Oxygen isotope composition of the Phanerozoic ocean and a possible solution to the dolomite problem

Uri Ryb and John M. Eiler

*Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125

Edited by Donald E. Canfield, University of Southern Denmark, Odense, Denmark, and approved May 16, 2018 (received for review November 10, 2017)

The 18O/16O of calcite fossils increased by ~8‰ between the Cambrian and present. It has long been controversial whether this change reflects evolution in the δ18O of seawater, or a decrease in ocean temperatures, or greater extents of diagenesis of older strata. Here, we present measurements of the oxygen and “clumped” isotope compositions of Phanerozoic dolomites and compare these data with published oxygen isotope studies of carbonate rocks. We show that the δ18O values of dolomites and calcite fossils of similar age overlap one another, suggesting they are controlled by similar processes. Clumped isotope measurements of Cambrian to Pleistocene dolomites imply crystallization temperatures of 15–158 °C and parent waters having δ18O-VSMOW values from ~2‰ to +12‰. These data are consistent with dolomitization through sediment-rock reaction with seawater and diagenetically modified seawater, over timescales of 100 My, and suggest that, like dolomite, temporal variations of the calcite fossil δ18O are largely driven by diagenetic alteration. We find no evidence that Phanerozoic seawater was significantly lower in δ18O than preglacial Cenozoic seawater. Thus, the fluxes of oxygen-isotope exchange associated with weathering and hydrothermal alteration reactions have remained stable throughout the Phanerozoic, despite major tectonic, climatic and biologic perturbations. This stability implies that a long-term feedback exists between the global rates of seafloor spreading and weathering. We note that massive dolomites have crystallized in pre-Cenozoic units at temperatures >40 °C. Since Cenozoic platforms generally have not reached such conditions, their thermal immaturity could explain their paucity of dolomites.

The δ18O-VSMOW of seawater at earlier times could be interpreted as a reflection of changes in the relative rates and/or conditions of weathering and hydrothermal alteration. Several studies have attempted to reconstruct the isotopic composition of seawater using marine carbonates (7–10), phosphorites and cherts (11–13), kerogens (14), and altered oceanic crust and iron ores (1). The interpretation of all of these records depends on assumptions regarding the temperatures at which the studied materials last exchanged oxygen with water. A common approach to this problem is to identify samples that grew at Earth-surface conditions; however, this method is only useful if we can reliably recognize materials that have escaped diagenesis.

Arguably the most abundant and influential record of this kind has examined calcite fossils (mostly brachiopods) that are inferred to have escaped diagenetic modification (7–10). Materials that pass these studies’ criteria for preservation record an 8‰ increase in δ18O between the Cambrian and the present. If this is a primary depositional signal, it implies a similarly large increase in the δ18O value of seawater, suggesting a decrease over time in the relative importance of weathering and an increase in the relative importance of hydrothermal alteration (2, 7, 10, 15). Alternatively, one might interpret these same materials as primary (free of diagenetic overprints) but conclude that their change in δ18O reflects a decrease in surface temperatures.

Significance

The elemental and isotopic compositions of seawater have evolved throughout Earth’s history, in tandem with major climatic, tectonic and biologic events, including the emergence and diversification of life. Over geological timescales, the oxygen isotope composition of seawater reflects a global balance between mineral-rock reactions occurring at the Earth’s surface (weathering and sedimentation) and crustal (hydrothermal alteration) environments. We put constraints on the oxygen isotope composition of seawater throughout the Phanerozoic and demonstrate that this value has remained stable. This stability suggests that the fluxes of globally averaged oxygen isotope exchange, associated with weathering and hydrothermal alteration reactions, have remained proportional through time and is consistent with the hypothesis that a steady-state balance exists between seafloor hydrothermal activity and surface weathering.
from as high as 80 °C during the early Paleozoic, rather than a change in the δ18O of seawater (12, 13). This conclusion has been criticized for its physical implausibility (16) but has been supported for the Archean and Proterozoic by studies of Si isotopes in cherts (17), δ18O of kerogens (14), and thermal stabilities of proteins that are conserved across diverse microbial taxa (18). It has also been argued that records of the δ18O of ancient altered oceanic crust, coupled with mass balance models, require that the δ18O of seawater has been buffered to values in the narrow range 0 ± 2‰ throughout the Phanerozoic (19). One solution to this debate suggests that the carbonate record reflects neither varying ocean δ18O nor surface temperatures; rather, it can be attributed to diagenetic alteration at elevated burial temperatures (20) and/or in the presence of low-δ18O meteoric water (21).

Part of the reason why this debate has failed to reach a consensus is that the measurements in question—δ18O values of minerals—depend on both temperature and the δ18O values of water from which those minerals grew. Carbonate clumped isotope composition provides a measure of the temperature of carbonate mineral crystallization (at least, in cases where minerals form at or near isotopic equilibrium). This temperature constraint is independent of mineral δ18O (or δ3C) value; in fact, when a clumped isotope temperature is combined with a mineral δ18O value, it allows one to independently calculate the δ18O of coexisting fluid, by assuming crystallization occurred at thermodynamic equilibrium and was not followed by solid-state isotopic alteration of the clumped isotope composition (22).

Several previous studies have applied clumped isotope thermometry to pre-Cenozoic fossil carbonates; briefly, these studies have demonstrated that (i) fossils that were previously suggested to be geochemically pristine were in fact diagenetically altered at elevated burial temperatures (23) and (ii) the least altered (coldest clumped isotope temperatures) samples last equilibrated at or near surface temperatures of 15–37 °C with waters having δ18O values of −1.6–0‰ during the Ordovician and Silurian (23–26), late Carboniferous (25), and late Cretaceous (27). These results suggest that between the late Ordovician and late Cretaceous the ocean has been stable in δ18O at near Cenozoic values and broadly similar to the range of modern Earth surface temperatures; these studies also suggest that the large ranges in δ18O of pre-Cenozoic carbonates are mostly the result of diagenetic alteration. These interpretations or involve potential problems (28, 29). Challenges (7) by a suggestion that the fossil-record argument is not consistent with observations of the coupled calcite or dolomite or δ18O of seawater (SI Appendix, Fig. S1). Based on stratigraphic relationships, several of the dolomite samples in the dataset are known to be associated with local mixing of seawater and meteoric water (33); these data are shown in Figs. 1 and 2 (gray filled symbols) but do not figure in our interpretations.

Fig. 24 plots the δ18OVPDB values of dolomites from this study against their stratigraphic ages, which represent the upper limit on the age of dolomitization. The δ18OVPDB of dolomites increases by ~5‰ between the Cambrian and the Pleistocene and overlaps the calcite record (Fig. 24). We acknowledge that our data compilation includes a limited number of samples and sampling sites. Nevertheless, a similar overlap has been observed in a comprehensive compilation of Precambrian dolomite and calcite δ18O values (10). We therefore consider the overlap in δ18O between coexisting calcite and dolomite to be a common feature of marine carbonate rocks and suggest that the observed temporal trends in Fig. 24 reflect a common process affecting the δ18O value of both mineral phases. Keeping in mind that the δ18O value of dolomite is controlled by the temperature of diagenetic alteration and the δ18O of seawater and basinal brines (Fig. 1A and B), we suggest the temporal trend in Fig. 24 is the result of older rock units’ having experienced, on average, a greater range of burial depths/temperatures for longer time spans,
and being more likely to have been preserved from erosion if they were deeply buried. Consistent with this interpretation, both the average and SD of the dolomite crystallization temperatures decreases from the Paleozoic (89 ± 33 °C) to Mesozoic (57 ± 30 °C) to Cenozoic (25 ± 6 °C) rock units (Fig. 3).

The similarity between the calcite and dolomite Phanerozoic δ^{18}O records in Fig. 2 suggests that calcite δ^{18}O is also largely a product of diagenetic alteration at elevated burial temperatures. Diagenetic alteration of early Paleozoic calcite fossils has been demonstrated for Silurian calcite fossils from Gotland, Sweden (23). There, samples have recorded a range of clumped isotope temperatures of 33–62 °C while preserving the original microstructures and Mg, Mn, and Sr compositions that are found in modern organisms and commonly used as indicators for diagenetic alteration. Importantly, these samples have experienced a common thermal history during burial and exhumation, and brachiopods and optical calcites have been shown to have common reordering kinetics (28). Therefore, any variation in clumped isotope composition must derive from the calcite temperature of crystallization, while solid-state isotopic reordering, if it occurred, would have shifted all clumped isotope temperatures toward higher values while slightly contracting the distribution of temperatures. A range of 29 °C is beyond the plausible variability of seawater temperatures and therefore must include elevated burial temperatures recorded by diagenetic alteration.

While the crystallization ages of dolomite we have studied are unknown, when one considers the range of depositional ages, dolomite crystallization temperatures, and the temperature histories of the basins from which these samples come, it is clear that the dolomites in our dataset have formed throughout the Phanerozoic (e.g., dolomites from the Paleozoic section at the western Colorado Plateau have formed throughout the Paleozoic and Mesozoic; SI Appendix, Fig. S2).

Our findings suggest that the record of δ^{18}O variations for Phanerozoic calcite fossils is largely a product of subsurface diagenetic alteration and not a record of Earth-surface environments. This result is inconsistent with previous interpretations which have associated low Paleozoic carbonate δ^{18}O values with low δ^{18}O seawater, ascribed to a higher proportion of weathering to hydrothermal alteration reactions, driven by a global increase in weathering rate (5) and/or a decrease in water circulation through midocean ridges that followed their “blanketing” by pelagic sediments and/or a lower sea level (2, 48). Clumped isotope and oxygen isotope constraints on δ^{18}O of waters parental to both dolomite and calcite in the Phanerozoic samples we considered indicate that all samples grew from waters that were either within the range of Cenozoic ice-free seawater δ^{18}O values or higher (which we interpret as a sign of water–rock reactions in basins). We find no indication for seawater lower in δ^{18}O than −2‰ (Fig. 2B). We conclude that the evidence we presented for diagenetic alteration of the δ^{18}O records of calcite and dolomite as well as the constraints we offer on the δ^{18}O of Phanerozoic seawater are most consistent with the uniformitarian hypothesis (19), that is, that the budget of oxygen isotope exchange fluxes associated with weathering and hydrothermal alteration had a balance of relative strengths similar to today’s throughout all of the Phanerozoic. Mass balance model results suggest that a persistent 20% decrease in the oxygen isotope flux associated with hydrothermal alteration reactions or a persistent 100% increase in the flux associated with weathering reactions (relative to their estimated values for the present) are required to drive seawater δ^{18}O value below −2‰; such values while slightly contracting the distribution of temperatures.

Fig. 1. (A) Dolomite δ^{18}O values are negatively correlated with clumped isotope-based crystallization temperatures (R^2 = 0.421, p = 0.913). Gray dots mark dolomites which were associated with local mixing with meteoric water (33); all other data are constrained between modeled δ^{18}O_dolomite compositions at equilibrium with water δ^{18}O_VSMOW of ~2% and ~12% (dashed lines), and dominantly (90%) of the data to ~1 to ~6‰. VSMOW (gray band) calculated using Horita (66) equation. (B) Calculated δ^{18}O_water is positively correlated with clumped isotope-based dolomite crystallization temperatures (R^2 = 0.406, p = 0.683). δ^{18}O_water is calculated from measured δ^{18}O_dolomite and clumped isotope temperatures using Horita (66) equation. Most data points follow the expected trend for buffering of seawater by dolomite with δ^{18}O_dolomite of ~2‰. Other samples diverge from this trend toward lower δ^{18}O compositions and may reflect dolomite crystallization at higher water/rock ratios (water-buffered) or mixing with meteoric water. Dashed lines are predicted water-to-rock ratio (W/R) contours (see Methods for details). (C) A histogram of log W/R values calculated for dolomite that have crystallized at temperatures >50 °C. These values reflect the minimum actual water-to-rock ratio during dolomite crystallization. W/R values are significantly higher than the range of pore water-to-rock ratio (67) and mostly lower than the W/R values required to fully dolomitize a low-Mg calcite (36).
perturbations are contraindicated by the findings of this study. While it is possible that the older, high-temperature dolomites grew from parental waters that were basinal brines derived from much lower δ¹⁸O initial seawaters (i.e., much lower than ~−2‰ VSMOW) there is no positive evidence for such waters, and any such scenario would require paths through temperature–δ¹⁸O space significantly different from that documented by the main trend of data; for example, early Paleozoic dolomites will have a negative offset of ~−8‰ from the general trend (marked by the gray trend in Fig. 1A), which is not the case.

It is significant that we find the proportions of weathering and hydrothermal alteration have remained similar through time, despite major tectonic, climatic, and biologic perturbations (e.g., the assembly and breakup of the Pangaea supercontinent, transitions from icehouse to greenhouse Earth climate, and the emergence of terrestrial plants) (Fig. 2B). These perturbations may persist for several times 10⁸ y and have the potential to drive a several per-mille decrease in the δ¹⁸O of seawater (49), yet their time-integrated effects are not detectable. The constant proportionality of weathering and hydrothermal exchange through these geological changes implies that a global feedback exists between weathering and seafloor spreading rates over timescales of 10⁸ to 10⁹ years. Such feedback was predicted by the “spreading rate hypothesis” (50), in which any increase in seafloor spreading rate is accompanied by a higher flux of CO₂ degassing from magmatic activity in spreading centers and subduction zones, leading to global warming, higher water acidity, and a global increase in weathering rates. A second possible feedback mechanism is that higher seafloor spreading rates will be accompanied by faster plate convergence, leading to the buildup of relief and faster erosion and weathering rates (51).

Dolomite is abundant in pre-Cenozoic strata but mostly absent from Cenozoic strata. This observation was referred to as the “dolomite problem” and has been attributed to the experimental finding that uptake of Mg²⁺ by Ca-carbonate minerals is kinetically limited, with a rate that depends strongly on temperature, and is prohibitively slow at average modern Earth-surface temperatures (52). Because marine temperatures are believed to have been higher during the Paleozoic and Mesozoic compared with the Cenozoic, cooling of marine waters and sediments are hypothesized to have driven a decrease in dolomite formation rate (52). This interpretation views dolomitization as an early (i.e., shallow sediment column) diagenetic process that was rapid and widespread in pre-Cenozoic marine sediments and slow and rare in Cenozoic and modern settings. The Bahamas platform is an example of a rare modern setting where locally high temperatures and salinities overcome these kinetic barriers and allow dolomite formation (53).

The findings presented here challenge this model, as they indicate that pre-Cenozoic dolomites mostly formed at temperatures significantly higher than plausible Phanerozoic ocean water or shallow sediment column conditions and commonly grew from isotopically evolved basinal fluids rather than unmodified seawater. This suggests that dolomite growth is promoted by protracted deep burial and that the increased proportion of dolomite in pre-Cenozoic strata simply reflects the increase with age in average temperature and time of burial. This finding suggests that dolomite is sparse in Cenozoic sediments not because of any peculiarity in their depositional conditions or compositions but simply because they have not yet undergone burial to deep elevated burial temperatures. The observed stability in seawater δ¹⁸O overlaps with major climatic and tectonic perturbations including the assembly and breakup of Pangaea and several transitions from an icehouse to greenhouse climate.

Fig. 2. The Phanerozoic carbonate and water δ¹⁸O records. (A) δ¹⁸Owater overlaps the δ¹⁸Owater record of well-preserved calcite fossils (7) and displays a similar ~8‰ increase between the early Paleozoic and the present. Calcite and dolomite are different in δ¹⁸O by ~4–3‰ when both grow from the same water at the same temperature, but this difference is subtle at the scale plotted. (B) δ¹⁸Owater record calculated from clumped and bulk isotope compositions of dolomite and well-preserved calcite fossils (23–27). For the calcite fossils we include only δ¹⁸Owater that has been associated with least-altered specimens (23–27). Except for dolomites that formed from local mixing between sea and meteoric water (gray dots) all δ¹⁸Owater values are > ~2‰ VSMOW, consistent with time-invariant seawater δ¹⁸O composition (gray rectangle) and inconsistent with the proposed time variation of seawater δ¹⁸O values (dashed black line (5)). δ¹⁸Owater that is >2‰ is explained by isotopic modification of seawater through water–rock reactions at
diagenetic settings. Assuming a seafloor temperature of 20 °C, a crustal thermal gradient of 25 °C km−1, and sedimentation rate in carbonate platforms of 0.01 mm y−1 [expected when averaged over timescales of 107 My (54)], Cenozoic deposits are expected to accumulate to a maximum thickness of 650 m and to reach a maximum temperature of 36 °C, which is in a range where dolomite formation from seawater is slow (36, 55) and below the range of temperatures we see associated with most dolomite formation. An implication of this hypothesis is that while Cenozoic strata generally fail to reach efficiently dolomitizing environments, dolomitization of at least some older strata took place during the Cenozoic (i.e., because they only reached deep burial in the recent geological past). This is a testable prediction, as it leads to the expectation that quantitative dating (such as by U-Pb techniques (46)) of at least some dolomites in pre-Cenozoic strata will yield Cenozoic ages.

An open question is how Mg2+ enters these rocks in the first place. Most simply, the temperatures we measure might represent the conditions at which Mg-rich fluids first convert calcite to dolomite. In this case, carbonate platforms have been commonly characterized by hydrological systems capable of transporting significant quantities of dissolved Mg2+ to deep diagenetic environments. Using the observed δ18O values and crystallization temperatures of dolomites, we estimate the minimum water to rock ratio at the sites of dolomite crystallization (Fig. 1 B and C) (see Methods for details). We find that the minimum ratio of low-δ18O water to primary sedimentary rock in which dolomites form is generally significantly higher than the range of typical pore volumes of carbonate rocks (Fig. 1C), indicating that these deep diagenetic environments have been flushed with surface waters (or basal fluids derived from surface waters). Although our quantification of this effect makes use of highly simplified arguments regarding the mass balance of fluid rock reaction, the first-order conclusion is not easily explained in any other way: As the δ18O values of carbonate rocks decrease consistently and progressively with increasing temperatures of last crystallization, the δ18O values we have calculated the expected water-to-rock ratio for these samples is very sensitive to the assumption of initial water and rock compositions and therefore highly uncertain (as implied by the convergence of W/R contours toward the assumed initial water δ18O value and temperature in Fig. 1B). To avoid this uncertainty, we confine our analysis of dolomites that have crystallized at temperatures <50 °C. Importantly, the results of this zero-dimension analysis should be regarded as minimum constraints on the actual water-to-rock ratio in the dolomite crystallization sites (58). Samples with δ18Owater significantly larger volumes of modified (isotopically heavier) seawater that have interacted with the rock (58). Alternatively, the data we present are also consistent with a more complex scenario in which Mg2+ was first bound in a disordered dolomite precursor during early diagenesis, and the temperatures we observe reflect the conditions where this precursor converted to ordered dolomite late in diagenesis, with little or no further input of Mg2+ from seawater. In this case, fluids need not deliver Mg2+ deep into platform carbonate sequences. However, the relationship between δ18O and formation temperature of dolomite still requires that final dolomite crystallization occurred at elevated temperatures and during reaction with large volumes of low-δ18O fluid, that is, this alternative allows that the Mg budget of dolomite-rich strata could be set by early diagenesis, but the data still require that such rocks typically undergo deep burial, and change in δ18O by reaction with surface-derived fluids at high water/rock ratios.

Methods
We collected 33 dolostone samples from carbonate rock units at the base, middle, and top of the Paleozoic section at the Grand Wash and the Upper Wash basins in Grand Canyon (Fig. S1), and six basinal carbonate samples from boreholes from the Paradox basin in the Plateau interior (SI Appendix, Fig. S3). Samples were cut, cleaned, and crushed using a mortar and pestle. Samples that contained multiple carbonate fabrics (i.e., cements, concretions, and veins) were selectively sampled using a microdrill, resulting in a total of 40 subsamples.

We analyzed the proportions of carbonate minerals (calcite, dolomite, and aragonite) in the powdered samples using a Bruker 2D-phase XRD system. All samples presented here consisted of >95% dolomite.

We analyzed bulk δ13C and δ18O and clumped (Δ47) isotope compositions following the procedures described in Ghosh et al. (59), Huntington et al. (60), and Passey et al. (61). In short, we dissolved ∼10 mg of sample at 90 °C in 103% phosphoric acid. Evolved CO2 was separated cryogenically and purified on a gas-chromatography column. We measured masses 44–49 of the purified CO2 gas using a Thermo MAT253 isotope ratio mass spectrometer. Measurements were replicated up to five times during different sessions and on two different mass spectrometers. Heated (1,000 °C) and equilibrium (25 °C) CO2 standard gases of variable δ13CO2 and δ18O2 were measured routinely to characterize and correct for the pressure baseline effect and isotopic “scrambling” in the ion source (62). We routinely measured in-house carbonate standards with long-term average Δ47 values and 5Ds of 0.408 ± 0.02 (CT Carrara) and 0.65 ± 0.029 (TV04).

Δ18O, δ13C, and Δ47 values were calculated following Huntington et al. (60) and Dennis et al. (62) and assuming the Brand isotopic ratios for oxygen (17/16 and 18/16) and carbon (13/12) in VPDB standard and slope of the triple oxygen isotope line (S3) (63). Δ47 values were calculated in the absolute reference frame using the ClumpyCrunch v1.0 online calculator (63) and corrected for acid fractionation by addition of 0.092‰ (64). When the average of the standards measured in a session deviated from either of the above values, we corrected our data to the standard using a linear transfer function, Δ47corrected = a × Δ47measured + b, where a and b are the slope and intercept of the standards measured versus known values, Δ47measured is the uncorrected value, and Δ47corrected is the Δ47 value after standard correction. Errors are reported as 1 SE of replicates, or for singly measured samples, the internal measurement SE. Clumped isotope temperatures were calculated using Bonfice et al. (65) calibration.

Using calculated and reported clumped isotope temperatures and δ18O values we have calculated the δ18O composition of water in thermodynamic equilibrium using the equation of Horita (66). Water-to-rock ratios have been calculated for a closed system (47) assuming an initial water δ18O value of 0‰ (VSMOW) and initial rock δ18O value of 3.6‰ (VPDB) which corresponds to dolomite in equilibrium with the assumed initial water at 15 °C—the minimum temperature observed in our dataset. Low-temperature dolomites have undergone relatively minor diagenetic modification of δ18O values (Fig. 1A). The calculation of water-to-rock ratio for these samples is very sensitive to the assumption of initial water and rock compositions and therefore highly uncertain (as implied by the convergence of W/R contours toward the assumed initial water δ18O value and temperature in Fig. 1B). To avoid this uncertainty, we exclude from this analysis dolomites that have crystallized at temperatures <50 °C. Importantly, the results of this zero-dimension analysis should be regarded as minimum constraints on the actual water-to-rock ratio in the dolomite crystallization sites (58). Samples with δ18Owater
values lower than the minimum value permitted under the assumptions of this analysis (<0% VSMOW) are considered water-buffered (W/R).

ACKNOWLEDGMENTS. We thank Yan Kiro, Max K. Lloyd, and Alex Lipp for assisting in the field and with sample preparation procedures; two anonymous reviewers for their detailed and constructive comments; and the Grand Canyon National Park and the US Geological Survey Core Research Center for facilitating the sample collection. This work was supported by NSF Grant EAR-1624827 (to J.M.E.). U.R. was supported by an O. K. Earl fellowship during this study.