Formation of dolomite at 40–80 °C in the Latemar carbonate buildup, Dolomites, Italy, from clumped isotope thermometry

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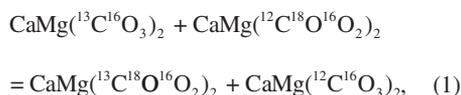
ABSTRACT

The temperature of formation of replacement dolomite and $\delta^{18}O(H_2O)$ of dolomitizing fluid in the Latemar carbonate buildup, Dolomites, Italy, were estimated independently from carbonate clumped isotope thermometry. Dolomite formed at $42–72 \pm 9–11$ °C (± 2 standard deviations, SD) from fluid with $\delta^{18}O(H_2O)$ that averages $-0.3‰ \pm 3.3‰$ (Vienna standard mean ocean water; ± 2 SD). The estimated temperature and $\delta^{18}O(H_2O)$ are similar to those of modern diffuse flow fluids at mid-ocean ridges, the kind of fluid that has been proposed previously as the dolomitizing fluid in the Latemar buildup, based on the trace element compositions of dolomite. Calcite in limestone preserves original $\delta^{18}O$, but records clumped isotope temperatures, $44–76 \pm 9–11$ °C (± 2 SD), that are higher than those at which the limestone formed. Temperature recorded by calcite, but not $\delta^{18}O$, was likely reset during dolomitization. Clumped isotope thermometry has great potential for application to studies of burial and diagenesis by retrieving independent estimates of temperature and $\delta^{18}O(H_2O)$ with uncertainties as low as ± 5 °C (± 2 standard errors, SE) and $\pm 0.75‰$ (± 2 SE), respectively, from a single stable isotope analysis of a carbonate mineral.

INTRODUCTION

Most dolomite in the geological record formed by replacement of calcite in limestone (Hardie, 1987; Budd, 1997; Machel, 2004). In these cases, there are fundamentally two requirements for formation of dolomite: a high Mg/Ca aqueous fluid and a mechanism that can pump large volumes of the fluid through limestone. Two important constraints on the source of the fluid and the mechanism that drives fluid flow are the temperature, T, of dolomitization and the oxygen isotope composition of the dolomitizing fluid, $\delta^{18}O(H_2O)$. Estimated $\delta^{18}O(H_2O)$ can distinguish among dolomitizing fluids that are unmodified seawater, evaporated seawater, or mixtures of seawater with meteoric water. Temperature can distinguish between fluid flow driven by hydrothermal activity and flow associated with burial along a normal geothermal gradient.

Measured $\delta^{18}O$ of dolomite, $\delta^{18}O(Dol)$, however, does not independently define both T and $\delta^{18}O(H_2O)$. Arguably the best means for estimating the T of dolomitization is the homogenization T (T_h) of fluid inclusions in dolomite (Machel, 2004). Unfortunately, most fluid inclusions in dolomite are too small for this purpose, and measurements of T_h in carbonates may be compromised by postentrapment leakage or stretching of inclusions. Precise estimation of both T and $\delta^{18}O(H_2O)$ from a single stable isotope analysis of dolomite, however, can now be made by clumped isotope thermometry.

Clumped isotope thermometry is based on the ordering of carbon and oxygen isotopes in carbonate minerals, governed (using dolomite as an example) by the reaction

$$CaMg(^{13}C^{16}O_3)_2 + CaMg(^{12}C^{18}O^{16}O_2)_2$$
$$= CaMg(^{13}C^{18}O^{16}O_2)_2 + CaMg(^{12}C^{16}O_3)_2, \quad (1)$$

(Ghosh et al., 2006; Schauble et al., 2006). The ordering of isotopes in carbonate minerals is inferred from the measured ordering in CO_2 released by acid digestion of the mineral. The T-dependent ordering parameter, Δ_{47}, is calculated as

$$\Delta_{47} = 1000\left[\left(R^{47}/R^{47*}\right) - \left(R^{46}/R^{46*}\right)\right.$$
$$\left. - \left(R^{45}/R^{45*}\right) + 1\right], \quad (2)$$

where the different R^i = (mass i/mass 44) are ratios of the various stable isotopologues of CO_2 in the gas (Affek and Eiler, 2006). The parameter R^{i*} refers to the mass ratio in the same gas with a fictive stochastic distribution of isotopologues. In practice, measured data for minerals are normalized to CO_2 gases heated to 1000 °C to achieve a stochastic distribution of isotopologues (Eiler and Schauble, 2004; Huntington et al., 2009). Precise values of $\delta^{18}O(Dol)$ are a by-product of measurements of Δ_{47}. Values of $\delta^{18}O(H_2O)$ then follow from the T estimated from Δ_{47} and published calibrations of the dolomite-H_2O oxygen isotope fractionation (e.g., Vasconcelos et al., 2005).

We report the first application of clumped isotope thermometry to the study of the formation of dolomite, specifically in the Latemar carbonate buildup, Dolomites, northern Italy. Dolomite was formed by replacement of Anisian and Ladinian limestones during the Middle Triassic, contemporaneous with plutonism and volcanism in the adjacent Predazzo igneous complex, which has radiometric ages of 232–238 Ma (see reviews by Wilson, 1989; Wilson et al., 1990; Carmichael et al., 2008, and references therein). Two models for dolomitization in the Latemar buildup differ in details that were resolved by this study. One model (Wilson, 1989; Wilson et al., 1990) considers that the dolomitizing fluid was unmodified seawater with formation of dolomite at 100–200 °C estimated from T_h of fluid inclusions in dolomite. Based on T_h for 7 samples and $\delta^{18}O(Dol)$ measured for 27 samples, they concluded that flow of dolomitizing fluid was uniform, pervasive, and defined a kilometer-scale plume driven by heat from the nearby plutonic activity. In contrast, Carmichael et al. (2008) and Carmichael and Ferry (2008) concluded, based on the elevated Fe, Mn, and Zn contents of dolomite compared to calcite in limestone, that the dolomitizing fluid was like modern diffuse flow fluid at mid-ocean ridges (Von Damm and Lilley, 2006), a fluid produced today by mixing of seawater with as much as ~25% hydrothermal fluid like that emitted from vents at mid-ocean ridges. A more extensive data set for replacement dolomite indicates that $\delta^{18}O(Dol)$ varies almost as much within individual outcrops as over the entire Latemar buildup (Fig. 1). These results, the geometry and spatial distribution of dolomite bodies in the field, and the crosscutting relationships between different dolomite bodies (Carmichael et al., 2008) imply pulsed and highly channelized fluid flow during dolomitization, like that observed at modern mid-ocean ridges. Assuming $\delta^{18}O(H_2O)$ of the dolomitzing fluids was ~0, like modern diffuse flow fluid, measured values of $\delta^{18}O(Dol)$ record significantly lower $T = 45–85$ °C (Fig. 1). We used independent estimates of T and $\delta^{18}O(H_2O)$ from clumped isotope thermometry to evaluate the two models for dolomitization in the Latemar buildup.

SAMPLE SELECTION AND ANALYTICAL METHODS

We chose 10 samples of dolomite and 5 samples of limestone that span almost the entire range of previously measured $\delta^{18}O$ in the Latemar buildup. In addition, two samples of dolomite grown at known T were analyzed. One sample was synthesized at 45 °C in the
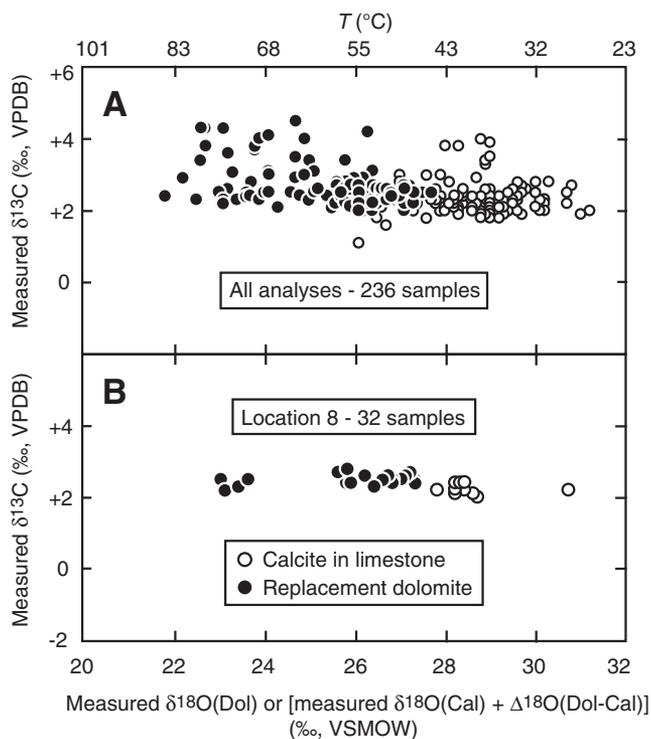
Figure 1. Oxygen and carbon isotope compositions of dolomite and calcite from Latemar buildup (Carmichael and Ferry, 2008). VSMOW—Vienna standard mean ocean water; VPDB—Vienna Peedee belemnite. Uncertainties are smaller than symbol size. Measured $\delta^{18}O(Cal)$ has been corrected for dolomite-calcite oxygen isotope fractionation so that top horizontal axis represents temperature, T, of equilibration of both minerals with H_2O fluid with $\delta^{18}O = 0\%$ VSMOW (Vasconcelos et al., 2005; O'Neil et al., 1969, calibrations for dolomite and calcite, respectively). A: All data for Latemar buildup. B: All data for one outcrop.

Figure 2. All measurements of Δ_{47} of dolomite and calcite from Latemar buildup and of natural (CVLV) and synthetic (CV45) dolomite grown at known temperature, T. Solid line represents theoretical temperature calibrations of Guo et al. (2009). The T values of data points for samples CV45 and CVLV correspond to their known growth Ts, whereas T values of Latemar dolomites and calcites are calculated from measurements of Δ_{47}. Error box (CVLV) and bars represent uncertainties in measurement and T described in text. Measured Δ_{47} of calcite has been corrected for equilibrium difference between dolomite and calcite so that horizontal axis represents T of formation of both minerals.

laboratory as part of a study to calibrate the oxygen isotope fractionation between dolomite and H_2O (Vasconcelos et al., 2005). The other was a natural sample of modern sediment from Lagoa Vermelha, Brazil, believed to have formed at 25–28 °C (Vasconcelos and McKenzie, 1997; Vasconcelos et al., 2005). A sample of dolomite marble, contact metamorphosed by the Predazzo igneous complex at ~710 °C (sample P1C of Ferry et al., 2002; T calculated from calcite-dolomite thermometry of rare calcite inclusions in forsterite), was analyzed to verify that high-temperature signals (small values of Δ_{47}) can be preserved in natural dolomite over geologic time scales.

All analyses were made at the California Institute of Technology. Analytical methods were described in detail by Passey et al. (2010). Briefly, for each analysis of dolomite and of calcite from limestone, ~8 mg of material was extracted from sawed, polished, and stained slabs using a 2-mm-diameter diamond-tipped drill. The sample from Lagoa Vermelha was treated with H_2O_2 to remove admixed organic material. Treatment of one aliquot of the synthetic dolomite with H_2O_2 demonstrated that the treatment does not measurably affect the value of Δ_{47}. Samples were reacted at 90 °C in 100% phosphoric acid in a custom-built, automated, online device. Product CO_2 was purified by passage through multiple cryogenic traps and a Porapak-Q gas chromatograph held at –20 °C and then passed into a ThermoFinnigan MAT 253 mass spectrometer. Values of Δ_{47} were calculated from measured ion intensity ratios

using Equation 2. A correction of +0.081‰ was made to all measurements of Δ_{47} to account for the difference between the T of reaction during analysis (90 °C) and the reference T (25 °C) of the calibrations of the T dependence of Δ_{47} in carbonates (Passey et al., 2010). The standard deviation (SD) of measured values of Δ_{47} and $\delta^{18}O$ was taken as the SD of measurements of the Fast Haga intralaboratory calcite standard at the California Institute of Technology that were frequently interspersed with analyses of the unknowns. During one analytical session in May 2008, when all samples of dolomite and limestone from the Latemar buildup and the dolomite marble were analyzed, the SD of Δ_{47} and $\delta^{18}O$ was 0.011‰ and 0.07‰, respectively (five standard analyses). During a second analytical session in August 2008, when synthetic dolomite and the sample from Lagoa Vermelha were analyzed, the SD of Δ_{47} and $\delta^{18}O$ was 0.009‰ and 0.06‰, respectively (six standard analyses) (see the GSA Data Repository[1]).

RESULTS

Measured values of Δ_{47} and $\delta^{18}O$ of dolomite and of calcite in limestone from the Latemar buildup are illustrated in Figures 2 and 3. The Δ_{47} of dolomite and calcite are 0.504‰–0.571‰ ± 0.022‰ (±2 SD) and 0.515‰–0.585‰

[1]GSA Data Repository item 2011181, Table DR1 (isotopic compositions of dolomite and calcite), is available online at www.geosociety.org/pubs/ft2011.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
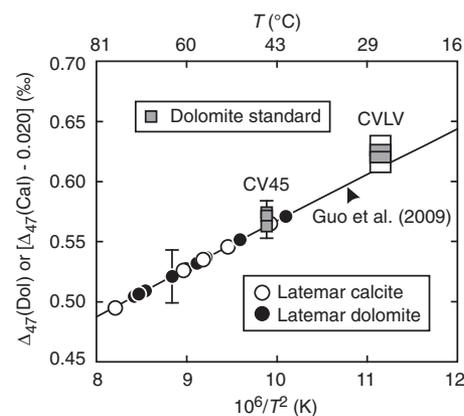
± 0.022‰, respectively. Values of $\delta^{18}O(Cal)$ are 26.1‰–29.0‰ ± 0.14‰ Vienna standard mean ocean water (VSMOW; ±2 SD). Because the acid fractionation factor for dolomite at 90 °C using the common acid bath technique used in the analyses has not been measured, values of $\delta^{18}O(Dol)$ in Figure 3 (21.6‰–27.2‰ ± 0.2‰ VSMOW, ±2 SD) are from Carmichael (2006), obtained by prior analysis of the same ~2-mm-diameter area sampled for Δ_{47} analysis with acid digestion at 90 °C in sealed reaction vessels. The mean Δ_{47} value of three analyses of the synthetic dolomite (0.563‰, 0.571‰, 0.574‰) is 0.569‰. The uncertainty is ±0.010‰, taken as twice the SD of analyses of the Fast Haga standard divided by √3. The mean Δ_{47} value of two analyses of the Lagoa Vermelha dolomite (0.620‰, 0.626‰) is 0.623‰. The uncertainty is ±0.012‰, taken as twice the SD of the Fast Haga standard divided by √2. The dolomite marble (sample P1C) has a $\Delta_{47} = 0.283‰$ ± 0.022‰ (±2 SD), the lowest measured value in an uncontaminated natural sample to date.

Temperature was calculated from measured values of Δ_{47} of the Latemar dolomites using the Guo et al. (2009) theoretical calibration, which builds on calculations by Schauble et al. (2006), because the one experimental calibration (Eiler et al., 2009) has not been published. The theoretical calibration of Guo et al. (2009) is a good representation of the experimental data. As further empirical validation of the calibration, the
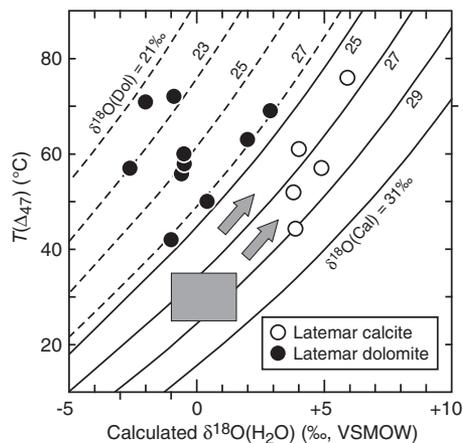
Figure 3. Temperature and δ¹⁸O(H₂O) recorded by Δ₄₇ and δ¹⁸O of dolomite and calcite from Latemar buildup (VSMOW—Vienna standard mean ocean water). Contours of δ¹⁸O(Dol) and δ¹⁸O(Cal) calculated from calibrations of Vasconcelos et al. (2005) and O'Neil et al. (1969) for dolomite and calcite, respectively. Shaded box represents likely conditions of formation of calcite (range δ¹⁸O of seawater from Shanks et al., 1995). Arrows indicate later closed-system [constant δ¹⁸O(Cal)] alteration paths for calcite.

analyses of the synthetic dolomite (CV45) and the dolomite from Lagoa Vermelha (CVLV) plot on the calibration curve within the uncertainties of measurement of Δ_{47} and in the T of formation (Fig. 2). Dolomites from the Latemar buildup record $T = 42–72$ °C with an uncertainty of 9–11 °C that represents the ±0.022‰ ±2 SD analytical uncertainty in Δ_{47} propagated through the dolomite calibration (Fig. 2). Temperature was calculated from measured values of Δ_{47} of calcite using the calibration of Guo et al. (2009) both for consistency with the dolomite calibration and because the empirical Ghosh et al. (2006) calibration is recommended only for $T = 1–50$ °C. Calcites from the Latemar buildup record $T = 44–76$ °C that substantially overlaps the range in T recorded by dolomites. Uncertainties of 9–11 °C represent the ±0.022‰ ±2 SD analytical uncertainty in Δ_{47} propagated through the calcite calibration (Fig. 2). For comparison, if the calibration of Dennis and Schrag (2010) for calcite is used, Δ_{47} of calcite records T in the range 43–82 °C.

Values of $\delta^{18}O(H_2O) = -2.6‰$ to $+2.9‰$ ± 1.5‰ with an average of –0.3‰ (Fig. 3) were calculated from $\delta^{18}O$ of the Latemar dolomites at the T recorded by Δ_{47}, using the calibration by Vasconcelos et al. (2005). The uncertainty in $\delta^{18}O(H_2O)$ represents the ±2 SD uncertainty in T and $\delta^{18}O(Dol)$ propagated through the calibration. Values of $\delta^{18}O(H_2O)$ calculated from $\delta^{18}O(Cal)$ at the T recorded by Δ_{47}, using the calibration of O'Neil et al. (1969), are larger, 3.8‰–5.9‰ ± 1.5‰ with an average of +4.5‰ (Fig. 3). The uncertainty in $\delta^{18}O(H_2O)$ repre-

sents the ±2 SD uncertainty in T and $\delta^{18}O(Cal)$ propagated through the calibration. Results are unchanged if the Kim and O'Neil (1997) rather than the O'Neil et al. (1969) calibration is used.

DISCUSSION

The value of $\Delta_{47} = 0.283‰$ recorded by the dolomite marble corresponds to $T = 317$ °C, using the calibration of Guo et al. (2009), much lower than $T \approx 710$ °C undergone by the rock during contact metamorphism (Ferry et al., 2002). The clumped isotope thermometer therefore fails to return very high temperatures of metamorphism, but rather records a "closure T" ≈ 300 °C. Closure T is defined as the T recorded by Δ_{47} of a carbonate mineral that has undergone reordering of carbon and oxygen isotopes (Equation 1) during cooling after crystallization. The closure T is similar to that inferred by Ghosh et al. (2006) and Dennis and Schrag (2010) for calcite. Although the closure T depends on cooling rate, the ~300 °C indicates that $T < 100$ °C obtained from clumped isotope thermometry of Latemar dolomites (Fig. 2) should faithfully represent the formation of dolomite even after more than 200 m.y. of burial, cooling, and uplift, unless the dolomite was recrystallized after formation. The preservation of fine-scale, ~10-μm-wavelength, oscillatory growth zoning of Fe in dolomite (Carmichael et al., 2008), however, indicates that later recrystallization of Latemar dolomite is unlikely. More broadly, clumped isotope thermometry should record the T of precipitation, diagenesis, and recrystallization of carbonate minerals up to at least 100–200 °C.

The T and average $\delta^{18}O(H_2O)$ recorded by Δ_{47} and $\delta^{18}O$ of dolomite are within the range of values of modern diffuse flow fluid at mid-ocean ridges, ~25–110 °C and –1‰ to +1‰ (Carmichael and Ferry, 2008), and are consistent with formation of Latemar dolomite by infiltration of limestone with a similar fluid. The range in T recorded by Δ_{47} of Latemar dolomite is within that considered typical for the formation of replacement dolomite worldwide, 50–80 °C (Machel, 2004). In contrast, measured values of Δ_{47} and $\delta^{18}O$ of Latemar dolomite are not consistent with dolomitization at 100–200 °C by heated but otherwise unmodified seawater (Wilson, 1989; Wilson et al., 1990). Dolomite with the measured values of $\delta^{18}O$ in Figure 3 would be in equilibrium with fluid with $\delta^{18}O(H_2O) = 1.5‰–7.0‰$ at 100 °C and 8.9‰–14.5‰ at 200 °C, using the Vasconcelos et al. (2005) calibration of dolomite-H_2O oxygen isotope fractionation. These values of $\delta^{18}O(H_2O)$ are inconsistent with a dolomitizing fluid like modern seawater (~0‰ ± 1‰). The higher temperatures inferred by Wilson (1989) and Wilson et al. (1990) for dolomitization in the Latemar buildup are explained if their measurements of T_h were made on fluid inclusions

that leaked or stretched following entrapment in dolomite (Prezbindowski and Larse, 1987). Disturbance of the fluid inclusions is indicated independently by a wide spread in T_h in excess of ~100 °C within individual samples for which at least five measurements were made. The average value of $\delta^{18}O(H_2O) = -0.3‰$, estimated from the isotopic composition of Latemar dolomite, validates estimation of the T of formation of dolomite in the Latemar buildup from measured $\delta^{18}O(Dol)$ assuming $\delta^{18}O(H_2O) \approx 0‰$ (Fig. 1). If fluid flow was prolonged (~1 m.y.) and pervasive, as envisioned by Wilson (1989) and Wilson et al. (1990), T differences over distances of ~10 m implied by the data in Figure 1B (Carmichael et al., 2008, their figure 9B) would not be preserved because they would be erased by heat conduction over a much shorter time, $t = 3.2$ yr ($t = x^2/\kappa$, where $x = 10$ m and thermal diffusivity, $\kappa = 10^{-6}$ m²/s). Observed differences in T at the 10 m scale, as well as the geometry of dolomite bodies and crosscutting relationships between dolomite bodies in the field (Carmichael et al., 2008), imply fluid flow during dolomitization in repeated, spatially restricted, temporally limited pulses.

The average difference between T recorded by Δ_{47} and that recorded by $\delta^{18}O(Dol)$, assuming $\delta^{18}O(H_2O) = 0‰$, is 0. The corresponding average difference for calcite, however, is 28 °C. Furthermore, the average $\delta^{18}O(H_2O)$ calculated from $\delta^{18}O(Cal)$ and the T recorded by Δ_{47} is +4.5‰, significantly higher than modern seawater. The Ts calculated from $\delta^{18}O(Cal)$, assuming $\delta^{18}O(H_2O) = 0‰$, 22–37 °C, are plausible values for the formation of marine limestone. The simplest explanation is that the original Δ_{47} of calcite was altered during closed-system recrystallization caused by heating of the Latemar buildup to ~40–80 °C by dolomitizing fluids. The preservation of original $\delta^{18}O$ of calcite can be explained in two different ways. First, there may have been no fluid flow through the analyzed limestones during dolomitization. Second, more plausibly, analyzed limestones occur downstream from the oxygen isotope reaction front associated with dolomitization, and were then infiltrated by fluid that had achieved oxygen isotope exchange equilibrium with limestone further upstream. In either case, the preservation of original $\delta^{18}O$ of calcite is further evidence for fluid flow during dolomitization that was highly channelized rather than pervasive. Calcite from the Latemar is an example that Δ_{47} of carbonate minerals can reset during heating without significant change in $\delta^{18}O$ (Fig. 3). Measurements of Δ_{47}, in general, may reveal thermal events that have little or no effect on $\delta^{18}O$.

Formation of dolomite in the range ~40–80 °C is inconsistent with many laboratory studies that failed to produce dolomite at $T < 100$ °C (Machel, 2004). The apparent discrepancy may

be explained by the recent recognition that disordered dolomite can form at $T < 100$ °C in the presence of fluid with dissolved sulfide species and/or CH_4 (Xu, 2010; Zhang et al., 2010). The sulfide species and CH_4 disrupt the hydration sphere around aqueous Mg ions, allowing them to react with calcite to form dolomite. Diffuse flow fluid is an ideal dolomitizing fluid in this regard because it contains $\sim 10^5$ times more CH_4 and at least 10^3 times more H_2S than normal seawater (Von Damm and Lilley, 2006). Dolomite in the Latemar buildup could also have formed at $T < 100$ °C under biological controls either induced during microbial metabolic activity (Vasconcelos and McKenzie, 1997) or when the kinetic barrier to precipitation was overcome by microbial processes that locally elevated the partial pressure of CH_4 and/or H_2S.

Precise estimates of T and $\delta^{18}O(H_2O)$ would further numerous studies in sedimentology and diagenesis. As demonstrated by this study, methods are now available to independently estimate both parameters from a single isotopic measurement of calcite or dolomite. With multiple analyses of the same sample, precision can be significantly improved over the measurements made in this study. For example, four measurements of Δ_{47} and $\delta^{18}O$ of a calcite or dolomite sample would reduce ±2 SD uncertainties by one-half, leading to uncertainties of ±5 °C in T and of ±0.75‰ in $\delta^{18}O(H_2O)$, representing a significant technical advance.

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