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A hydrothermal origin for isotopically anomalous cap dolostone cements from south China

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The release of methane into the atmosphere through destabilization of clathrates is a positive feedback mechanism capable of amplifying global warming trends that may have operated several times in the geological past[1–3]. Such methane release is a hypothesized cause or amplifier for one of the most drastic global warming events in Earth history, the end of the Marinoan 'snowball Earth' ice age, ~635 Myr ago[4–7]. A key piece of evidence supporting this hypothesis is the occurrence of exceptionally depleted carbon isotope signatures ($\delta^{13}C_{PDB}$ down to −48‰; ref. 8) in post-glacial cap dolostones (that is, dolostone overlying glacial deposits) from south China; these signatures have been interpreted as products of methane oxidation at the time of deposition[5,6,8]. Here we show, on the basis of carbonate clumped isotope thermometry, $^{87}Sr/^{86}Sr$ isotope ratios, trace element content and clay mineral evidence, that carbonates bearing the ^{13}C-depleted signatures crystallized more than 1.6 Myr after deposition of the cap dolostone. Our results indicate that highly ^{13}C-depleted carbonate cements grew from hydrothermal fluids and suggest that their carbon isotope signatures are a consequence of thermogenic methane oxidation at depth. This finding not only negates carbon isotope evidence for methane release during Marinoan deglaciation in south China, but also eliminates the only known occurrence of a Precambrian sedimentary carbonate with highly ^{13}C-depleted signatures related to methane oxidation in a seep environment. We propose that the capacity to form highly ^{13}C-depleted seep carbonates, through biogenic anaerobic oxidation of methane using sulphate, was limited in the Precambrian period by low sulphate concentrations in sea water[9]. As a consequence, although clathrate destabilization may or may not have had a role in the exit from the 'snowball' state, it would not have left extreme carbon isotope signals in cap dolostones.

A common sedimentary motif marking the end of the severe Marinoan ice age (~635 Myr ago[10]) is observed in rocks on almost all of the present day continents. Glaciogenic deposits, formed at equatorial latitudes in some places, are sharply overlain by metre-scale intervals of dolostone[11]. These cap dolostones contain enigmatic sedimentary structures and unusual stable carbon and sulphur isotope signatures hypothesized to reflect climate change associated with deglaciation[11]. Proposed drivers of global warming during this period include deep-ocean CO_2 outgassing during post-glacial ocean overturn[12], ice–albedo feedback[11] or methane release caused by the destabilization of clathrates[4].

The lithologies and sedimentary structures observed in the cap dolostone of south China, which forms the basal 3–5 m of the Doushantuo Formation, are typical of cap dolostones worldwide[6,11] (Supplementary Discussion). But unlike other cap dolostones that have mildly negative $\delta^{13}C_{PDB}$ values (−2 to −4‰; ref. 11), three sections in the Yangtze Gorges area host highly ^{13}C-depleted calcites ($\delta^{13}C_{PDB}$ down to −48‰; ref. 8). Petrographic textures of the highly ^{13}C-depleted calcites exclusively from calcite cements with exceptionally low $\delta^{13}C_{PDB}$ values. Areas drilled for isotopic analysis are highlighted in yellow (Supplementary Fig. 2 shows unmarked images of the samples) and labelled (J*x* and H*y* refer to sample spots from Jiulongwan and Huajipo, respectively) for cross-referencing with data in Supplementary Table 1. The temperatures and isotope values shown are the mean of two or three replicate measurements of the same powder.

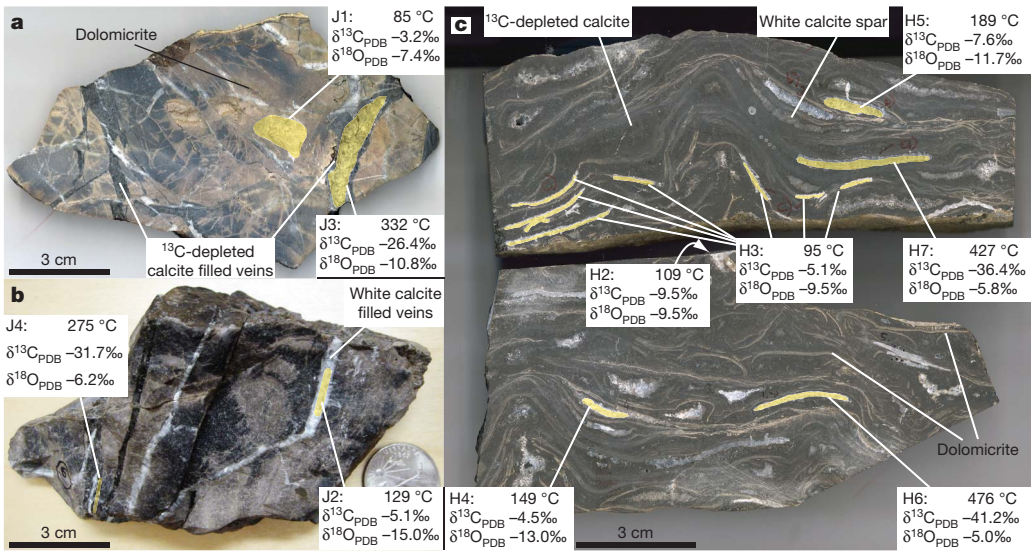

Figure 1 | Crystallization temperatures (based on Δ_{47} measurements) and C and O stable isotope data from various carbonate phases in two samples of the Doushantuo Formation cap dolostone. **a**, **b**, Two views of sample 1, collected from the lower unit of the cap at Jiulongwan (Fig. 3; Supplementary Fig. 1). **c**, Two pieces of sample 3, collected from the middle of the cap dolostone at Huajipo (Fig. 3; Supplementary Fig. 1). The highest temperatures come

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and associated carbonates have been likened to modern methane seeps[5,6,8]. Additionally, $\delta^{18}O_{PDB}$ values as high as −4‰ in some of the most ^{13}C-depleted calcites are close to values expected in equilibrium with sea water at Earth-surface temperatures, and have been used to support the hypothesis that methane oxidation occurred at the time of deposition[5].

To test this interpretation, we examined the paragenetic history of three representative samples that contain, amongst other phases, highly ^{13}C-depleted calcite. The samples were collected from the lower and middle units of the cap dolostone from two sections of the Doushantuo Formation in the Yangtze Gorges area at Jiulongwan and Huajipo (see below; Supplementary Fig. 1). Samples consist of: (1) early dolomicrite; (2) highly ^{13}C-depleted grey calcite, with crystals up to 1 mm in length, filling fractures that cross-cut dolomicrite and forming isopachous cements lining voids and bed-parallel lenses; and (3) late-stage white calcite spar filling voids and veins cross-cutting ^{13}C-depleted calcite (Fig. 1; Supplementary Figs 2–6).

Application of carbonate clumped isotope thermometry to these materials provides new constraints on their origin and diagenetic history. This technique measures the degree of 'clumping' of heavy isotopes of carbon and oxygen (^{13}C and ^{18}O, respectively) in the carbonate lattice in comparison with a random distribution. The degree of clumping, expressed as Δ_{47} in units of ‰, shows a systematic dependence on temperature[13]. This thermometer can be used to reconstruct the temperature of carbonate precipitation and the oxygen isotope composition of the fluids ($\delta^{18}O_{SMOW}$) from which analysed carbonates formed.

The cap samples examined in this study have Δ_{47} values ranging from 0.487‰ to 0.265‰, corresponding to temperatures of 86–476 °C (Figs 1 and 2a; Supplementary Table 1). In all samples, dolomicrite records the lowest temperatures (mean, 112 °C; $n = 4$), whereas the strongly ^{13}C-depleted grey calcite has the highest temperatures (mean, 378 °C; $n = 4$), with white calcite spar showing intermediate temperatures (mean, 156 °C; $n = 3$). The possibility that high carbonate clumped isotope temperatures result from nonlinear mixing or kinetic effects has been considered and ruled out (Supplementary Discussion). Further discussion of data from dolomicrite and white calcite spar is provided in the Supplementary Discussion; here we focus on the origin of highly ^{13}C-depleted calcite.

Carbonate clumped isotope temperatures from highly ^{13}C-depleted calcite are up to 200–300 °C higher than in any natural carbonate sample analysed to date. Even marbles that experienced ~500 °C during regional metamorphism have lower apparent carbonate clumped temperatures (~200 °C) because cooling over millions of years allowed C–O bonds to keep rearranging until a final 'blocking' temperature was reached[13]. Preservation of high temperatures in the Doushantuo Formation therefore requires faster cooling rates, which we propose are related to a local, short-lived thermal anomaly. More specifically, we suggest that highly ^{13}C-depleted calcite precipitated from a pulse of hot hydrothermal fluid. The exact dependence of blocking temperature on cooling rate is currently unknown. The only potentially relevant constraint is that rearrangement of oxygen by self-diffusion at 500 °C over length scales similar to a unit cell is likely to occur in minutes[14]. Conversely, carbonate blocking temperatures of ~200 °C show that the rate of oxygen diffusion drops rapidly with decreasing temperature. Therefore, the lowest temperatures measured in highly ^{13}C-depleted calcite (~275 °C) could have persisted over geological timescales.

A series of independent observations are consistent with a post-depositional, hydrothermal origin for the highly ^{13}C-depleted calcite. First, by combining temperatures with $\delta^{18}O_{PDB}$ values of carbonate, we calculate that ^{13}C-depleted calcite precipitated from ^{18}O-enriched fluids ($\delta^{18}O_{SMOW} \geq +18$‰), which were distinct from the fluids that precipitated dolomicrite and calcite spar ($\delta^{18}O_{SMOW}$ of 1 ± 1‰ and 13 ± 2‰, respectively; Fig. 2b, Supplementary Table 1). ^{18}O-enrichment of fluids in seep environments can be caused by clathrate dissociation[7,15]. However, the maximum oxygen isotope fractionation during clathrate formation is +3.2‰ relative to the water source[16]; therefore clathrate dissociation cannot account for the degree of $\delta^{18}O_{SMOW}$ enrichment calculated for fluids precipitating ^{13}C-depleted calcites. Conversely, high-$\delta^{18}O_{SMOW}$ fluids (similar to those that precipitated ^{13}C-depleted calcite) are reported from other ancient continental hydrothermal systems where ^{18}O-rich carbonate host rocks control oxygen isotope fluid compositions[17]. Therefore, we think that the high $\delta^{18}O_{PDB}$ values observed in ^{13}C-depleted calcite (Fig. 2c) are not a sign of exceptional preservation (as previously suggested, ref. 5), but instead are a result of precipitation from hot fluids buffered by ^{18}O-enriched carbonate host rocks (i.e. at low water/rock ratios).

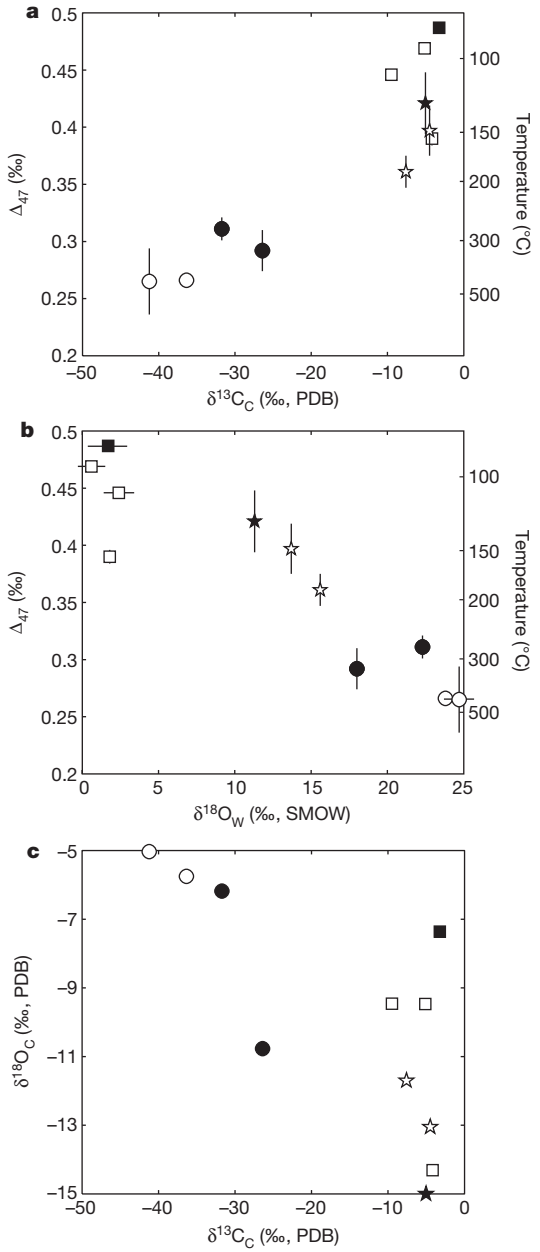

Figure 2 | Cross-plots of Δ_{47} and conventional stable isotope data from the three carbonate phases identified in cap dolostone samples. **a**, Mean Δ_{47} (left axis) and derived temperature (right axis) versus $\delta^{13}C_{PDB}$ of carbonate ($\delta^{13}C_C$). **b**, Mean Δ_{47} (left axis) and derived temperature (right axis) versus the calculated mean $\delta^{18}O_{SMOW}$ of water precipitating carbonates ($\delta^{18}O_W$). **c**, Mean $\delta^{18}O_{PDB}$ of carbonate ($\delta^{18}O_C$) versus $\delta^{13}C_{PDB}$ of carbonate. Error bars, ±1 s.d. based on two or more replicate analyses of the same powder. Error bars are less than the width and height of the symbol where not apparent. Open symbols, samples from the Huajipo section; filled symbols, samples from Jiulongwan. Stars, white calcite spar; squares, dolomicrite; and circles, ^{13}C-depleted grey calcite.

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Second, elemental analysis shows that highly ^{13}C-depleted calcite has Mn/Sr ratios >100 (Supplementary Table 2). These cements also have ^{87}Sr/^{86}Sr values (0.7090 to 0.7130) that are radiogenic in comparison with the best-preserved Marinoan cap dolostones (0.7072 to 0.7080)[18] and the low Mn/Sr (<1) carbonates from argillaceous dolomites overlying the Doushantuo Formation cap (~0.7080, ref. 19; Fig. 3, Supplementary Table 3). In contrast, most well preserved Phanerozoic seep carbonates have ^{87}Sr/^{86}Sr values close to contemporaneous sea water and Mn/Sr ratios <1 (Supplementary Tables 4 and 5). However, it is noteworthy that dolomicrite and white calcite spar also have relatively high Mn/Sr and ^{87}Sr/^{86}Sr ratios (Supplementary Table 2), indicating they were diagenetically altered[20]. This raises the possibility that the Mn/Sr and ^{87}Sr/^{86}Sr ratios of ^{13}C-depleted calcite may not be uniquely diagnostic of its origin (Supplementary Discussion). And it also makes conceivable the preservation of depositional $\delta^{13}C_{PDB}$ values in highly ^{13}C-depleted calcite, if Δ_{47} were to be reset during exchange of isotopes and trace elements between pre-existing carbonate and hot, carbon-poor fluid with high δ^{18}O, high Mn and high ^{87}Sr/^{86}Sr. But such a process strikes us as unlikely, because it should have affected other phases in the cap dolostone rather than being exclusive to highly ^{13}C-depleted calcite.

Highly ^{13}C-depleted diagenetic carbonates (with $\delta^{13}C_{PDB}$ values down to −41‰), interpreted as a product of thermogenic oxidation of low-$\delta^{13}C_{PDB}$ hydrocarbons such as methane, have been reported from several other sedimentary basins[21,22]. Similarly, we infer that the extremely low-$\delta^{13}C_{PDB}$ calcite in Doushantuo formed via thermochemical oxidation of hydrothermal methane. We think methane was sourced from organic-rich marls of the Doushantuo Formation, as there are no older source rocks in the Yangtze Gorges area. This is an appealing hypothesis, because the most ^{13}C-depleted methane (down to −51‰, PDB) previously observed in continental hydrothermal systems is produced by the thermogenic breakdown of organic matter in host sediments[23]. In addition, we suggest that the low permeability of overlying clay-rich lithologies of the Doushantuo Formation acted as a seal, causing preferential hydrothermal fluid flow through the porous cap dolostone. This explains why highly ^{13}C-depleted carbonates have only been reported from the cap.

Systematic variations in the degree of clay mineral diagenesis indicate a localized thermal anomaly at the base of the Doushantuo Formation, thus supporting the hypothesis of focused hydrothermal flow. The main clay mineral in the lower 80 m of the Doushantuo Formation in this area is saponite, an Mg-rich trioctahedral smectite interpreted as forming at the time of deposition, based on the unusual mineralogy[24]. However, X-ray diffraction (XRD) data[24] and a decrease in cation exchange capacity (CEC) normalized to the total clay content (Fig. 3; Supplementary Discussion) show that saponite is increasingly altered to corrensite (ordered mixed-layer trioctahedral smectite/chlorite) and chlorite down-section, as the cap dolostone is approached. Because the extent of chloritization of saponite during diagenesis increases with temperature and duration of thermal activity, and does not require extensive fluid exchange, it is a useful means of monitoring maximum palaeotemperatures and is therefore commonly used to study the diagenetic history of sedimentary basins[25]. At temperatures >300 °C, indicated by carbonate clumped isotopes, chloritization takes place at timescales of hundreds to thousands of years[25], consistent with our hypothesis that low Δ_{47} values in carbonates were preserved by rapid cooling.

The thermal gradient implied by clay minerals in the basal 25 m of the Jiulongwan section (Fig. 3) also requires that hydrothermal activity took place after deposition of at least this much sediment. U–Pb zircon ages of 635.2 ± 0.5 Myr and 632.5 ± 0.6 Myr from ash beds within the cap dolostone and 5 m above the top of the cap, respectively[10], show that hydrothermal activity occurred more than 1.6 Myr after deposition of the cap dolostone and is therefore unrelated to deglaciation. We suspect a much younger age, however, coinciding with a regionally extensive Early Cambrian hydrothermal episode in south China (ref. 26; Supplementary Discussion).

Our findings show that the highly ^{13}C-depleted calcite in the Doushantuo Formation is not a record of clathrate destabilization associated with Marinoan deglaciation. The results also highlight a broader puzzle. Before this study, the Doushantuo Formation was considered to contain the oldest examples of carbonates derived by methane oxidation at a cold seep, despite evidence for metabolism of methane dating back to the Archaean[27] and predictions of higher

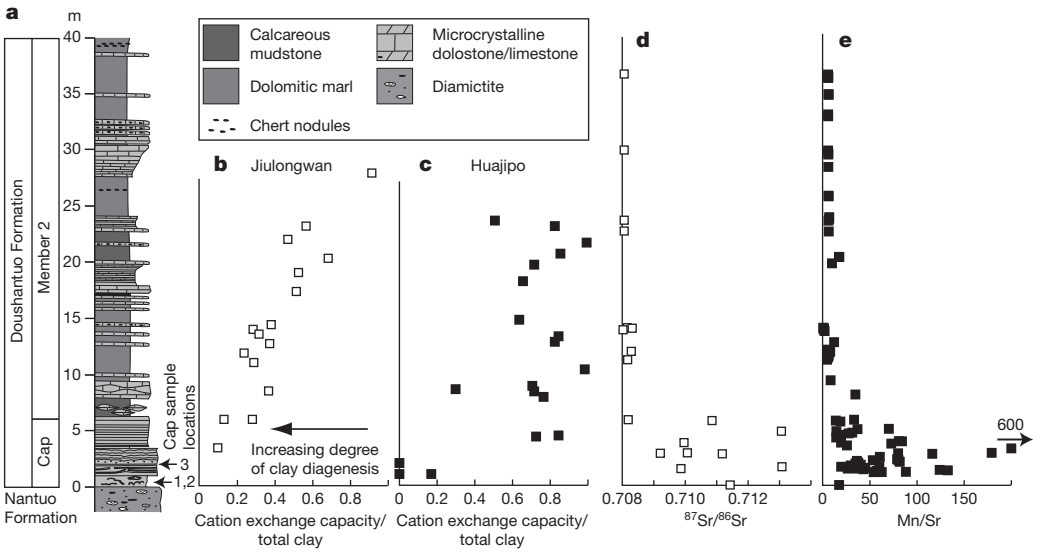

Figure 3 | Stratigraphic variability in trace element content, ^{87}Sr/^{86}Sr ratios and degree of chloritization of trioctahedral clay minerals of the lower Doushantuo Formation from the two sections examined in this study. **a**, Stratigraphy. **b**, **c**, Stratigraphic trends in the cation exchange capacity (CEC) of a sample normalized to the total trioctahedral clay content. This ratio is used as an indicator of the extent of clay mineral diagenesis (Supplementary Discussion). Samples with lower normalized CEC contain more corrensite and chlorite and are more diagenetically altered. The stratigraphic position of mineral transformations is different in each section; this is an expected consequence of the heterogeneity of a thermal anomaly induced by hypothesized hydrothermal activity. ^{87}Sr/^{86}Sr ratios (**d**) and Mn/Sr data (**e**) are from ref. 19 and are consistent with phase specific trace element and ^{87}Sr/^{86}Sr data from the cap dolostone (Supplementary Tables 2 and 3). The sampling locations of cap dolostone samples analysed are shown next to the stratigraphic column. Sample 1 comes from Jiulongwan, samples 2 and 3 come from Huajipo.

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fluxes of biogenic methane in the Precambrian[28]. However, our reinterpretation of the highly ^{13}C-depleted calcite, combined with a survey of seep occurrences through Earth history[15] and a recent survey of Precambrian carbon isotope data (including over 11,000 analyses)[29], show that Precambrian carbonates are devoid of cements with $\delta^{13}C_{PDB}$ values less than −30‰, which are characteristic of methane seep carbonates in the Phanerozoic[15].

We propose that this absence reflects the importance of anaerobic oxidation of methane (AOM), using sulphate, in generating exceptionally low $\delta^{13}C_{PDB}$ signatures in carbonate rocks associated with methane seeps. AOM is a biologically mediated reaction that generates ^{13}C-depleted carbonate alkalinity, promoting subsequent precipitation of carbonate with exceptionally low $\delta^{13}C_{PDB}$. Incubation experiments on cold seep sediments, naturally enriched in methanotrophic communities, show that decreased sulphate concentrations result in reduced rates of AOM[30]. Therefore, low sulphate concentrations that characterized Precambrian oceans[9] would have reduced AOM rates, making conditions less favourable for the precipitation of highly ^{13}C-depleted carbonates[11]. Our reinterpretation of the highly ^{13}C-depleted carbonates in the Doushantuo Formation thus highlights the influence of ocean chemistry on methane cycling through Earth history.

METHODS SUMMARY

We characterized the petrography and mineralogy of three cap dolostone samples using visible light microscopy, elemental mapping (with the electron microprobe JEOL JXA 8200 at the California Institute of Technology and an XGT X-ray fluorescence scanner at the Jet Propulsion Laboratory) and quantitative elemental spot analysis of carbonates by electron microprobe. Representative carbonates were micro-drilled from slabs for isotope measurements. Sr isotope measurements were made on acetic acid digestions of carbonate powders using a Neptune MC-ICPMS at the Keck Laboratory, University California, Santa Cruz. Clumped and traditional carbon and oxygen isotope analysis were made on a MAT 253 at the California Institute of Technology. The degree of chloritization of clay minerals was quantified by measuring the CEC to total clay content ratios of 35 samples of the cap and 25 m of overlying sediments collected at Huajipo and Jiulongwan. Quantitative XRD and CEC measurements were carried out at the University of California, Riverside, on whole-rock powders (see Methods and Supplementary Discussion for more details).

Full Methods and any associated references are available in the online version of the paper at www.nature.com/nature.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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Author Contributions T.F.B. and J.P.G. conceived the study. M.B. carried out clumped and conventional isotope analysis and wrote part of the Supplementary Discussion. J.M.E. provided laboratory facilities for isotope work. A.D. and T.F.B. carried out clay mineral analysis. T.F.B. carried out petrographic work and trace element analysis and wrote the manuscript. All authors discussed results, planned analyses and contributed to the manuscript.

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METHODS

Clumped and traditional isotope measurements. CO_2 was extracted from all carbonate samples by phosphoric acid digestion at 90 °C using the automatic laboratory methods described elsewhere[31]. CO_2 was analysed at the California Institute of Technology using a Finnigan MAT 253 gas source mass spectrometer configured to collect masses 44–49. Each measurement consisted of eight acquisitions, with typical standard deviations of 0.01‰ to 0.04‰ for Δ_{47} measurements. Values of $\delta^{18}O$ and $\delta^{13}C$ were acquired as part of each analysis and typically show standard deviations one order of magnitude lower (averages of 0.008‰ and 0.004‰, respectively). Carbonate powders with known compositions and heated CO_2 standards were run with unknown samples for offset correction and standardization. Heated gas (CO_2 heated for two hours at 1,000 °C to achieve a stochastic isotopic distribution) with a range of bulk stable isotope compositions similar to samples ($\delta^{13}C \ll 0$‰) were analysed to minimize the potential errors associated with mass spectrometric nonlinearities. For this study, data were normalized relative to a fixed heated gas line model (for each of the three sessions of analyses run) and raw data corrected for instrument nonlinearity and scale compression as described in ref. 32. Δ_{47} data were then corrected for an acid reaction temperature of 90 °C, with the correction factor of 0.081‰, as experimentally determined[31]. Finally, Δ_{47} data were normalized to working carbonate standards: a vein calcite named 102-GC-AZ01 and an Italian marble named Carrara marble. This last correction stage is typically less than 0.02‰. Fourteen distinct extractions of Carrara marble standard during this period yielded a mean Δ_{47} value of 0.356 ± 0.012‰, a $\delta^{13}C_{PDB}$ of 2.34 ± 0.04‰ and a $\delta^{18}O_{PDB}$ of -1.75 ± 0.07‰. Five separate extractions of 102-GC-AZ01 yielded a Δ_{47} of 0.646 ± 0.009‰, a $\delta^{13}C_{PDB}$ of 0.51 ± 0.06‰ and a $\delta^{18}O_{PDB}$ of -14.32 ± 0.06‰. Accepted Δ_{47} values for these standards from >60 analyses by multiple analysts in our laboratory are 0.352‰ and 0.654‰ for Carrara marble and 102-GC-AZ01, respectively.

Fractionation factors of 1.00821 and 1.0093 were used to account for the temperature-dependent oxygen isotope fractionation between CO_2 gas and carbonates resulting from the reaction with phosphoric acid at 90 °C, for calcitic samples[33] and dolomitic samples[34], respectively. Measured values of Δ_{47} (in ‰) were used to estimate carbonate growth temperature, using the empirically derived polynomial determined using high temperature experimental carbonates[13], hydrothermal dolomite (M.B. *et al.*, manuscript in preparation) and inorganic synthetic calcites[13]. Paired temperature and carbonate $\delta^{18}O_{PDB}$ data were used to calculate the $\delta^{18}O_{SMOW}$ values of hydrothermal and/or formation waters that interacted with analysed carbonates, using temperature dependent carbonate–water fractionations described in ref. 35 for calcite and ref. 36 for dolomite. All samples were analysed at least twice using sub-fractions of the same powder, to account for heterogeneity. Uncertainties in temperature estimates and isotopic data (Fig. 2; Supplementary Table 1) are based on a minimum of two analyses of the same powder. A minimum error for Δ_{47} measurements of 0.02‰ has been applied based on the maximum external precision expected from counting statistics; see, for example, ref. 32.

Sr ratios. Because of the relatively large amount of sample required for combined Δ_{47} and Sr isotope analysis, powders for Sr isotope analysis of sample 3 were collected from the same phases in a companion slab cut from the sample used to obtain powders for isotope measurements. For other samples, powders were obtained by re-drilling holes initially used to collect powder for Δ_{47} measurements. To avoid potential contamination from silicate phases, Sr isotope measurements were made on acetic acid digests of carbonate powders, using a Neptune MC-ICPMS at the Keck Laboratory, University California, Santa Cruz. The precision of these measurements is 0.00002, based on repeated measurements of an internal standard that yielded a mean Sr ratio of 0.71030 ($n = 5$). The accepted value of this standard is 0.71025 and this offset was applied in correcting measured sample ratios. A repeat measurement of a sample of highly ^{13}C-depleted calcite from sample 3 yielded Sr ratios that were within 0.00002.

Elemental mapping and analysis. Two methods were used in elemental mapping. Areas of samples 1 and 3, outlined in blue in Supplementary Fig. 4 and 5, were scanned using an XGT X-ray fluorescence scanner at the Jet Propulsion Laboratory, Pasadena, California. The images give qualitative information about the elemental abundances in various phases of the samples, with the brightest areas containing the highest relative abundance of a particular element.

A highly polished, large format (51 × 75 mm) thin section, of part of sample 3, corresponding to the area inside the blue box shown in Supplementary Fig. 5, was carbon coated for electron probe analysis using the JEOL JXA 8200 instrument at the Division of Geological and Planetary Sciences Analytical Facility, California Institute of Technology. A representative 6 × 6 mm area that contained each of the three main carbonate phases was selected for elemental mapping. The elemental maps shown in Supplementary Fig. 6 give qualitative information about elemental abundance, with brighter areas containing higher concentrations of an element.

Quantitative measurements of Mg, Ca, Sr, Fe, Mn, Si, Al and Ba in the various carbonate phases were made using multiple spot analyses, with a defocused 10 μm spot at 15 kV and 15 nA.

Quantitative XRD and CEC measurements. These analyses were made at the University of California, Riverside, on powdered samples from the same sections of the Doushantuo Formation (at Huajipo and Jiulongwan) that cap dolostone samples were collected from (Fig. 3). The methods used for analysis are described elsewhere[24,37].

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