Stable Isotope Geochemistry
Carbon Chemistry Project

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——————————————— **Abstract** ———————————————

Samples of barium carbonate ($BaCO_3$) were produced by reacting Na_2CO_3 with $BaCl_2$ at a range of temperatures from 6-75°C. These isotope values of these were measured and used to produce a palaeothermometer calibration curve after Kim and O'Neil (1997). Systematic offsets from the expected line suggest kinetic isotope effects due to fast precipitation. A range of hard rock carbonate samples were measured for their $\delta^{18}O$ and $\delta^{13}C$ values. Literature and measured (for modern samples) values of water $\delta^{18}O$ were used to estimate a formation temperature of the carbonates using the Kim and O'Neil (1997) paleothermometer equation. Carbon isotope values have a much smaller temperature dependence than oxygen isotopes (ref). Therefore, those measured from the hard rock samples were used to give insights into the environmental chemistry and DIC of the water they formed from. Temperatures obtained from the paleothermometer are reasonable given the location and age of the samples.

Contents

1 Introduction

Equilibrium reactions are temperature dependent. The fractionation that occurs under equilibrium conditions is therefore also temperature dependent, so isotopes are used as thermometers. Given a set of values, the temperature of formation of a given mineral can be determined, making isotopic measurements paleothermometers. Isotopic compositions of primary carbonates in particular are widely used as geological archives of past environments (Huntington and Petersen, 2023). However, there is much debate in the published literature as to whether most carbonates actually precipitate under equilibrium conditions (Coplen, 2007). Kinetic effects which lead to a departure from equilibrium are often cited as the reasons why paleothermometers do not accurately represent the conditions of the past. In addition, effects of diagenesis are thought to have the potential to rewrite the isotopic signal of a particular carbonate (Hodgskiss, Crockford, and Turchyn, 2023). Nevertheless, in the absence of better paleothermometers, oxygen and carbon isotopes are good starting points to assess at what temperature a particular carbonate formed. In this study, barium carbonate is precipitated under known temperature in an attempt to recreate a paleothermometer equation. In addition, carbonates from a range of localities are measured for oxygen and carbon isotopes, and where the oxygen isotopic composition of the water is known, their temperature at the time of formation is calculated.

2 Literature review: the temperature dependence of α

Fractionation is defined as the phenomenon that occurs during a chemical or physical process whereby differences in mass between isotopes cause the partitioning of these isotopes into different substances. Stable isotope (i.e. non-radiogenic) fractionation occurs under equilibrium and kinetic conditions. Different fractionation types have different fractionation factors.

The isotopic fractionation factor, α, is defined as the ratio of ratios for the rare to heavy isotope for any two substances A and B (Sharp, 2017).

$$\alpha_{\text{A-B}} = \frac{R_{\text{A}}}{R_{\text{B}}} = \frac{\frac{\text{rare} A}{\text{common} A}}{\frac{\text{rare} B}{\text{common} B}}; \quad eg. for \ O \quad \alpha = \frac{\left(\frac{^{18}O}{^{16}O}\right)_{\text{A}}}{\left(\frac{^{18}O}{^{16}O}\right)_{\text{B}}}$$

When $\alpha = 1$, there is no fractionation. The definition for α can also be expressed in terms of δ:

$$\alpha_{\text{A-B}} = \frac{1000 + \delta_{\text{A}}}{1000 + \delta_{\text{B}}}$$

Where:

$$\delta_A = \left(\frac{\frac{\text{rare } X}{\text{common } X} \text{sample}}{\frac{\text{rare } X}{\text{common } X} \text{standard}} - 1 \right) \times 1000, \quad X \text{ is an element, eg. } \quad \delta^{18}O = \left(\frac{\frac{^{18}O}{^{16}O} \text{sample}}{\frac{^{18}O}{^{16}O} \text{standard}} - 1 \right) \times 1000$$

Fractionation factors are temperature dependent. As the temperature increases, the fractionation factor decreases, leading to less isotopic discrimination. This is due to the temperature dependence of the equilibrium and kinetic isotope fractionation mechanisms. Urey (1947) was one of the first to use this temperature dependence to quantitatively calculate the temperature at which marine carbonates formed in the past. Since Urey, there have been discussions in the published literature as to how this temperature dependence can be modeled.

There is general consensus that under normal temperature ranges above 20°C or 293K, α is dependent on $1/T^2$ in Kelvin (Clayton and Epstein, 1961).

$$1000 \, ln \, \alpha = \frac{C \cdot 10^6}{T^2} + D, \quad \text{C and D constants}$$

α is also proposed to be sensitive to the concentration of solution. O'Neil and Trusdell (1991) propose "critical concentrations" for thermodynamically distinct structural states which therefore possess different fractionation factors. Kim and O'Neil (1997) take this further, suggesting that the lower the concentration of solution studied, the closer the fractionation factor obtained is to equilibrium conditions. Indeed, precipitation of minerals under equilibrium conditions is heavily debated in the literature. One of the most notable examples is that of Coplen (2007), where mammillary calcite coating the walls of Devil's Hole cave in Nevada was found to have a significantly higher $1000 \, ln \, \alpha$ for its temperature, suggesting that the Kim and O'Neil (1997) data was precipitated out of equilibrium. Analyses in Laghetto basso near Corchia Cave in Italy by Daëron et al. (2019) confirmed the displacement found by Coplen (2007).

3 Materials and Methods

Generation of Barium Carbonate

Barium carbonate samples were precipitated at a range of temperatures. 10 mM solutions of Na_2CO_3 and $BaCl_2$ were prepared with DI water with known isotopic composition. Syringes filled with 5 ml of these solutions were submerged in water at measured temperatures and left to reach the temperature of the water. These solutions were then mixed in an Exetainer® vial also submerged in the water. This

resulted in almost immediate precipitation of $BaCO_3$ as it is highly insoluble in water. The resultant precipitate was filtered out and left to dry.

Other carbonate samples

A range of other carbonate samples from different locations, time periods and formation mechanisms were collected to be measured, these are described in Table 1, with their collection locations in Fig. 1.
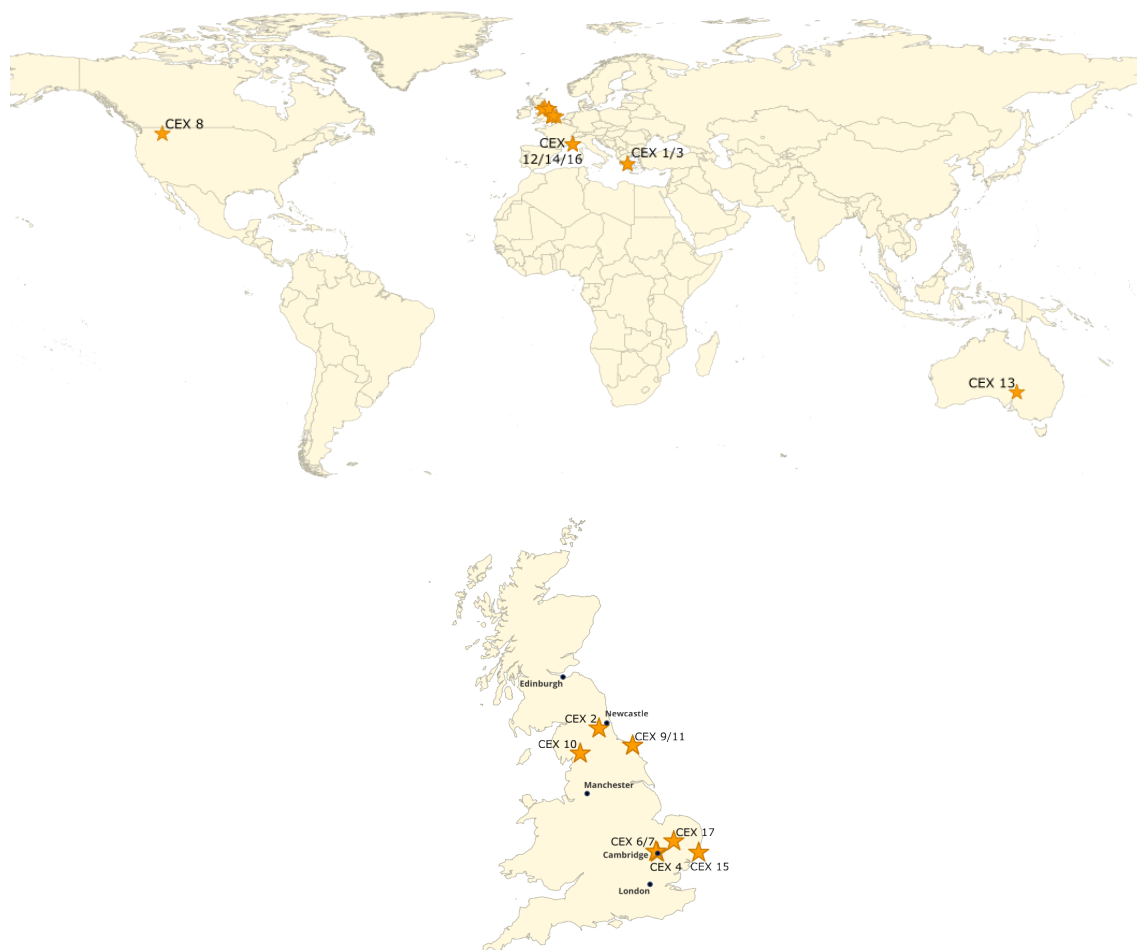

Figure 1: Map showing the locations of where all samples were collected

Sample ID	Type	Source	Latitude	Longitude	Age
Biogenic calcite					
CEX1	Shell	Greece	37.94	22.93	Recent
CEX3	Shell	Greece	37.94	22.93	Unknown
CEX9	Limpet	Whitby, UK	54.49	-0.61	Modern
CEX10	Coral	Sedbergh, UK	54.32	-2.53	Carboniferous
CEX11	Gastropod	Whitby, UK	54.49	-0.61	Modern
CEX14	Gryphaea	Castellane, France	43.85	6.51	Hettingian, Cretaceous
CEX15	Shell	Sussex, UK	52.15	1.60	Pliocene, Neogene
CEX13	Stromatolite	Australia	-30.33	139.37	Tonian

Sample ID	Type	Source	Latitude	Longitude	Age
Carbonate rocks					
CEX2	Carbonate	Consett, Durham, UK	54.86	-1.84	Modern
CEX4	Chalk	Cherry Hinton, UK	52.18	0.17	Cretaceous
CEX5	Oolite	Unknown	n/a	n/a	Jurassic
CEX12	Carbonate	Castellane, France	43.85	6.51	Cretaceous
CEX16	Carbonate	Castellane, France	43.85	6.51	Berriasian, Cretaceous
CEX17	Carbonate	Thetford, UK	52.41	0.75	Unknown
CEX8	Mudstone	Clarkia, Idaho, USA	47.04	-116.26	Miocene, Neogene
Anthropogenic carbonate					
CEX6	Kettle precipitate	Cambridge, UK	52.21	0.12	Modern
CEX7	Kettle precipitate	Cambridge, UK	52.21	0.12	Modern

Table 1: Table detailing the types, collection locations and ages of the carbonate samples

Isotope measurements

All carbonate samples were analysed for $\delta^{18}O$ and $\delta^{13}C$ values using a Thermo Delta V isotope ratio mass spectrometer coupled to a GasBench II on-line gas preparation/introduction system. Carbonate samples were ground up into a homogenous powder, and 0.5 mg of each sample was sealed in a borosilicate glass Exetainer® vial with a silicone rubber septum and loaded into the Thermo Gasbench autosampler that holds 40 samples. Each batch of samples included 10 reference carbonates of the in-house standard Carrara Z (calibrated to VPDB using the international standard NBS 19) and two control samples of Fletton Clay. Samples and standards were first flushed with helium and then acidified with 10.4% orthophosphoric acid for 1 hour at 70 °C and analysed with the mass spectrometer in continuous flow mode. Precision of Carrara Z was ± 0.06‰(1σ) or better for $\delta^{18}O$ and $\delta^{13}C$.

4 Results

4.1 Barium Carbonate Results

Kim and O'Neil report the oxygen isotopic composition of barium carbonate with respect to the V-SMOW standard, so a conversion is necessary. The conversion from $\delta^{18}O_{VPDB}$ to $\delta^{18}O_{V-SMOW}$ is:

$$\delta^{18}O_{V-SMOW} = 1.03091 \cdot \delta^{18}O_{VPDB} + 30.91$$

(Coplen, Kendall & Hopple, 1983). In order to calculate the fractionation factor α, or in this case $1000 \, ln \, \alpha$, one can use the approximation:

$$10^3 \, ln \, \alpha_b^a \approx \delta_a - \delta_b = \delta^{18}O_{carb} - \delta^{18}O_{water}$$

Where $\delta^{18}O_{water}$ of the water used for dissolution was -7.56.

Sample	Temperature (°C)	δ^{13}C (VPDB)	δ^{18}O (VPDB)	δ^{18}O (SMOW)	1000lnα
1	6.0	-7.36	1.26	32.21	39.78
2	23.2	-7.24	-12.43	18.11	25.67
3	40.0	-7.20	-13.26	17.25	24.81
4	50.0	-7.51	-12.32	18.22	25.78
5	59.0	-7.22	-13.70	16.80	24.36
6	75.0	-7.46	-15.83	14.60	22.16

Table 2: Isotopic data for precipitated barium carbonate including temperature, δ^{13}C, and δ^{18}O values.

4.2   Hard Rock Carbonate Results

Sample	δ^{18}O (VPDB)	δ^{13}C (VPDB)	Category	Sample type
CEX1	-2.43	0.64	Biogenic carbonate	Shell
CEX2	-8.31	-13.03	Carbonate rocks	Carbonate
CEX3	-7.74	-6.46	Biogenic carbonate	Shell
CEX4	-2.94	2.86	Carbonate rocks	Chalk
CEX5	-4.44	-1.35	Carbonate rocks	Oolite
CEX6	-15.90	-9.12	Anthropogenic carbonate	Kettle precipitate
CEX7	-16.57	-9.27	Anthropogenic carbonate	Kettle precipitate
CEX8	-9.34	12.94	Carbonate rocks	Mudstone
CEX9	2.14	-0.29	Biogenic carbonate	Limpet
CEX10	-6.35	1.34	Biogenic carbonate	Coral
CEX11	1.97	0.90	Biogenic carbonate	Gastropod
CEX12	-4.92	-5.16	Carbonate rocks	Carbonate
CEX13	-4.12	-4.33	Biogenic carbonate	Stromatolite
CEX14	-3.76	1.42	Biogenic carbonate	Gryphaea
CEX15	0.54	0.38	Biogenic carbonate	Shell
CEX16	-3.26	0.90	Carbonate rocks	Carbonate
CEX17	-5.55	3.40	Carbonate rocks	Carbonate

Table 3: Isotopic data for carbonate samples. The δ^{18}O and δ^{13}C values are relative to VPDB.

5 Discussion

5.1 Barium Carbonate Discussion
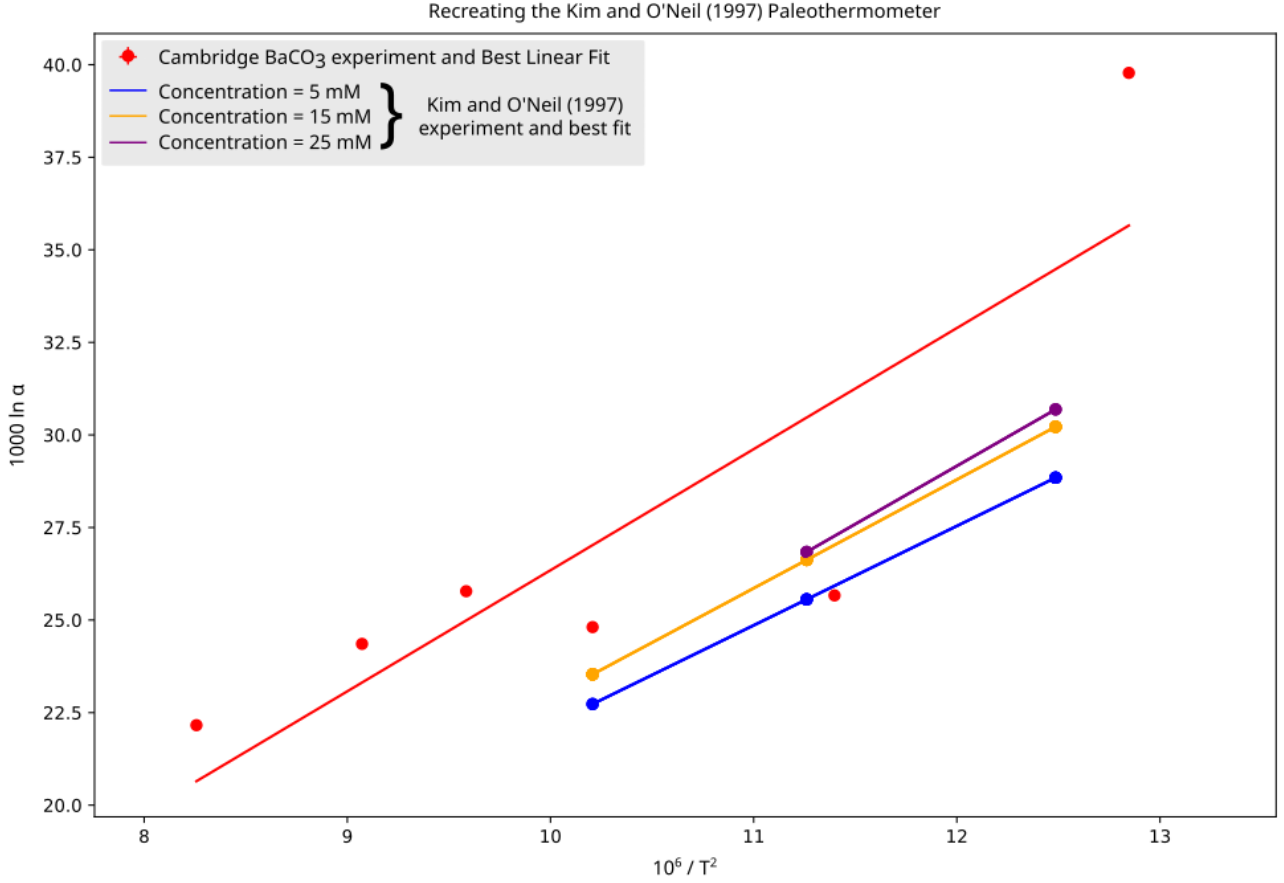

Figure 2: Recreating the barium carbonate thermometer. Red dots and line indicate measurements in Table 2. Temperature uncertainty of $\pm$ 2° is shown on Cambridge measurements. Uncertainty in 10^3 ln α is $\pm$ 0.1 0/00. Other colour dots and lines indicate measurements made by Kim and O'Neil (1997) on witherite for different concentrations.

$BaCO_3$ precipitated in this study was done at a concentration of 10 mM:

$$Na_2CO_{3(aq)} + BaCl_{2(aq)} \rightarrow BaCO_{3(s)} + 2NaCl_{(aq)}$$
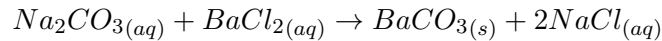
$BaCO_3$ is almost completely insoluble in water (Clarkson, 2001). Once precipitated, therefore, there is little scope for reequilibration unless the water is saturated in CO_2, in which case its solubility slightly increases. Kim and O'Neil (1997) report two different methods of isotope measurements; one is the total oxygen method, and other other is the phosphoric acid method. The total oxygen methods uses fluorination to release all the oxygen in $CaCO_3$, whereas the phosphoric acid method produces CO_2 (2 out of 3 atoms of oxygen) which results in an "acid fractionation factor". Kim and O'Neil used the phosphoric acid method for witherite precipitation so their methods are comparable with this study.

6

Given an initial concentration of 10 mM, one would expect witherite precipitated under similar conditions to plot in between the 5 mM and 15 mM lines (blue and yellow respectively) in Fig. 2. This is because the fractionation factor will change depending on the initial concentration at a given temperature. Because there is only one equilibrium fractionation at any temperature, most carbonates logically precipitate out of oxygen isotope equilibrium with the water, and the lowest concentrations display the closest values to isotopic equilibrium (Kim and O'Neil, 1997). This study's experiments are clearly deviating from the ideal concentration line, which is likely closest to the Kim and O'Neil (1997) 5mM line. There is a ≈ 4 0/00 offset in the y axis to be explained.

There are two possible reasons for this deviation. One is related to the rate of precipitation differing: slow in their experiments and fast (instantaneous) in this study. The other is related to the speciation of the Dissolved Inorganic Carbon (DIC) and the kinetic isotope effects related to that as the reaction progresses.

5.1.1 Precipitation Rate Investigation

At faster precipitation rate, kinetic isotope effects dominate. Some studies suggest that carbonate precipitation is not found to have a dependence on fractionation (Tarutani et al., 1969). However, these findings are generally for much slower rates than the next-to-instant one found in the Cambridge experiment setting. It is likely that there is therefore a kinetic isotope effect related to precipitation rate, just the rate in the Cambridge experiment is magnitudes faster than that already studied in Tarutani et al. (1969). Indeed, in the Kim and O'Neil (1997) paper, samples took as much as many days to precipitate. However, samples reported to have precipitated in isotopic equilibrium, such as mammilary calcite (Coplen et al., 2007) plot above the Kim and O'Neil (1997) line, just like the Cambridge experiment ones do. However, mammillary calcite precipitation rates are far slower than both experiments. This suggests that precipitation rate is not the main factor contributing to the observed offset.

5.1.2 DIC Speciation Investigation

Witherite is insoluble in most settings unless in the presence of CO_2. Differences between the Cambridge and Kim and O'Neil (1997) experiment involving the bubbling of CO_2 over the sample in the latter. This likely kept much of the Ba^{2+} and CO_3^{2-} dissolved, contributing to much lower precipitation rates. The addition of CO_2 also arguably changed the speciation of the dissolved inorganic carbon (DIC) of the system. At pH 8, which is the pH of the water in which the Cambridge samples were dissolved, the dominant carbonate species is the bicarbonate, HCO_3^- ion. The change in carbonate speciation is associated with a kinetic isotope effect, as detailed by Sade et al. (2020). Their study finds that the witherite precipitation pathway (that is, the main carbonate ion through which $BaCO_3$ is precipitated) changes depending on the percentage of DIC precipitated. It follows that the fractionation will change

depending on the carbonate species dominating the precipitation pathway. Therefore, by bubbling CO_2, the methods of Kim and O'Neil (1997) are leading to a different DIC speciation pathway compared to the Cambridge experiment, and so a different fractionation, but both are out of equilibrium. It is this difference in method that arguably causes the observed kinetic isotope effect, and deviation from their line.
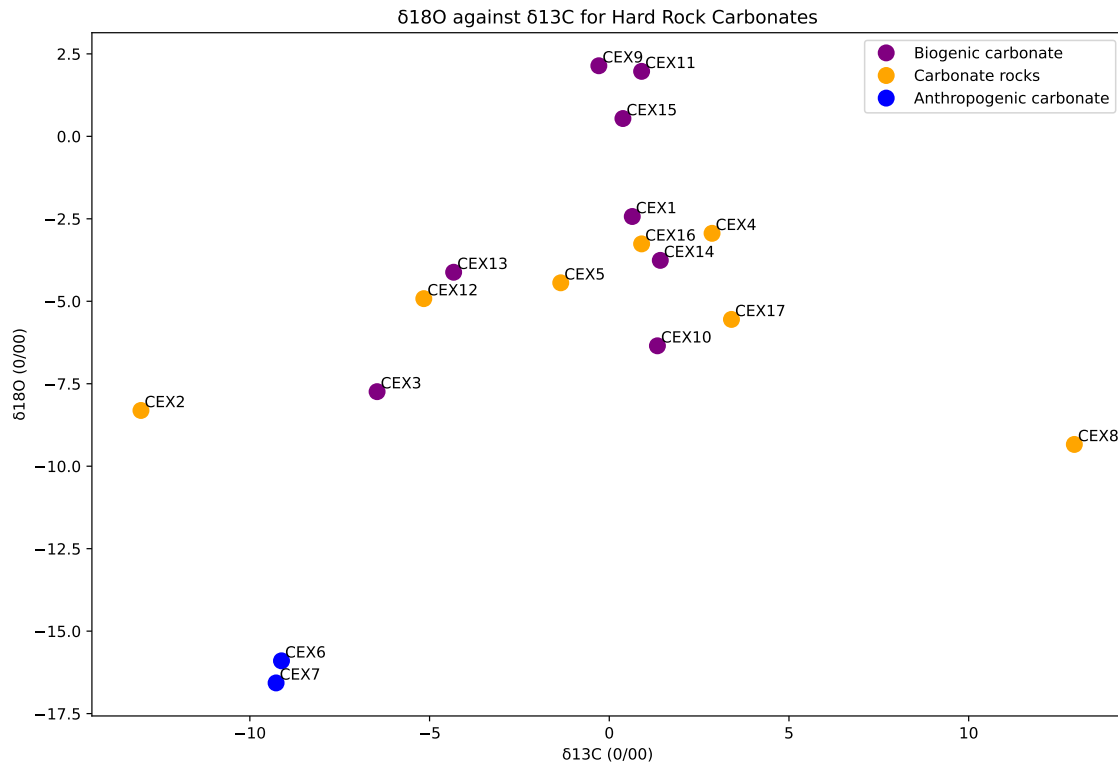
5.2 Hard Rock Carbonate Discussion

Figure 3: Scatter plot of $\delta^{18}O$ (PDB) against $\delta^{13}C$ (PDB)

The carbon isotopic composition of biogenic samples cluster around 0 ‰. This is consistent with a biological origin in a closed system carbonate isotope box model.
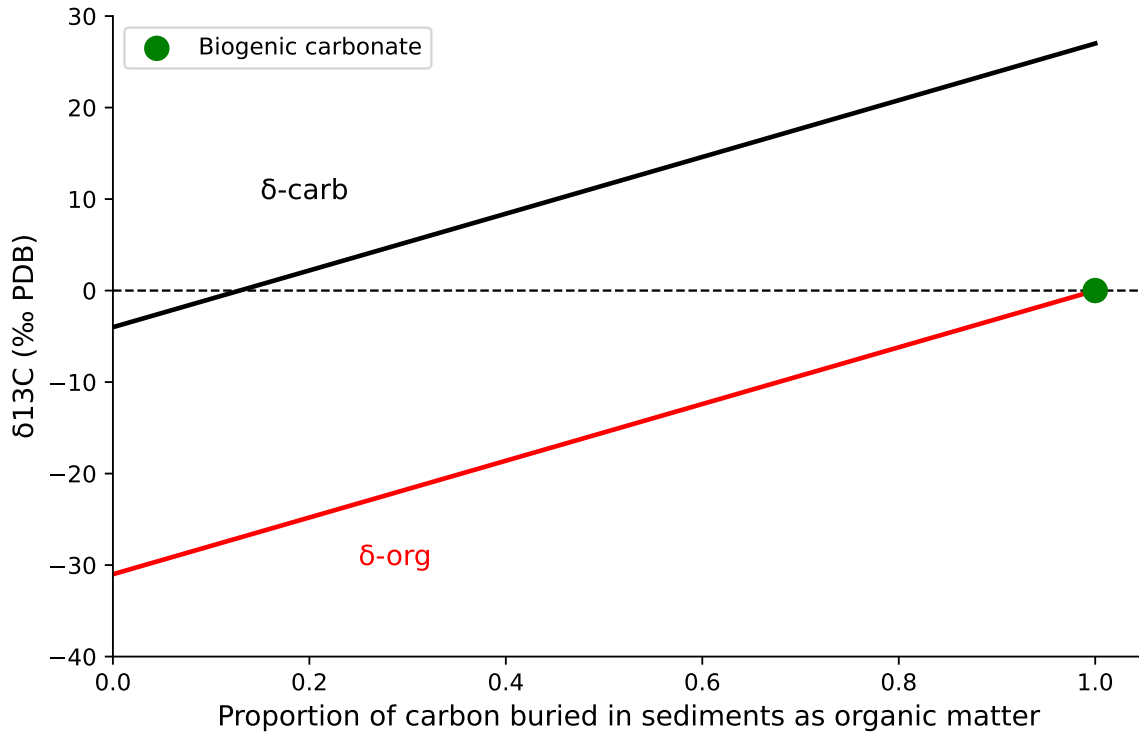
Figure 4: Closed system box model of δ^{13}C for a fractionation factor of 27 ‰(Turchyn Part II lectures). Biogenic carbonates should plot around x=1, which corresponds to a δ^{13}C ≈ 0

Biogenically precipitated carbonates display a broader range in δ^{18}O values compared to carbonate rocks, which have a wider range in δ^{13}C. Sample CEX-8 displays a very positive δ^{13}C value, which suggests it precipitated from DIC depleted in ^{12}C. This is consistent with the presence of methanogenesis in the anoxic Clarkia lake, which preferentially removes ^{12}C, producing methane with δ^{13}C values in the range of -70 to -100 ‰. Kettle precipitates CEX-6 and CEX-7 have a significantly more negative δ^{18}O compared to the biogenically precipitated carbonates. This is consistent with them having been precipitated at higher temperatures. In fact, for those samples for which the oxygen isotope composition of the water is known, a temperature can be estimated. According to Kim and O'Neil (1997), the calcite thermometer equation is the following:

$$1000 \ln \alpha(\text{Calcite-H}_2\text{O}) = 18.03 \left(10^3 T^{-1}\right) - 32.42$$

After having converted the δ^{18}O to V-SMOW, it is possible to use this equation to back-calculate the temperature at which the carbonates precipitated. The δ^{18}O of the water was obtained from water samples collected at the time of carbonate collection, or otherwise inferred. For example, for samples CEX-12 and CEX-16 which are of Cretaceous age, an ice-free world assumption was used to estimate a

$\delta^{18}O_w$ of -1 ‰(VSMOW). Note this has only been done for samples which are actually calcium carbonate given that the paleothermometer is for calcite.

Sample	Sample type	Carbonate type	$\delta^{18}O_{carb}$ (VSMOW)	$\delta^{18}O_w$	T (°C)
CEX6	Kettle precipitate	Anthropogenic carbonate	14.53	-7.34	59.14
CEX7	Kettle precipitate	Anthropogenic carbonate	13.84	-7.34	63.42
CEX9	Limpet	Biogenic carbonate	33.13	-0.09	1.68
CEX11	Gastropod	Biogenic carbonate	32.95	-0.09	2.42
CEX12	Carbonate	Carbonate rocks	25.85	-1.00	31.21
CEX16	Carbonate	Carbonate rocks	27.56	-1.00	22.67

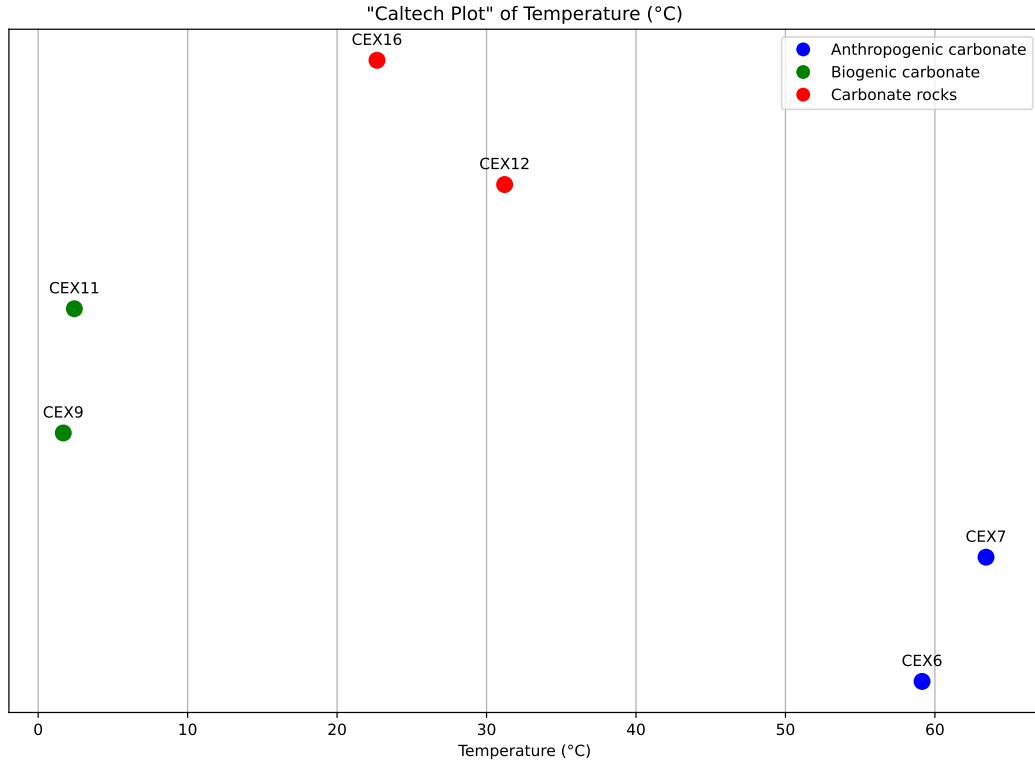Table 4: Isotopic and temperature data for various carbonate samples.

Figure 5: Plot displaying the temperature obtained from the paleothermometer for different samples. Error propagation uncertainty in temperature is on the order of ±0.5°C

The temperatures obtained for CEX-9 and CEX-11 are consistent with the formation of biogenic carbonate in seawater at low temperatures, although there is clearly a larger uncertainty than just that calculated from error propagation. This is because the lowest temperature recorded at Whitby beach is 3°C. This is supported by the fact that the kettle precipitates report temperatures of ≈60°C, which is

far lower than the boiling point of water. There is a point to be made here though, that perhaps that temperature is recording the average temperature of formation, and that the precipitation of calcite does not necessarily occur at 100°C. Lastly, the samples formed in the Cretaceous record high temperatures consistent with an ice-free world.

6 Conclusion

Barium carbonate fractionation factors in a plot against temperature obtained from an experiment aiming to recreate Kim and O'Neil (1997) display more positive lnα values. Because the precipitation rate was so much quicker, and the kinetic isotope effect for faster-than-equilibrium precipitation is in the opposite direction to that observed, it is likely the difference in methods that causes the difference in outcome. Indeed, CO_2 bubbling in the Kim and O'Neil (1997) experiment caused the DIC speciation to change. Given that changes from one DIC species to another is associated with a fractionation factor, the observed difference is due to a different DIC composition between the two experiments.

The hard rock carbonate isotopic compositions are consistent with the provenance of each sample. Of note is the samples that plot near zero ‰ δ^{13}C, which agree with their biogenic origin under a closed system box model assumption. Anoxic lake siderite has very positive δ^{13}C, which suggests it precipitated in an area in which methanogenesis was occurring. Paleothermometry was conducted according to Kim and O'Neil (1997), and yields temperatures consistent with the setting each sample was found in.

7 Recommendations for Practical Exercise

- Samples for the witherite experiment should be kept at the desired temperature for longer, and the headspace of the tube be kept to a minimum.

- Witherite experiment samples should be run with both Na_2CO_3 and $NaHCO_3$ to see if there is a significant effect from DIC speciation.

- Hard rock carbonates should be chosen so that they have a water sample associated with them, meaning less assumptions going into the paleothermometer equation.

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