

Paleoclimates, ocean depth, and the oxygen isotopic composition of seawater

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Abstract

A recurrent interpretation of ancient climate based on the oxygen isotopic composition of marine carbonates and cherts suggests that Earth's climate was substantially warmer in the distant past and remained so until as recently as 400 Myr ago. This interpretation is difficult to reconcile with the long-term glacial record, with evidence for modest weathering rates during most of Earth's history, with biomarker and fossil evidence for eukaryotes and even vertebrates at times of anomalously low $\delta^{18}\text{O}$ values, and with the predicted faintness of the young Sun. We argue here, following earlier suggestions, that the low $\delta^{18}\text{O}$ values in ancient rocks are a consequence of the low $\delta^{18}\text{O}$ of ancient seawater. A modest increase in ocean depth with time, together with progressive increases in pelagic sedimentation on midocean ridge flanks since about 550 Ma, could account for the variation in seawater isotopic composition. The required change in ocean depth, coupled with thinning of the oceanic crust, is a natural consequence of the decline in heat flow over time. Contrary to previous assertions, such a model is not inconsistent with data from ophiolites. It seems likely that Earth's climate remained largely within Phanerozoic norms throughout the past 3.5 Ga.

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1. Introduction

Oxygen isotopes in sedimentary rocks are widely used to infer paleotemperatures. Minerals precipitated from seawater at low temperatures are enriched in ^{18}O compared to the parent solution, while minerals formed at higher temperatures show less enrichment. Variations in oxygen isotopic composition are typically expressed in terms of $\delta^{18}\text{O}$, which represents the per mil (‰) difference in the ratio $^{18}\text{O}/^{16}\text{O}$ between the sample and

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Standard Mean Ocean Water (SMOW). (Bio)chemical marine sedimentary rocks of Archean, Proterozoic and early Phanerozoic age, that is older than about 0.4 Ga, typically have $\delta^{18}\text{O}$ values that are lower than those of modern carbonates, by $\sim 6\text{--}10\text{‰}$ [1–6]. Data from ancient carbonates are shown in Fig. 1. The chert data show a roughly similar trend towards isotopically lighter values in the distant past, although the change during the Phanerozoic is somewhat less and the difference between the Archean and Proterozoic is more marked [6]. The highest estimated temperatures are derived from Archean cherts dated at ~ 3.3 Ga [5]. Even taking into account the second order effects of glaciation at modulating global seawater $\delta^{18}\text{O}$, mean surface ocean temperatures during the Precambrian are estimated to have been 60 ± 20 °C.

Even though the Sun was substantially less luminous in the geological past, such temperatures could in theory have been sustained by a dense greenhouse atmosphere rich in CO_2 and H_2O [8], and perhaps CH_4 as well [9]. Yet, new calculations [10] indicate that about 2–6 bars of CO_2 would be required to produce these high temperatures at 3.3 Ga, assuming atmospheric CH_4 concentrations of $<1\%$ by volume. While such high CO_2 concentrations have been predicted by some models that assume delayed formation of continents [11], contrasting models show low early CO_2 levels because of enhanced seafloor weathering [12].

High CO_2 levels at this time, and high surface temperatures throughout the Precambrian, are difficult to reconcile with well-documented glacial intervals between 0.75 Ga and 0.58 Ga [13] and 2.45 and 2.22 Ga

[14], and with possible evidence for regional glaciation at 2.9 Ga [15]. High surface temperatures should also have caused intense continental weathering, yet the geologic record suggests that weathering in the distant past was not significantly more intense than it is today [16–18]. The paleobiological record, too, appears at odds with high temperatures on the early Earth. Molecular and fossil evidence for eukaryotes as far back as the Neoproterozoic and Paleoproterozoic [19] appears to rule out temperatures at the higher end of the estimated range. Similarly, the evolution of vertebrates during the Ordovician Period [20], clearly within the interval of anomalously low $\delta^{18}\text{O}$ values, is incompatible with even the minimum O-isotope estimate of 40 °C. These clear contradictions have led many researchers to search for alternative explanations for the marine oxygen isotope record.

The explanation offered most frequently for the high estimated paleotemperatures is that they reflect diagenetic alteration within sediments rather than ocean temperatures [21,22]. In this view, the alteration of sedimentary rocks is proportional to their age due to continuous post-depositional equilibration with meteoric and/or warm basinal waters. Careful analyses by many different workers [3,5,7,23,24], though, show that this explanation is unlikely to be valid, or, at least, that significant secular trends in the data remain after diagenetic effects have been taken into account. Our reasoning is as follows: First, the secular trends are parallel for limestones, dolostones and cherts. If continuous alteration was the cause, the trends would

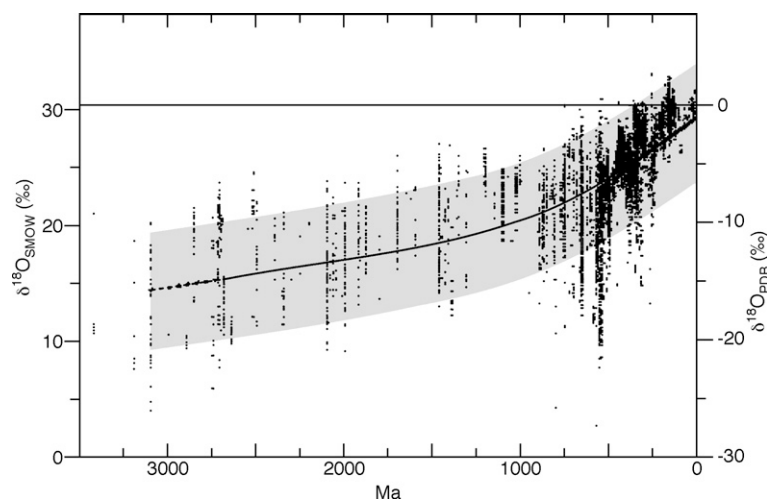


Fig. 1. $\delta^{18}\text{O}$ values from 9957 ancient marine calcites, based on published analyses of Precambrian to Ordovician limestones [4] and Phanerozoic calcitic fossils [7]. All data can be downloaded at http://www.science.uottawa.ca/geology/isotope_data/. The thick line through the database is a cubic smoothing spline. Note that diagenetic resetting and most post-depositional alteration phenomena tend to shift $\delta^{18}\text{O}$ values downwards. We therefore argue that the upper envelope of the band represents the best approximation of the original $\delta^{18}\text{O}$ signal.

diverge with age, reflecting the relative stabilities of these lithologies [25]. Second, the biggest shift in $\delta^{18}\text{O}$ values, for carbonates in particular, occurs during the Phanerozoic. Here the same trend is evident not only for the whole rocks, but also for exceptionally well-preserved low-Mg calcitic and aragonitic fossils [7] and marine cements [26]. Third, the demonstrably early nature of most marine calcite cements of the Precambrian carbonate record, likely related to a higher CaCO_3 saturation state [27], also implies limited diagenetic alteration by later fluids. The observed O isotope trend in sedimentary rocks is almost certainly related to the properties of ancient seawater. The question is whether it reflects temperature or isotopic composition.

2. Controls on the oxygen isotopic composition of seawater

On long time scales, the oxygen isotope composition of seawater is controlled by exchange of oxygen with silicate rocks [28–32]. Unaltered silicate rocks are enriched in ^{18}O relative to seawater by $\sim 5.7\%$. High-temperature interactions between seawater and rock that occur during hydrothermal circulation at axial midocean ridges drive the isotopic composition of seawater towards that of the rock, *i.e.*, towards increasing $\delta^{18}\text{O}$. Low-temperature interactions, such as those that occur in off-axis vent systems and during continental weathering, drive seawater isotopic composition towards low $\delta^{18}\text{O}$. Today, the isotopic crossover point between interactions that raise and lower seawater $\delta^{18}\text{O}$ is $\sim 350^\circ\text{C}$ [33]. For typical water-rock interaction rates, the maximum change in seawater $\delta^{18}\text{O}$ is $\sim 1\%$ per 10^8 year [30]. If one assumes that the system remains in steady state, and that the conditions within the vent systems remain constant, the seawater isotopic composition should not change with time [28,31,34].

We shall argue below that the above assumptions are *not* valid and that seawater isotopic composition does indeed change with time. This, in itself, is not a new idea. Various mechanisms for altering the balance between high- and low-temperature water–rock interactions have been proposed by different authors. Perry et al. [29] suggested that higher heat flow in the Archean could have resulted in a higher percentage of magma being extruded as pillow basalts and pyroclastic material, leading to average water–rock interaction temperatures below 200°C . Walker and Lohmann [30] proposed that the Archean oceans might have been shallower and that the midocean spreading ridges were mostly subaerial, also leading to cooler seawater–rock interactions. But these mechanisms fail to explain the large changes in

sedimentary $\delta^{18}\text{O}$ values during the Phanerozoic [4,7] and are in apparent contradiction with evidence for high-temperature seawater–rock reactions from ophiolites dated at 2 Gyr ago [35] and older [36]. Wallmann [37] suggested that blanketing of midocean ridges by pelagic sediment during the last few hundred million years reduced the rate of cooler, off-axis hydrothermal alteration, thereby altering the balance in favor of high-temperature interactions. This mechanism by itself has difficulty in explaining the long-term (multi-billion year) trend in marine sedimentary $\delta^{18}\text{O}$, as most of this sedimentary blanket today is composed of the shells of calcareous plankton that only evolved around 250 Myr ago, by which time marine carbonate $\delta^{18}\text{O}$ had already reached almost modern values [38]. It is unclear to what extent siliceous plankton and faecal pellets, both of which originated around 550 Ma, could have played a similar role in suppressing low-temperature hydrothermal alteration.

We suggest here, following Walker and Lohmann [30], that a secular increase in sea level over time has been the primary factor driving long-term changes in seawater oxygen isotopic composition. The required change, however, is much less than previously estimated. Most midocean spreading ridges today have ridgecrest depths ranging from 2.5–2.9 km for fast-spreading ridges like the East Pacific Rise [39] to 3.5 km or more for slow-spreading ridges like the Mid-Atlantic Ridge [40]. The pressures within the axial hydrothermal circulation systems are thus in the range of 250–450 bars. By comparison, the critical pressure for seawater is 285–302 bars [41]. Exit temperatures from the axial vents are $\sim 350^\circ\text{C}$, just below the critical temperature of seawater, $403\text{--}406^\circ\text{C}$ [41]. Seawater circulating in these systems is thus near the critical point where the convective heat transport properties are at a maximum. The circulation within these systems is said to be in the “superconvective” regime [42]. If the ridgecrests were less deeply submerged in the distant past, the pressure within the hydrothermal systems would have been lower, and the circulation would have been less effective at transporting heat upwards. As a result, both the penetration depth and the temperatures within the hydrothermal circulation systems would have been reduced. This, in turn, could have reduced the amount of oceanic crust exposed to high-temperature water–rock interactions. Circulating seawater may also have boiled more frequently in hydrothermal systems operating at less than the critical pressure. Both of these factors should have led to a lower $\delta^{18}\text{O}$ value for seawater.

We explore these phenomena quantitatively in Sections 4 and 6 below. First, however, we review some concepts governing simple models of convection.

3. One-dimensional porous convection models: effect of water properties on hydrothermal penetration depth

The characteristics of midocean ridge hydrothermal systems can be estimated from one-dimensional convection theory [43–46]. At this level of approximation, the important parameters are the Rayleigh number, R , and the Nusselt number, N . The Rayleigh number is a measure of the tendency of the system to convect and is defined mathematically by the relation [[46], p. 394]

$$R = \frac{\alpha_w g \rho_w c_{pw} D \Delta T h}{\nu_w \lambda_m} \quad (3.1)$$

Here, variables with the subscript ‘w’ represent physical properties of water: α_w =coefficient of thermal expansion, ρ_w =density, c_{pw} =specific heat capacity at constant pressure, and ν_w =kinematic viscosity. The other parameters are: g =gravity, D =rock permeability, ΔT =temperature difference between the bottom and top of the convecting layer, h =layer thickness, and λ_m =thermal conductivity of the water–rock medium. The ratio of water properties can be written as: $R_w = \alpha_w \rho_w c_{pw} / \nu_w$. Both α_w and c_{pw} have strong maxima near the critical point; thus, R_w is even more strongly peaked at that point [45] (see also Fig. 2).

The Nusselt number, N , represents the ratio of the heat flow carried by porous convection to the heat flow

that could be maintained by the same temperature gradient through solid rock. It is defined mathematically as [43]

$$N = \frac{Qh}{\lambda_m \Delta T} \quad (3.2)$$

where Q represents the convective heat flow through the system. The Nusselt number is related to the Rayleigh number in different ways depending on the intensity of convection. For “active”, axial circulation systems with $R > 1000$, the approximate relationship is [43,46]

$$N \propto R_a^{1/3} \quad (3.3)$$

For “passive”, off-axis circulation systems, the relationship between N and R_a is linear [43,46] and the analysis presented here does not apply.

We focus here on the axial circulation systems. In this flow regime, the three equations, (3.1)–(3.3), can be combined to estimate the dependence of hydrothermal penetration depth on water properties and heat flow [45]

$$h \propto \frac{R_w^{1/2}}{Q^{3/2}} \quad (3.4)$$

Physically, this relationship implies that the depth of hydrothermal convection within the midocean ridges should be greatest when R_w is at a maximum and when heat flow is relatively small. High axial heat flow, or low R_w , would require a shallower porous convective layer in order to get the heat out. Heat flow at 2.0 Gyr ago was probably higher than today by a factor of 2–3 [48]. This alone would imply a decrease in h by a factor of 3–5, according to Eq. (3.4). This change, however, could also be accommodated by an increase in ridge length with no change in Q . Changes in ocean depth, by contrast, would affect R_w , and hence penetration depth, at all midocean ridges. This analysis ignores the complex feedbacks between hydrothermal circulation and rock permeability, D , that more ambitious modelers [43] have attempted to simulate.

4. Calculation of hydrothermal penetration depth vs. ridgecrest depth

We are now ready to explore the hypothesis presented in Section 2. As just shown, the penetration depth, h , of “active” hydrothermal systems is proportional to $R_w^{1/2}$, where $R_w = \alpha_w \rho_w c_{pw} / \nu_w$ is a ratio of seawater physical properties. We calculated the properties of water using the computer model of Haar et al. [47], following Kasting and Holm [45]. This model

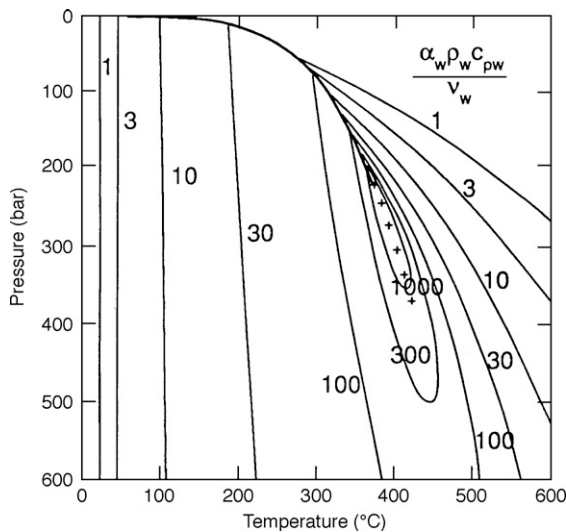


Fig. 2. Contours of the ratio of water properties, $R_w = \alpha_w \rho_w c_{pw} / \nu_w$, as a function of temperature and pressure. See text for definitions of the parameters. Values shown are for pure water [47]. Plus signs indicate 1-km increments along an adiabat extending downwards from the critical point. (From [45]).

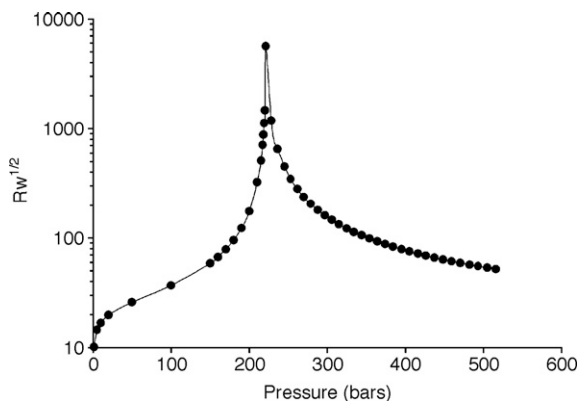


Fig. 3. Variation in the water-property parameter, R_w , with pressure along the saturation vapor pressure curve (below 220.55 bars) and along the critical adiabat. Properties shown are for pure water.

applies to pure water; the properties of saline water can be estimated from the theory of corresponding states [49]. The actual behavior of seawater in the 2-phase regime is more complicated because of differences in salinity between vapor and brine phases [41,50]. However, as discussed below, these complications are probably more important for chemistry (including isotopic fractionation) than for fluid flow.

Fig. 3 shows the quantity $R_w^{1/2}$ for pure water as a function of pressure. The critical pressure for pure water is 220.55 bars. At pressures below the critical pressure, the values were computed at a temperature just slightly (0.1 °C) below the saturation vapor pressure curve. Above this temperature, the liquid vaporizes, ρ_w decreases dramatically, and so R_w decreases. Above the critical pressure, R_w was computed along an adiabat extending downward from the critical point. This P-T curve, which we refer to as the “critical adiabat,” is shown by the ‘+’ signs in Fig. 2. These values also represent local maxima with respect to temperature. Hence, the values shown correspond to the maximum possible value of R_w at a given pressure. The fact that axial vent fluids typically emerge at close to the critical temperature suggests that real circulation systems self-adjust so as to be close to these conditions and thus transport heat upwards with maximum efficiency [43]. A more sophisticated, 2-D flow simulation might reveal the extent to which this assumption is actually valid (see below and Section 7).

In Fig. 4, we translate this curve into a plot of hydrothermal penetration depth versus ridgecrest depth. In making this plot, seawater density above the ridgecrest was assumed to be 1.03 g/cm³, and the pressures from Fig. 2 were scaled up by a factor of 290/220 to account for the difference in critical pressures between

pure water and seawater. We assumed a penetration depth of 5 km for a circulation system in which the fluid emerges at the critical point, *i.e.*, at the top of the critical adiabat. The average value of R_w over this adiabat was 1.4×10^6 , substantially lower than the value at the critical point itself because it is averaged over the vertical column. We next computed adiabats starting from pressures above and below the critical pressure. The high-pressure adiabats were assumed to extend downwards from P-T points along the critical adiabat. The depth of these curves was scaled by the factor $(R_w/1.4 \times 10^6)^{0.5}$, where R_w was computed as the average along the adiabat. Iterations were necessary to achieve convergence because the penetration depth changed as R_w was recomputed. Adiabats originating from below the critical pressure were started from 0.1 °C below saturation and were assumed to remain parallel to the saturation vapor pressure curve until it intersected the critical point, after which they followed the critical adiabat. Their penetration depths were assumed to be small (0.2 km) initially and were adjusted iteratively by the scaling factor given above.

The results plotted in Fig. 4 reveal the following behavior: Hydrothermal penetration depths are predicted to be small, 0.6 km or less, at ridgecrest depths below ~2.4 km. Seawater circulating in such systems would vaporize, and this would limit its penetration depth. Once the ridgecrest depth exceeds 2.4 km, the circulation system extends downwards through the critical region, and the penetration depth jumps to ~5 km. The critical adiabat itself begins at a depth of 2.9 km. At ridgecrest depths exceeding this value, the penetration depth again

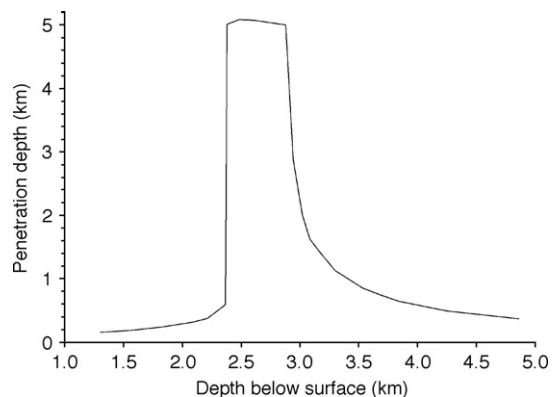


Fig. 4. Predicted hydrothermal penetration depth as a function of ridgecrest depth. The saline nature of seawater has been taken into account, as described in the text. Water properties are calculated along adiabats originating along the critical adiabat (at high pressure) or along the liquid side of the saturation vapor pressure curve (at low pressure).

drops off sharply because the critical region is again excluded from the circulation system.

The dependence of hydrothermal penetration depth on ridgecrest depth predicted here is crude because it relies on 1-D convective theory and thus ignores such factors as the geometry of the circulation system and variations in rock properties. In real, axial hydrothermal flow systems, seawater descends in cooler, off-axis regions and then moves towards the ridge axis, where it is heated and rises. A 2-D simulation would be needed to represent this behavior accurately. And, as noted in Section 3, “passive” circulation systems that are well off axis may behave in a different manner. Indeed, 1-D theory yields no prediction of the penetration depth of such systems. This is an important point, as data on ancient ophiolites (described below) indicate that these rocks were aqueously altered to depths of several kilometers. However, the interaction temperatures in such off-axis systems would presumably have been much lower, and so they would not have affected seawater $\delta^{18}\text{O}$ values in the same way.

Shallow ridgecrest depths would also have led to increased boiling of circulating seawater, and this should have had a direct effect on the isotopic exchange with the surrounding basalts. When seawater boils, the remaining brine is enriched in ^{18}O . The isotopic fractionation between liquid water and vapor increases with decreasing temperature [51], and the boiling temperature of seawater is reduced at low pressures [41]. Consequently, brines formed at shallow ridges are strongly enriched in ^{18}O compared to seawater and to brines formed at deeply submerged ridges. Dense brines often reside within oceanic crust for long periods of time before they are finally recycled into the ocean, while vapor escapes rapidly from the system and is unlikely to chemically interact. Therefore, much of the isotopic exchange between ancient oceans and midocean ridge basalts probably proceeded through brine-rock interactions at shallow ridges. Since these brines were enriched in ^{18}O , the heavy isotope was efficiently transferred from the ocean into oceanic crust even at low seawater $\delta^{18}\text{O}$ values and high temperatures.

The implications of these results for the isotopic composition of seawater are straightforward: If the oceanic ridge systems were significantly shallower in the past, then the region of high-temperature interaction between seawater and the seafloor could have been greatly diminished. Seawater oxygen isotopic composition would have been dominated by low-temperature water–rock interactions within the vent systems and in continental weathering, and isotopic exchange within some of the vent systems would have been further altered

by boiling. This combination of factors would have driven ancient seawater to low $\delta^{18}\text{O}$ values, explaining the low $\delta^{18}\text{O}$ values measured in cherts and carbonates.

We explore the effect of changes in penetration depth on seawater isotopic composition quantitatively in Section 6. First, though, let us consider the critical question of whether this hypothesis has any support other than the fact that it can successfully explain the observed trend in the $\delta^{18}\text{O}$ values of sedimentary rocks. Are there other reasons to believe that the mean depth of the ridgecrests has varied with time?

5. Does ridgecrest depth vary with time?

Ridgecrest depth could vary with time for a number of reasons. One is that the volume of the oceans may itself be increasing with time [45]. Water is currently being exchanged between the crust and the mantle at rates that could alter ocean volume substantially on billion-year time scales [45]. The downward flux of water is associated with subduction of hydrated oceanic crust. If ridgecrest depth was shallower in the past because of reduced ocean volume, then hydrothermal penetration depths would have been smaller, the downward flux of water would also have been smaller, and mantle outgassing may have dominated the water balance. So, the oceans may have deepened with time until the ridgecrests were in the superconvective regime.

The above hypothesis is attractive and could be correct. However, the mean ridgecrest depth could also have increased with time for reasons that do not depend on a change in ocean volume. One of these reasons comes from considering how plate tectonic processes have evolved in response to decreasing mantle heat flow. Several authors [52–58] have argued that the thickness of the oceanic crust has decreased with time in response to this change. According to Moores [57], the thickness decreased from perhaps 25 km in the Archean to ~ 7 km in the Phanerozoic. The thicker oceanic crust, being buoyant, would have risen isostatically, displacing seawater, and leading to a decrease in continental freeboard compared to today. Indeed, in Moores’ model, the continents would have remained submerged until the Neoproterozoic. Although the author does not discuss the issue explicitly, this model implies decreased ridgecrest depth in the past, as the ocean volume would have been distributed over a greater fraction of Earth’s surface. In a detailed analysis, Sleep [58] also concludes that the ridgecrests should have been shallower in the distant past for this same reason (but see below).

Some empirical support for this hypothesis is provided by Kitajima et al. [36], who have analyzed what

they interpret to be a preserved segment of Archean midocean ridge. They estimate that phase separation (boiling) of the hydrothermal fluid occurred at a temperature of ~ 350 °C and a depth of about 1 km below the seafloor. This is consistent with a ridgecrest depth of ~ 1.6 km—significantly shallower than most modern midocean ridges and well out of the supercritical regime where deep hydrothermal penetration can occur (Fig. 4). Additional support is provided by Arndt [59], who points out that large portions of the continental crust appear to have been submerged during the Archean, consistent with Moores' hypothesis.

An attractive feature of this mechanism is that it could potentially explain one of the most perplexing features of the O isotope data shown in Fig. 1, namely, that much of the observed variation in the $\delta^{18}\text{O}$ values of carbonates occurred fairly recently in geologic time. One interpretation of the carbonate data is that there was a large secular decrease in $\delta^{18}\text{O}$ values going back through the Phanerozoic, and that the mean value of $\delta^{18}\text{O}$ was essentially constant (even though the data are scattered) throughout the Precambrian. Our model might be able to explain this pattern because, even if tectonic evolution was continuous, a threshold should have been reached when the mean ridgecrest depth reached ~ 2.4 km (Fig. 4). However, enthusiasm for this hypothesis should be tempered by the realization that this threshold type of behavior should be moderated by two factors: 1) Modern midocean ridgecrests span a range of depths from above sea level (Iceland) to 3.5 km or greater (the Mid-Atlantic and other slow-spreading ridges). The deeper, slow-spreading ridges (spreading rate < 50 mm/yr) occupy more than half the total midocean ridge length, but account for only ~ 25 percent of total magma production [60]. Accounting for these deeper ridges would broaden the peak in penetration depth shown in Fig. 4. 2) A more realistic, 2-D hydrothermal flow model should also broaden the peak in Fig. 4 by allowing seawater to descend off axis. In Section 7, we discuss future steps that could be taken to reduce these uncertainties and to test our hypothesis in more detail. We also explore (in Section 6) an alternative mechanism for causing a marked change in ocean isotopic composition during the Phanerozoic.

Not all authors agree that the Archean ridgecrests must have been shallow. Bickle et al. [61] suggested that if the volumes of Archean oceans and continents were the same as today, the oceanic ridgecrests would have been ~ 1 km deeper than today because increased spreading rates would have decreased the topographic difference between the ridges and the deep ocean basins. However, others [62] have suggested that the required increase in heat flow from the Earth's interior would have been accommodated

by increased ridge length, rather than by increased spreading rates. Davies [63] favors thin (5 km thick) Archean oceanic crust rather than the thick oceanic crust predicted by Sleep and Moores, but makes no explicit predictions about ridgecrest depth. Even thin ridgecrests could be shallow if the continents were smaller or partially submerged. It is difficult to make definitive statements about sea level and ridgecrest depth during the Archean, as our understanding of plate tectonics is still largely empirical.

All tectonic models of the Archean must account for the widespread emplacement of greenstone belts. These belts consist of aqueously altered basalt and have been interpreted by some to represent ancient oceanic seafloor [52,64], although others disagree [61]. Moores [57] suggested that they form by accumulation of "flakes" of thick oceanic crust [65] that were scraped off onto continents during subduction. Arndt [59] considered them to be flood basalts that erupted onto submerged continental crust. Regardless of which model one accepts, greenstone belts appear to have been volumetrically important during the Archean, and they have clearly exchanged oxygen isotopes with the water that percolated through them [66]. These rocks could therefore have played an important role in governing Archean seawater isotopic composition.

6. Modeling the evolution of marine $\delta^{18}\text{O}$ values

It remains to be shown that the mechanism proposed above is consistent with the oxygen isotope record preserved in sedimentary rocks and in ophiolites. In this section, we demonstrate this explicitly. We make no attempt, however, to directly calculate average ridgecrest depth and hydrothermal penetration depth versus time. Doing so would require a detailed model of tectonic evolution that is beyond the scope of this paper. Instead, we parameterize these processes by their presumed effect on the fraction (f_{deep}) of deep oceanic crust subject to high-temperature hydrothermal alteration.

6.1. Model description

The ^{18}O evolution model used in this paper is an enhanced version of the model presented by Wallmann [32]. It includes mantle degassing, continental weathering, alteration of oceanic crust at high and low temperatures, water uptake in crust and continental weathering products, as well as recycling of water at subduction zones. The parameterization of isotopic exchange was improved to maintain isotopic equilibrium between seawater and alteration products of ocean crust (see also [37]). The isotopic exchange processes during alteration of the upper volcanic section at low temperatures ($F_{\text{ex}}^{\text{up}}$)

and the deeper section at high temperatures ($F_{\text{ex}}^{\text{deep}}$) are formulated as:

$$F_{\text{ex}}^{\text{up}} = (\Phi_{\text{up}}^{\text{i}} - \Phi_{\text{bas}}) f_{\text{sp}} r_{\text{up}} P_{\text{up}} \quad (6.1)$$

$$F_{\text{ex}}^{\text{deep}} = (\Phi_{\text{deep}}^{\text{i}} - \Phi_{\text{bas}}) f_{\text{sp}} r_{\text{deep}} P_{\text{deep}} \quad (6.2)$$

where Φ_{bas} is the model fraction of ^{18}O in fresh oceanic crust, f_{sp} is the spreading rate normalized to its present value, P_{up} and P_{deep} are the modern production rates of shallow and deep crust (in mol crustal oxygen yr^{-1}) and r_{up} and r_{deep} are the corresponding fractions of ocean crust subject to alteration and isotopic exchange. The modern production rates of crustal oxygen are calculated assuming a spreading rate of $3 \text{ km}^2 \text{ yr}^{-1}$, an oxygen concentration of 44 wt-% in crustal rocks, and crustal densities of 2.5 and 3.0 g cm^{-3} for upper (P_{up}) and lower crust (P_{deep}), respectively.

The model fractions of ^{18}O in instantaneous products of alteration at low and high temperatures are given as:

$$\Phi_{\text{up}}^{\text{i}} = \frac{\alpha_{\text{up}} \cdot \Phi_{\text{sw}}}{\alpha_{\text{up}} \cdot \Phi_{\text{sw}} + 1 - \Phi_{\text{sw}}} \quad (6.3)$$

$$\Phi_{\text{deep}}^{\text{i}} = \frac{\alpha_{\text{deep}} \cdot \Phi_{\text{sw}}}{\alpha_{\text{deep}} \cdot \Phi_{\text{sw}} + 1 - \Phi_{\text{sw}}} \quad (6.3)$$

Here, $\alpha_{\text{up}} (=1.015)$ and $\alpha_{\text{deep}} (=1.000)$ define the isotopic fractionation between seawater and alteration products at low and high temperatures, respectively. At high temperatures the fractionation is strongly suppressed so that alteration products in deep crust attain the isotopic composition of seawater (Φ_{sw}).

6.2. Effect of hydrothermal circulation and crust alteration on the isotopic composition of seawater

In agreement with previous models, the new model shows that the isotopic composition of seawater ($\delta^{18}\text{O}_{\text{sw}}$) is largely determined by the isotopic exchange between seawater and oceanic crust at high and low temperatures. In upper crustal levels, low-temperature alteration decreases the $\delta^{18}\text{O}_{\text{sw}}$ but increases the $\delta^{18}\text{O}$ value of the rock. Deeper in the crustal section, at temperatures of 350°C , the polarity of exchange reverses and the $\delta^{18}\text{O}_{\text{sw}}$ is increased at the expense of the rock. The “isotopic neutral point” is located at mid depths where the altered rocks attain the $\delta^{18}\text{O}$ value of fresh basalts (5.7‰ SMOW). This point is located above the sheeted dykes at a shallow crustal level (700 m depth) in 6 Myr oceanic crust drilled at a ridge flank of Costa Rica [67], while the Cretaceous Oman ophiolite contains ^{18}O -enriched crust throughout the top 1.5 km and the isotopic neutral point is located within the lower sheeted dyke complex.

In the modelling, we assume that the upper 1 km of the oceanic crust is enriched in ^{18}O by low temperature alteration ($<350^\circ\text{C}$) occurring mainly at the ridge flanks, while the underlying 6 km of ocean crust are depleted in ^{18}O due to the circulation of hot seawater through spreading centers. Applying modern rates of alteration, where 20% of the upper crust is altered at low temperatures ($r_{\text{up}}=0.2$), and 10% of the lower crust at high temperatures ($r_{\text{deep}}=0.1$), seawater is indeed buffered close to the modern value at -1‰ SMOW.

The alteration of upper and lower crust was varied systematically to investigate the sensitivity of $\delta^{18}\text{O}_{\text{sw}}$ values with respect to high and low temperature alteration processes (Figs. 5 and 6). A decrease in the fraction of oceanic crust altered at high temperatures (r_{deep}) has a strong effect on the isotopic composition of seawater (Fig. 5). The calculated $\delta^{18}\text{O}_{\text{sw}}$ values decrease to the very low values observed in the Cambrian and Precambrian carbonate record when r_{deep} is reduced by one order of magnitude. Considering that modest changes in sea level and ridge depth may reduce the intensity of axial circulation dramatically, the model results presented in Fig. 5 suggest that the very negative $\delta^{18}\text{O}$ values observed in the marine carbonate record may indeed reflect the isotopic composition of seawater in shallow oceans with low rates of high temperature water–rock interactions.

Low temperature alteration and fluid flow through oceanic crust are limited by the deposition of carbonate oozes comprising the remains of coccolithophores and foraminifera on the flanks of modern midocean ridges. Prior to the evolutionary expansion of skeletal

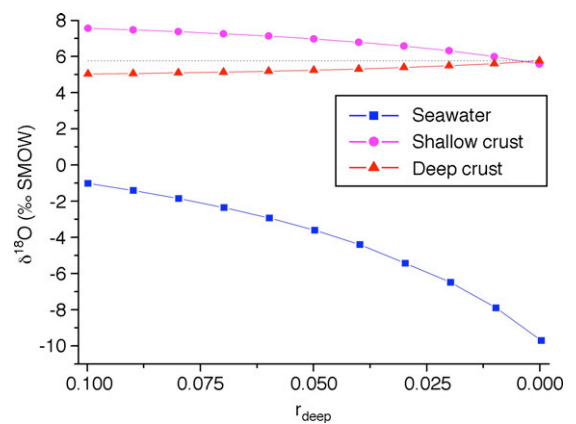


Fig. 5. Change in the isotopic composition of seawater, shallow and deep crust as a function of high temperature alteration in deep crustal levels (1–7 km depth). The parameter r_{deep} defines the fraction of deep crust exchanging oxygen isotopes with seawater at high temperatures. In the steady state model runs, the spreading rate and the intensity of low temperature alteration were maintained at their modern values ($f_{\text{pb}}=1$, $r_{\text{up}}=0.2$).

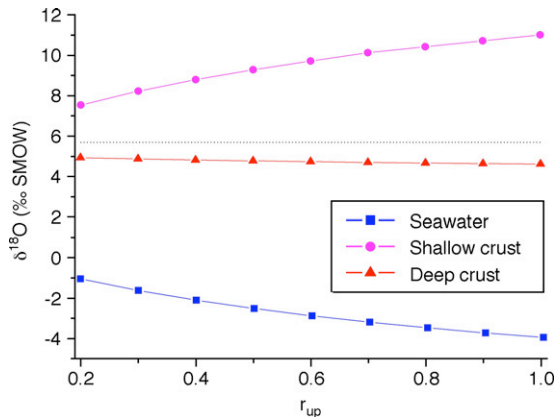


Fig. 6. Change in the isotopic composition of seawater, shallow and deep crust as a function of low temperature alteration at shallow crustal levels (0–1 km depth). The parameter r_{up} defines the fraction of shallow crust exchanging oxygen isotopes with seawater at low temperatures. In the steady state model runs, the spreading rate and the intensity of high temperature alteration were maintained at their modern values ($f_{pb}=1$, $r_{deep}=0.1$).

organisms into the pelagic realm at about 550 Ma, almost barren seafloor was exposed to Precambrian seawater; thus, circulation and alteration at ridge flanks could affect large proportions of the oceanic crust. An increase in the fraction of shallow crust affected by low temperature isotopic exchange (r_{up}) causes a significant decrease in $\delta^{18}O_{sw}$ (Fig. 6). It is thus likely that the negative Precambrian $\delta^{18}O_{sw}$ values suggested by the marine carbonate record were partly caused and maintained by enhanced rates of fluid flow and low temperature alteration.

6.3. Simulating the isotopic evolution of seawater

The model was run in a non-steady state mode to reproduce the evolution of seawater suggested by the marine carbonate record (Fig. 7). The negative $\delta^{18}O_{sw}$ values in ancient seawater were attained by reducing the r_{deep} value to zero. Starting at 3.5 Ga, the r_{deep} values were slowly increased to reproduce the positive shift suggested by the data. At the end of the Precambrian, r_{deep} was adjusted to the modern value to mimic the strong increase in $\delta^{18}O_{sw}$ observed over the Phanerozoic. This external model forcing may be justified by the strong effect of ridge depth on the intensity and axial hydrothermal circulation. We have to postulate that the midocean ridges were shallower than today over the Precambrian and attained the modern depth level close to the beginning of the Phanerozoic.

The intensity of low temperature alteration was set to a very high value over the entire Precambrian to mimic

the more intense circulation at ridge flanks through barren seafloor and was reduced to the low modern value at the beginning of the Phanerozoic when skeletal organisms started to evolve. This model forcing helped to maintain negative Precambrian $\delta^{18}O_{sw}$ values and to reproduce the rapid positive shift over the Phanerozoic. Changes in r_{deep} had however a larger effect on $\delta^{18}O_{sw}$ than r_{up} changes (see also Figs. 5 and 6) suggesting that the isotopic evolution of seawater is mainly controlled by the intensity and depth of axial hydrothermal circulation systems.

6.4. The ophiolite record

The model results shown in Figs. 5–7 clearly demonstrate that the average composition of shallow and deep oceanic crust is affected by the intensity of low and high temperature alteration. Thus, the isotopic composition of deep crust approaches the value of fresh basalt (5.7‰ SMOW) when r_{deep} is strongly reduced (Fig. 5), while

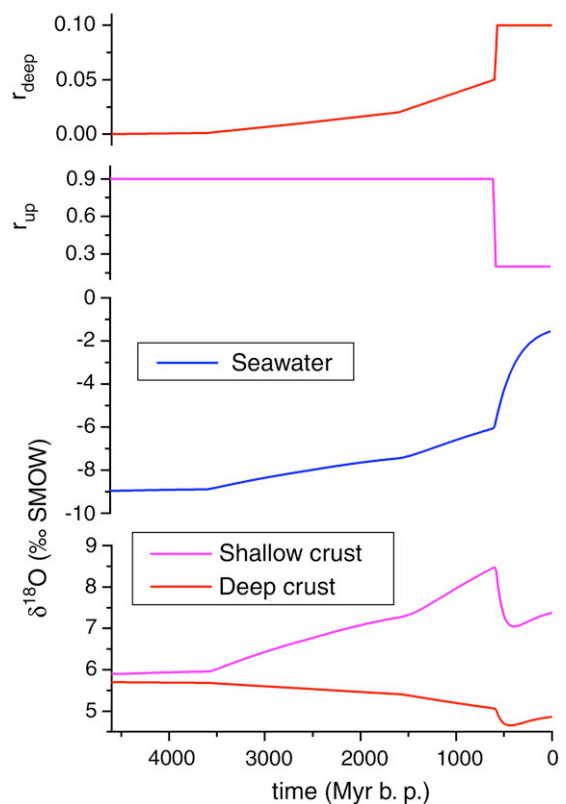


Fig. 7. Evolution of marine $\delta^{18}O$ values as calculated in the model. The upper panels show the r_{deep} and r_{up} values used as forcing to the model. They were tuned to simulate the changing intensities of high and low temperature alteration and to reproduce the isotopic evolution of seawater suggested by the marine carbonate record.

an increase in upper crustal alteration results in more positive $\delta^{18}\text{O}$ in upper crustal rocks (Fig. 6). It is, however, important to note that the isotopic composition of oceanic crust does not mimic the changing isotopic composition of seawater. Hence, the strong increase in $\delta^{18}\text{O}_{\text{sw}}$ over the Precambrian and Phanerozoic is not accompanied by a corresponding change in bulk crustal composition (Fig. 7). The modelling rather shows that the $\delta^{18}\text{O}$ values in shallow and deep crustal rocks attained modern values already two billion years ago when $\delta^{18}\text{O}_{\text{sw}}$ was much more negative than today. The bulk isotopic composition of crustal rocks should thus not be used as a proxy for the isotopic composition of ancient seawater.

Ancient oceanic crust is conserved in the Silurian Trinity ophiolite and two billion years old Purtuniqu ophiolite. Detailed $\delta^{18}\text{O}$ studies showed that both ophiolites are isotopically enriched in the pillow basalts, over the entire sheeted dykes complex and even in the underlying gabbros [35,68]. Contrary to the conclusions reached by the original authors of the Purtuniqu study [35], these findings do not require that seawater isotopic composition has remained constant with time. Rather, they are consistent with our hypothesis that axial hydrothermal penetration depths were smaller and that ridge flank circulation at low temperatures was more intense and deep reaching than today due to the missing sedimentary apron on ancient ridge flanks.

7. Conclusions and suggestions for further research

Our analysis suggests that seawater was isotopically lighter in the distant past by perhaps as much as 10‰, largely as a consequence of changes in midocean ridge-crest depth associated with higher heat flow. If so, then the low $\delta^{18}\text{O}$ values of ancient carbonates and cherts cannot be taken as evidence for hot climates during the Precambrian. This result is in accord with other constraints from the paleoclimate record, notably the occurrence of glaciations in the early and late Proterozoic, and possibly during the mid-Archean.

Our conclusions depend critically on the supposition that tectonic styles were different in the past, particularly the idea that the oceanic crust was thicker, and thus more buoyant. This hypothesis is supported by theoretical analysis and is broadly consistent with observed changes in rock types over time, *e.g.*, the widespread occurrence of greenstone belts during the Archean.

This said, it is clear that more work needs to be done to quantify the proposed change in seawater oxygen isotopic composition. A straightforward, but time-consuming task would be to develop a 2-D model of axial hydrothermal flow, and to use this model to investigate isotopic

exchange between seawater and basalt as a function of ridgecrest depth. Such a model would need to include the thermodynamic properties of seawater emphasized here, along with fractionation of oxygen isotopes during boiling. Coupled with a detailed map of the depth distribution of the ridges (not currently available, as far as we could tell), such a model could be used to obtain a more quantitative estimate of the dependence of seawater isotopic composition on sea level. Predicting how sea level would have changed as a function of heat flow and tectonic style is obviously more difficult, as is calculating how rock properties (especially porosity) might have varied. So, it may not be possible to obtain a definitive calculation of seawater isotopic composition versus time. But by recognizing that significant changes in seawater isotopic composition are possible, and by understanding the control mechanism, we may be able to use the oxygen isotope data from ancient rocks to help constrain how the tectonic-ocean-climate system has evolved.

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