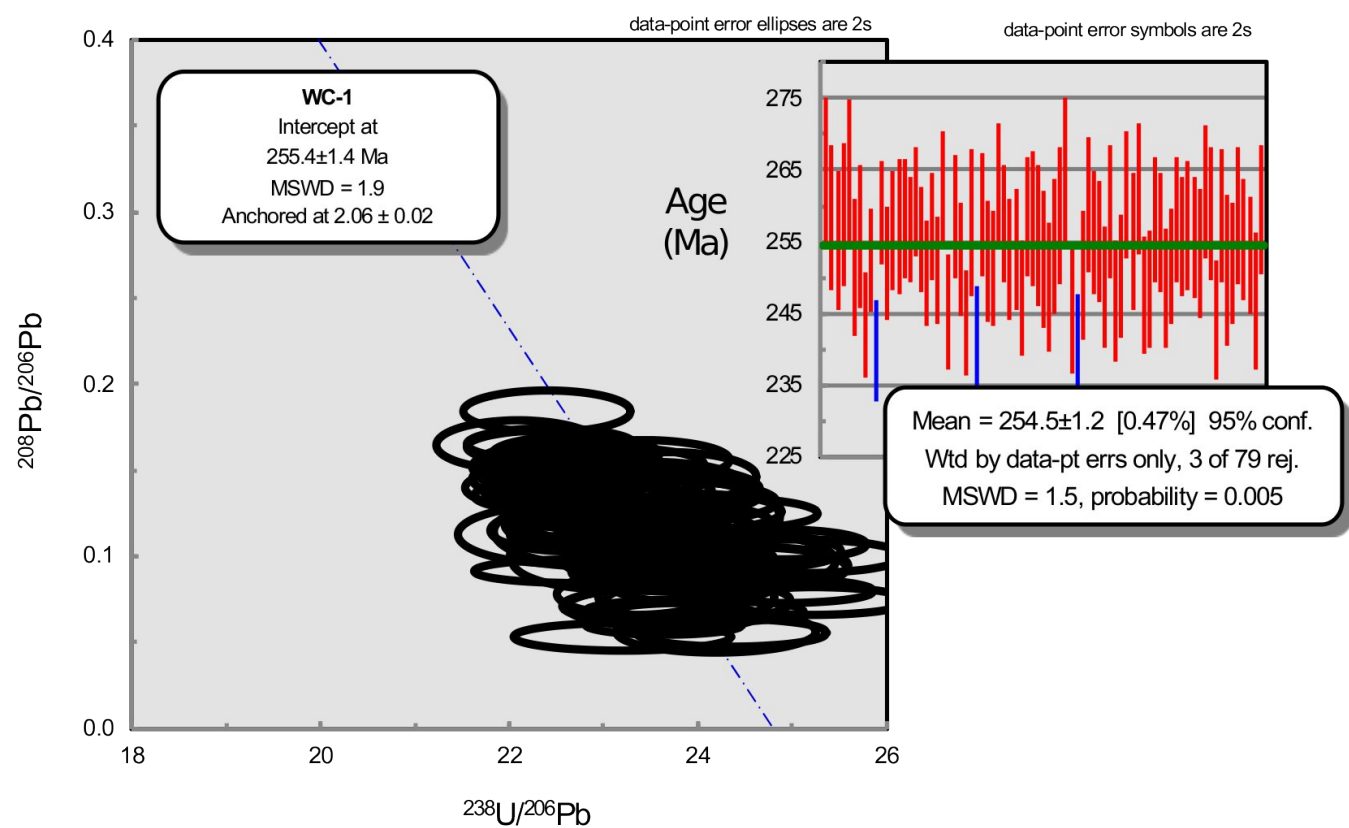
Sample Information (data- time of taken measurement)	Counts sec ⁻¹ . concentrations								Corrected ratios						Commo n Pb	Common Pb- corrected ratios and ages						
																Projected T-W age corrected via 207 for Pbc		²⁰⁸ Pb _C -cor ²⁰⁶ Pb- ²³⁸ U		²⁰⁸ Pb _C -cor Age		
	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²³⁸ U	²³² Th	Pb	U	Th	²³⁸ U/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁸ Pb _C / ²⁰⁶ Pb	2s				f206c via208	(Ma)	2s	ratio	2s
						ppm										(Ma)	2s		ratio	2s	(Ma)	2s
28/09/2016 (4) 16:43:49.48	31830	2002	4877	278236	129843	0.380	11.51	5.821	8.7	0.3	0.063	0.001	0.010	0.003	0.005	f206c via208	(Ma)	2s	ratio	2s	(Ma)	2s
28/09/2016 (4) 16:47:07.17	32110	2020	4924	278964	130595	0.384	11.56	5.862	8.7	0.2	0.063	0.001	0.010	0.003	0.005		702	17.6	0.1146	0.0035	699.1	20.1
03/10/2016 (2) 17:15:09.18	33940	2163	5186	291462	135791	0.374	11.26	5.773	8.6	0.2	0.065	0.001	0.010	0.003	0.005		708	17.4	0.1159	0.0034	706.7	19.9
03/10/2016 (2) 17:43:16.66	33890	2070	5215	284312	131926	0.380	11.23	5.718	8.4	0.2	0.062	0.001	0.012	0.003	0.006		726	17.7	0.1185	0.0035	722.1	20.1
03/10/2016 (2) 18:07:55.03	34880	2145	5215	294294	135588	0.383	11.68	5.889	8.4	0.2	0.063	0.001	0.008	0.003	0.004		722	17.4	0.1180	0.0034	719.3	19.7
03/10/2016 (2) 18:27:41.38	33330	2096	5041	281565	130062	0.374	11.42	5.755	8.4	0.2	0.064	0.001	0.010	0.003	0.005		720	17.6	0.1178	0.0035	717.9	20.0
04/10/2016 (3) 11:02:00.69	35230	2275	5312	308948	142560	0.387	11.77	5.942	8.8	0.3	0.065	0.001	0.010	0.003	0.005		694	18.4	0.1135	0.0036	693.0	20.9
04/10/2016 (3) 11:28:47.51	34380	2191	5167	298064	139259	0.386	11.78	5.966	8.7	0.3	0.064	0.001	0.007	0.003	0.004		702	18.4	0.1149	0.0036	701.4	20.7
04/10/2016 (3) 11:49:10.49	32850	2126	5022	287491	136026	0.378	11.28	5.750	8.8	0.3	0.065	0.002	0.008	0.004	0.004		695	18.6	0.1138	0.0036	694.9	21.0
04/10/2016 (3) 12:07:55.37	32640	2066	4886	284365	133953	0.370	11.32	5.735	8.7	0.3	0.063	0.001	0.005	0.004	0.003		699	18.6	0.1145	0.0036	698.7	21.0
04/10/2016 (3) 12:34:31.51	32750	2055	5099	282121	133068	0.389	11.30	5.729	8.6	0.3	0.063	0.001	0.011	0.003	0.005		708	18.6	0.1155	0.0037	704.4	21.1
04/10/2016 (3) 13:30:05.07	34650	2183	5351	304494	143185	0.406	12.02	6.070	8.8	0.2	0.063	0.001	0.010	0.004	0.005		694	17.0	0.1132	0.0033	691.5	19.3
04/10/2016 (3) 13:56:39.92	34130	2175	5186	299739	139546	0.400	11.91	6.038	8.8	0.2	0.064	0.001	0.009	0.003	0.005		693	16.7	0.1133	0.0033	692.1	19.1
04/10/2016 (3) 14:12:14.19	34000	2120	5138	299104	137739	0.403	12.08	6.143	8.8	0.2	0.063	0.001	0.010	0.003	0.005		694	16.7	0.1131	0.0033	690.9	19.0
04/10/2016 (3) 14:38:51.02	33160	2071	5109	239555	110700	0.400	11.88	6.045	7.2	0.2	0.063	0.001	0.013	0.003	0.006		839	22.5	0.1376	0.0044	830.9	25.0
04/10/2016 (3) 14:57:35.02	33680	2112	5167	244958	113210	0.402	12.08	6.116	7.3	0.2	0.063	0.001	0.012	0.003	0.006		833	22.3	0.1367	0.0044	825.9	24.9

Counts for ²⁰⁶Pb are taken from Iolite;

Counts for ²⁰⁶Pb are taken from Iolite; Counts for ²⁰⁷Pb adjusted using mass-bias using one mass unit and power law; Counts for ²⁰⁸Pb adjusted using final 206 counts and mass bias power law and two mass units; ²³⁸U counts are derived by multiplying the ²⁰⁶Pb counts by the ²³⁸U/²⁰⁶Pb ratio; Ppm values are derived from Iolite where they are adjusted to accepted values; F206c via 208 is the common lead proportion and is derived by subtraction of ²⁰⁸Pb_{rad} from ²⁰⁸Pb_{total} using T-W age; ²⁰⁸Pb_{com} – corrected ratios and ages are derived by 8-6TW regressions with X-axis .

Table 1. (Continued)

Name	U(ppm)	Th(ppm)	Pb(ppm)	²⁰⁶ Pb/ ²³⁸ U	2s (Ma)	n	MSWD	²⁰⁷ Pb/ ²⁰⁶ Pb	2s (Ma)	n	MSWD	²⁰⁸ Pb _C / ²⁰⁶ Pb	2s(Ma)	n	MSWD
NIST 614	0.823	730	2.6	0.738	0.172	35	0.98	0.851	0.0096	38	0.98	2.002	0.0214	38	1.5



Appendix 3.2. Figure 1. 86 T-W diagram illustrating measured data for WC-1 standard. The weighted mean plot of individual analyses is presented in the upper right corner of the 86 T-W diagram. Detailed results are presented in Table 1. Appendix 3.2. Common $^{208}\text{Pb}/^{206}\text{Pb}$ used to calculate the age with the value of 2.06 ± 0.02 . Isoplot was used to calculate the weighted mean value.