

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 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. Literature and measured (for modern samples) values of water $\text{d}18\text{O}$ 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.

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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: 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.

Kinetic isotope fractionation is explained by the principle that, for the same kinetic energy, lighter isotopes travel faster than heavier isotopes. Equilibrium fractionation is instead driven to the degree to which bond vibrational energy is reduced by heavy isotope substitution. The former is a kinetic process, and the latter is a quantum mechanical process which depends on the vibrational energies of bonds between atoms. 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 Cite]

$$\alpha_{A-B} = \frac{R_A}{R_B} = \frac{\frac{\text{rare } A}{\text{common } A}}{\frac{\text{rare } B}{\text{common } B}}$$

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

$$\alpha_{A-B} = \frac{1000 + \delta_A}{1000 + \delta_B}$$

Where:

$$\delta_A = \left(\frac{\frac{\text{rare } X}{\text{common } X} \text{ sample}}{\frac{\text{rare } X}{\text{common } X} \text{ standard}} - 1 \right) \times 1000, \quad X \text{ is an element}$$

For example, for oxygen isotopes:

$$\delta^{18}O = \left(\frac{\frac{^{18}O}{^{16}O} \text{ sample}}{\frac{^{18}O}{^{16}O} \text{ standard}} - 1 \right) \times 1000$$

$$\alpha = \frac{\left(\frac{^{18}O}{^{16}O} \right)_A}{\left(\frac{^{18}O}{^{16}O} \right)_B}$$

Fractionation factors are temperature dependent. Qualitatively, 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 lively 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).

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

However, α is more generally thought to follow a dependence on temperature like so:

$$\ln \alpha = C/T^2 + D/T, \quad C \text{ and } D \text{ constants}$$

Bottinga and Javoy (1973) discuss the fractionation factor from a kinetic standpoint, concluding that the consensus equation does not have a theoretical basis, and is not valid at temperatures above 500°C or 773K. They do not, however, propose an alternative, suggesting that whilst perhaps not fully based, it is the best isotope geochemists have.

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, prompting Coplen to agree 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.

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. ??.

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
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 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ 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 $\pm 0.06\text{‰}$ (1σ) or better for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$.

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)	d13C (VPDB)	d18O (VPDB)	d18O (SMOW)	1000ln α
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, d13C, and d18O values.

4.2 Calcium Carbonate Results

5 Discussion

5.1 Barium Carbonate Discussion

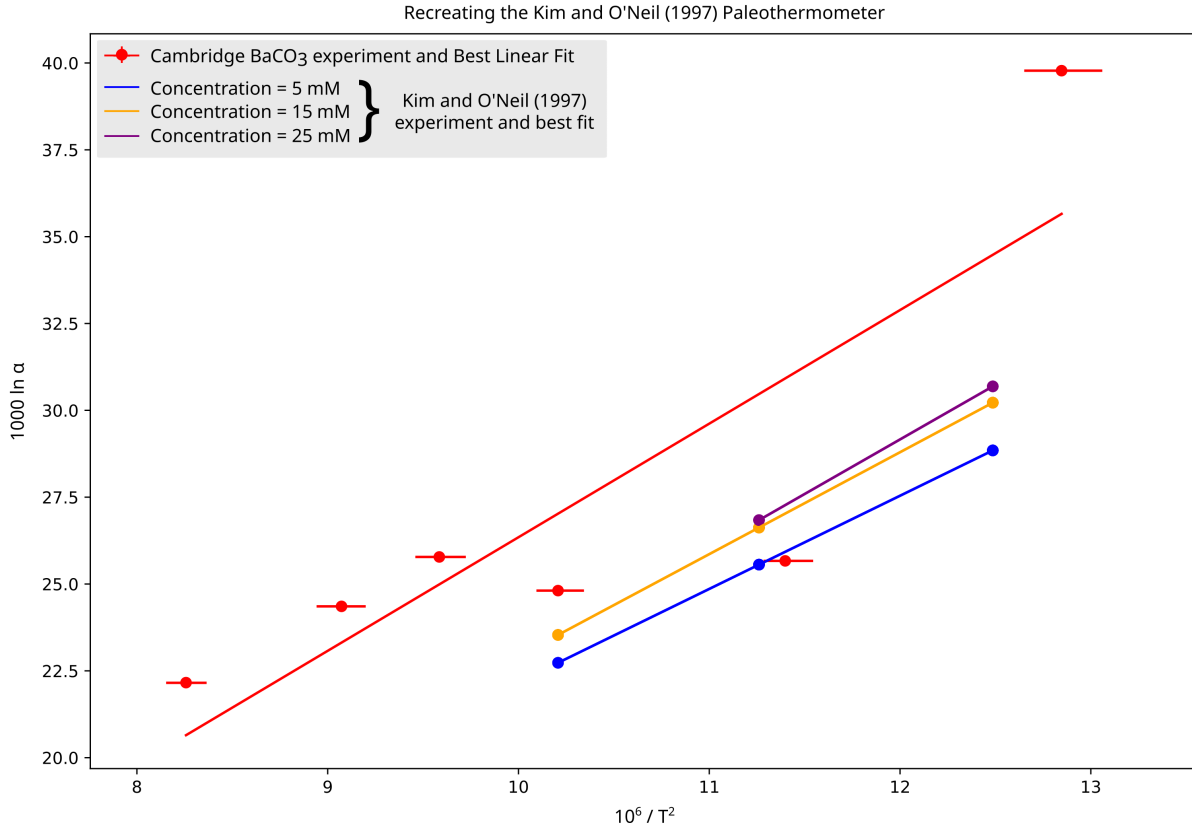
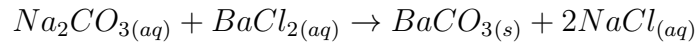


Figure 1: Recreating the barium carbonate thermometer. Red dots and line indicate measurements in Table 2. Temperature uncertainty of $\pm 2^\circ$ is shown on Cambridge measurements. Uncertainty in $10^3 \ln \alpha$ is ± 0.1 ‰. Other colour dots and lines indicate measurements made by Kim and O’Neil (1997) on witherite for different concentrations.

BaCO₃ precipitated in this study was done at a concentration of 10 mM:



BaCO₃ is almost completely insoluble in water (Clarkson, 2001). Once precipitated, therefore, there is little scope for reequilibration unless the water is saturated in CO₂, 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 CaCO₃, whereas the phosphoric acid method produces CO₂ (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.

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. 1. 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 (Coplen, 2007; Kim and O’Neil, 1997). This study’s experiments are clearly deviating from the ideal concentration line. Assuming the only differences between this study and the Kim and O’Neil (1997) values are the isotopic values, there is a ≈ 4 ‰ 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 required is magnitudes faster than that already studied. Indeed, in the Kim and O’Neil (1997) paper, samples took as much as many days to precipitate. This is arguably due to the bubbling of CO_2 that occurred in their experiment.

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 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. This causes the observed kinetic isotope effect, and deviation from their line.

5.2 Calcium Carbonate Discussion

6 Conclusion

Recommendations for Practical Exercise

References