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Oxygen isotope history of seawater revisited: Timescales for boundary event changes in the oxygen isotope composition of seawater

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Abstract—Oxygen isotopic data from hydrothermally altered oceanic pillow lavas suggest that the $\delta^{18}O$ value of seawater has not changed very much over geologic time. However, several studies on sedimentary rocks attribute 3–6 per mil changes in the $\delta^{18}O$ values of carbonate rocks to changes in the $\delta^{18}O$ of the coexisting seawater. These changes appear to occur over very short time intervals (<20 Ma), and therefore it is important to examine the characteristic times associated with processes that can affect the isotopic composition of seawater. Material-balance equations describing the secular change in the $\delta^{18}O$ of seawater resulting from isotopic exchange between the lithosphere and the hydrosphere have solutions that give the steady-state value of seawater as: $\sum k_i(\delta_i^0 - \Delta_i)/\sum k_i$, where the Δ_i are the bulk fractionation factors between the various rock reservoirs (i) and water, the δ_i^0 are the initial $\delta^{18}O$ values of the various rock reservoirs, the k_i are the rate constants in units of 1/time, and $\sum k_i$ is the total rate. For a global ridge system, typical of present-day Earth, with a spreading rate of 3 km^2/yr and a 4 km depth of seawater penetration, the k value for exchange between the oceanic crustal reservoir and seawater is $\approx$0.008/Ma with a mean lifetime ($1/k$) of 125 Ma. Similarly, a continental weathering rate of 2.5 km^3/yr yields a rate constant for the seawater cycle of 0.002/Ma with a mean lifetime of 420 Ma. Even for high estimates of continental weathering rates ($\approx$7 km^3/yr), the mean life for the weathering process is still 150 Ma, which is longer than the mean lifetime of the ridge crest cycle. By these mechanisms, a 6 per mil change in the $\delta^{18}O$ value of seawater requires 60–150 km^3/yr of continental weathering, which would occur over $\approx$15 Ma at the expense of processing up to a third of the continental crust! Clearly, if such changes in the ^{18}O composition of the oceans do in fact occur, they should be reflected in dramatic and easily identifiable changes in the tectonic regime of the Earth, and no such changes are documented in the rock record. From this analysis of the time constants involved in the global cycles, it would seem that apparent boundary event changes in the $\delta^{18}O$ values of carbonates must be attributable to other mechanisms.

INTRODUCTION

NEW $\delta^{18}O$ DATA on the Darb Zubaydah ophiolite, Saudi Arabia, and the Yilgarn and the Pilbara blocks, Western Australia, complement earlier data sets (*e.g.*, MUEHLENBACHS, 1986; GREGORY and TAYLOR, 1981; BEATY and TAYLOR, 1982; KERRICH, 1987; SMITH *et al.*, 1984; HOFFMAN *et al.*, 1986) that show that there is little or no variation over geologic time in the range of $\delta^{18}O$ values of the upper crustal products of seafloor hydrothermal alteration (Fig. 1). In the Pilbara block, over 100 analyses of samples from a pillow lava section covering over 600 km^2 display a range of $\delta^{18}O$ values nearly the same as that for Cenozoic and Mesozoic oceanic pillow lava sections. The simplest interpretation of the data shown in Fig. 1 is that the isotopic composition of seawater has not changed much through geologic time.

Conflicting ideas regarding the secular change in the isotopic composition of seawater come from the studies of sedimentary carbonates, cherts, and phosphates (*e.g.*, DEGENS and EPSTEIN, 1962; VEIZER *et al.*, 1986; POPP *et al.*, 1986; LOHMANN and WALKER, 1989; BURDETT *et al.*, 1990; KNAUTH and EPSTEIN, 1976; LUZ *et al.*, 1984). In these studies, there is a clear conflict in the interpretation of the cause of a general lowering of the $\delta^{18}O$ values of sedimentary materials back through geologic time. One group of researchers invariably interprets the change in terms of changes in the isotopic composition of seawater; a second group interprets the change in isotopic composition in terms of higher surface temperatures (warmer paleoclimates); and a third group interprets the change in terms of a later-stage, secondary alteration of the original isotopic compositions of the rocks. The first two interpretations require that the secular change in oxygen isotopes of sedimentary rocks is a primary feature which has not been affected by diagenesis or metamorphism.

Paleoclimatic constraints derived from models of atmospheric evolution argue for the stability of temperature distributions on the ancient Earth (*e.g.*, KASTING, 1989). Numerical simulations of atmospheric circulation predict only a $\approx$5°C change between global mean temperatures of glacial and nonglacial epochs (*e.g.*, BARRON and WASHINGTON, 1984). Also, because the types of continental shelf marine sediments that have been subjected to stable isotopic studies formed over a restricted range of latitude, large changes in apparent paleotemperature are unlikely (unless the climatic models are in serious error).

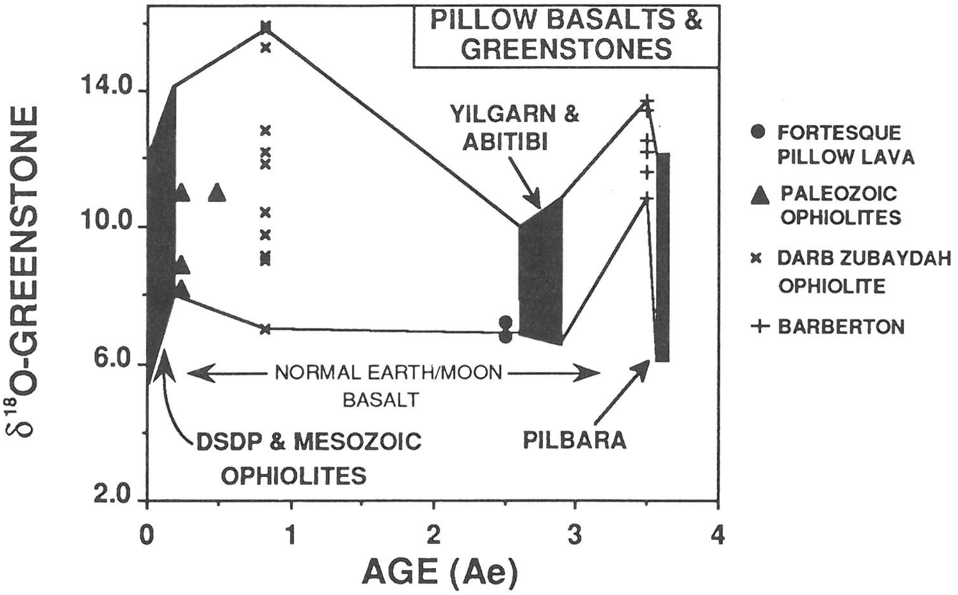

FIG. 1. The $\delta^{18}O$ values of pillow basalts and greenstones are shown as a function of age in Ga. These data suggest that the range of $\delta^{18}O$ values of metabasalts altered on the seafloor has not changed throughout geologic time. The ^{18}O-enriched character of greenstones of any age is difficult to reconcile with oceans that were depleted in ^{18}O in the past. The areas shown in black represent rock localities and types where there are many analyses. The DSDP & Mesozoic ophiolite field represents the data summarized by MUEHLENBACHS (1986); the Yilgarn & Abitibi (Australia and Canada, respectively) field is from the work of BEATY and TAYLOR (1982), KERRICH (1987), and unpublished data; the Pilbara (Australia) field represents the range of over 100 new data points. The triangles, X's, dots, and crosses represent limited data from greenstones of all ages. The Paleozoic samples are from the Bay of Islands complex and the Canyon Mountain ophiolite, North America (GREGORY and TAYLOR, 1981), the X's from the Darb Zubaydah ophiolite complex, Arabia (GREGORY and QUICK, 1990); the dots from the Fortescue Group, Australia, and the crosses from the Barberton greenstone belt (SMITH *et al.*, 1984; HOFFMAN *et al.*, 1986).

In view of interpretations which attribute 3–6 per mil changes in the $\delta^{18}O$ values of carbonate rocks to changes in the $\delta^{18}O$ of coexisting seawater, as well as the interpretations that these changes occur over very short time intervals (*e.g.*, VEIZER *et al.*, 1986; LOHMANN and WALKER, 1989), it is important to examine the characteristic times associated with processes that affect the $\delta^{18}O$ value of seawater. Recent work toward the development of isotopic chronostratigraphies, in which oxygen isotope data are represented side by side with carbon, sulfur, and strontium isotopic data, must recognize the major differences in the behaviour of these systems. It is clear that secular trends in the carbon and sulfur isotopic composition of sedimentary materials are related to the interplay on short time scales between oxidized and reduced species that results from the exchange between the biosphere and the reservoirs of these elements in the atmosphere, hydrosphere, and lithosphere (*e.g.*, HOLSER *et al.*, 1988; BERNER, 1989).

HOLLAND (1984) reviews the isotopic composition of Sr and O in seawater and concludes that both isotopic systems are mainly controlled by a competition between seafloor processes and continental weathering. This phenomenon is by now reasonably well understood (*e.g.*, MUEHLENBACHS and CLAYTON, 1976; HOLLAND, 1984; PALMER and EDMOND, 1989). It is interesting to note that the Sr isotopic composition of Phanerozoic seawater changes by only 4 per mil with Sr present at ≈8 ppm (*e.g.*, PETERMAN *et al.*, 1970; VEIZER *et al.*, 1986), a minor perturbation compared with the rapid 6 per mil change in the $\delta^{18}O$ value of seawater (89 wt.% oxygen) required by interpretations of the sedimentary oxygen record. For oxygen isotopes, because seawater is predominantly oxygen, the mass of the ocean must have a large damping effect on possible changes in the oxygen isotopic composition of seawater. The purpose of this paper is to investigate the stability of the $\delta^{18}O$ value of seawater in relation to the various plausible perturbations away from steady state.

MASS BALANCE RELATIONSHIPS

The general material balance equation describing the change in the $\delta^{18}O$ of seawater as a function of time resulting from isotopic exchange between the lithosphere and the hydrosphere is given by

$$d\delta W/dt = -\sum k_i(\delta W + \Delta_i - \delta_i^0) \quad (1)$$

where δW is the instantaneous $\delta^{18}O$ value of seawater, the Δ_i are the bulk fractionation factors between the various rock reservoirs (i) and water, the δ_i^0 are the initial $\delta^{18}O$ values of the various rock reservoirs, and the k_i are the rate constants in units of 1/time. Equation (1) is similar to the types of material-balance equations put forward in GREGORY and TAYLOR (1981), CRISS *et al.* (1987) and GREGORY *et al.* (1989). The main difference is that the rate constants are rock cycling rates normalized to the mass of the oceans.

Equation (1) can be solved analytically as long as the k_i, the Δ_i and the δ_i^0 are held constant by separating variables and integrating from δW_0 and $t = 0$ to δW and t to obtain

$$\delta W = (\delta W_0 - \delta W_{\text{steady state}}) \times \exp - (\sum k_i t) + \delta W_{\text{steady state}}. \quad (2)$$

From the definition of the Δ_i, $\delta_i^0 - \Delta_i$ is the value seawater would obtain if steady state was achieved with the ith reservoir. Thus, the steady state δ value of seawater is given by

$$\delta W_{\text{steady state}} \equiv [\sum k_i(\delta_i^0 - \Delta_i)]/\sum k_i. \quad (3)$$

If seawater exchanged with a single massive crustal reservoir, the steady-state δ value of the oceans would simply be the initial composition of the crustal reservoir minus the bulk fractionation factor (Δ) of the interaction. If the formation of sediments by weathering of pristine igneous rocks with $\delta^{18}O = +8$ occurs at a bulk $\Delta^{18}O$ of +20, the steady-state $\delta^{18}O$ value of seawater would be −12. Similarly, if the $\delta^{18}O$ of seawater is dominated by the ridge-crest interaction with the oceanic crust ($\delta^{18}O \approx +6$ per mil) at a bulk $\Delta^{18}O$ of approximately +6 in the style dictated by the present-day plate tectonic regime, the steady-state δ value of seawater would be roughly zero. Crudely over geologic time seawater should vary between these extremes, unless one process dominates (*e.g.*, MUEHLENBACHS and CLAYTON, 1976; GREGORY and TAYLOR, 1981). From Eqn. (3), the process with the largest k value is proportionally the most important control on the isotopic composition of seawater.

In the following discussion of the ridge crest-seawater interaction, the low- and high-temperature interactions are not treated separately but as parts of the same process. This is a departure from the approach used by MUEHLENBACHS (1986) and HOLLAND (1984) where the low- and high-temperature ridge interactions are treated as separate processes. In the present treatment, one bulk fractionation factor applies to the whole ridge system, and thus the rates of exchange of oxygen isotopes can be more directly related back to plate tectonic processes. The major problem with treating the ridge-crest interaction as a single process revolves around the uncertainty in the choice of the bulk fractionation factor, Δ. Because this factor, Δ, is ultimately related to the average temperature of isotopic exchange in the oceanic crust, its value is tied to the mechanics of the accretion of new oceanic crust and to the contrast between the temperature of mid-ocean ridge magmas and surface oceans. GREGORY and TAYLOR (1981) argued that as long as a plate tectonic regime obtains (*i.e.*, global spreading rates greater than ≈ 1 km^2/yr), the value of the bulk fractionation factor would be close to +6.

Assuming that Cretaceous seawater was close to its steady-state oxygen isotopic composition during a time of rapid seafloor spreading, the material balance for the ^{18}O distribution in the altered Cretaceous oceanic crust achieves special significance. When the isotopic composition of seawater approaches a steady-state relationship with a single dominant reservoir, the average value of this rock reservoir should not change as a result of subsequent interaction. This means that the amount of ^{18}O enrichment will balance the amount of ^{18}O depletion in the altered oceanic crust (*e.g.*, MUEHLENBACHS and CLAYTON, 1976). If the oxygen isotope balance in a section of oceanic crust is real, then it implies that seawater was indeed at its steady-state isotopic composition and that the ridge-crest interaction dominates the system. However, if another reservoir exchanges at a fast enough rate to make a proportionally significant contribution to the isotopic composition of seawater, then the oxygen isotope profile of the oceanic crust *should not* balance.

Alternatively, if the mechanism of ocean-crust formation changes as a function of spreading rate, some changes in the bulk fractionation factor might occur as the average temperature of exchange changes. Thus, it might be possible for some oceanic ridge segments to exhibit a local oxygen isotope imbalance, while others forming at spreading rates closer to the global average would be in oxygen isotopic balance. Because it is difficult to differentiate between the effect of another important exchange reservoir from possible fluctuations that might occur as a result of the accretion of the oceanic crust, it is particularly important to constrain the exchange rates for oxygen isotopes between seawater and the various crustal reservoirs. Obviously, these rates would have to be consistent with rates of tectonic processes.

In Fig. 2, the behavior of oxygen isotopes is shown to be strikingly different than that of Sr isotopes for profiles of the composite Ibra section of the Cretaceous Samail ophiolite (GREGORY and TAYLOR, 1981; LANPHERE *et al.*, 1981; MCCULLOCH *et al.*, 1981). The oxygen isotope profile exhibits rocks which are both depleted and enriched in ^{18}O relative to their primary igneous $\delta^{18}O$ values. Because the integrated average bulk $\delta^{18}O$ value of the altered oceanic crust is close to the initial $\delta^{18}O$ value, there was little or no flux of ^{18}O in or out of the oceans. This balance for oxygen isotopes obtains even though there is abundant evidence for fluid flow throughout the oceanic crust. From the profile of $^{87}Sr/^{86}Sr$, it is clear that the Sr isotopic system was not close to a condition of steady-state. Because of the major differences in the behavior of these two isotopic systems, by casting the rates of exchange in terms of volumetric rates, we can discern whether the behavior of the two dissimilar systems is qualitatively correct and compatible with observation.

RATES

Ridge crest-seawater interaction

Following GREGORY and TAYLOR (1981), the rate constant, k, for seawater exchange with the oceanic crust would be $[\phi/(\phi + 1]Rc/W$, where R is the global spreading rate in km^2/yr, ϕ is the actual water/rock ratio for the rocks exchanged at the ridge, W is the mass of the oceans (in oxygen units), and c is a constant that takes into account the depth of alteration (in terms of oxygen isotopes) and the oxygen content of the oceanic crust. The mean life of the process is simply $1/k$. For a global ridge system with a spreading rate of 3 km^2/yr, $\phi = 2$, and a 4 km depth of seawater penetration, the rate constant is 0.008/Ma for the ocean crust-seawater interaction, and the mean lifetime is 125 million years.

Note that the term $\phi/(\phi + 1)$ takes into account the actual water/rock ratio (in oxygen units) in the ridge system, and this is related to the integrated fluid flux. Because of the near balance between ^{18}O depleted and enriched rocks in the altered oceanic crust (MUEHLENBACHS and CLAYTON, 1976; GREGORY and TAYLOR, 1981), it is difficult to estimate the water/rock ratio for the overall ridge system from oxygen isotope data. This, by itself, is a statement that the oxygen isotopic composition of seawater is close to a steady-state value and that the bulk fractionation for the ridge crest-seawater interaction is close to +6. When the difference between the oxygen isotope composition of seawater and pristine oceanic crust is close to the value of the bulk fractionation factor, the water/rock ratio calculated from oxygen isotopes becomes indeterminate.

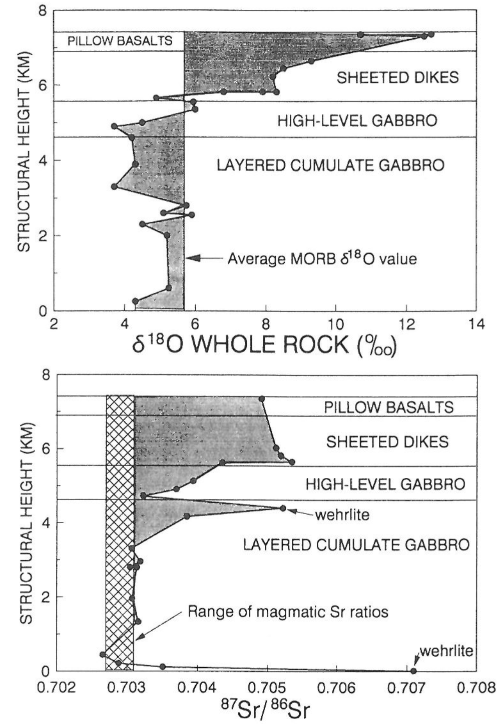

FIG. 2. A comparison of oxygen and strontium isotope profiles through the Cretaceous oceanic crust is shown using the Ibra section of the Samail ophiolite. This figure clearly illustrates the major difference in the behavior of Sr and O isotopes in the altered oceanic crust. In each diagram, the primary isotopic composition is shown as a vertical line, $\delta^{18}O = 5.7$, or as a field for $^{87}Sr/^{86}Sr$. The shaded areas represent the deviations from the primary magmatic composition. It is clear that the hydrothermal alteration resulted in a net transfer of ^{87}Sr into the crust. Excluding the wehrlite samples which have almost no Sr, the average $^{87}Sr/^{86}Sr$ of the altered Samail crust is approximately 0.7036, enriched relative to a primary value of less than 0.703. In contrast, the inferred bulk $\delta^{18}O$ of the altered section is approximately the same as the original primary magmatic value of the rocks; i.e., the shaded areas representing enriched and depleted rocks are nearly equal. This means that there was no net transfer of ^{18}O in or out of seawater as a result of the hydrothermal interaction. The data are from GREGORY and TAYLOR (1981), LANPHERE *et al.* (1981) and MCCULLOCH *et al.* (1981).

Strontium isotopes display a different behavior (*e.g.*, Fig. 2), and thus can be used to infer the actual water/rock ratio of the ridge. In a recent summary of estimates for the ridge-crest water flux based on thermal and chemical constraints, PALMER and EDMOND (1989) concluded that the ridge-system water flux is in the vicinity of 0.9 to 1.3 × 10^{14} kg/yr. For a 3 km^2/yr global spreading rate, this flux would translate into an integrated water/rock ratio of 3.6 to 5.2 in oxygen units. These numbers are similar to an independent estimate from the Sr-isotope work on the Ibra section of the Samail ophiolite.

This latter calculation can be done by integrating the profiles for $^{87}Sr/^{86}Sr$ and Sr content as a function of depth in the Samail ophiolite to get averages for these parameters. Then the water/rock ratio can be calculated in the normal way (*e.g.*, MCCULLOCH *et al.*, 1981). Using the data on the Ibra section from LANPHERE *et al.* (1981) and MCCULLOCH *et al.* (1981), the water/rock ratio for the Samail ridge system is estimated to be about 4–6 in oxygen units. This estimate, derived from material-balance considerations, suggests that the term $\phi/(\phi + 1)$ is probably greater than 0.8. Note that if the water/rock ratio is very large, $\phi/(\phi + 1)$ approaches one, and the rate constant reflects the fastest rate that seawater can approach steady state through the ridge-crest interaction. In all of the calculations below, a conservative value of ϕ equal to 2 ($\phi/(\phi + 1) = 0.67$) has been used. Thus, uncertainties about the magnitude of the fluid flux will not affect the results.

The variability of global spreading rates over geologic time is related to heat generation in the mantle. Plate velocities follow the mean velocity of mantle convection, which is related to the square root of the Rayleigh number (TURCOTTE and SCHUBERT, 1982). The Rayleigh number in turn is proportional to heat generation in the mantle. Considering that heat generation due to radioactive decay has approximately halved over the last three billion years (TURCOTTE and SCHUBERT, 1982; LEE, in YODER, 1976), global spreading rates in the past were probably at least as high as at present.

The constant c reflects the depth of penetration of seawater into the oceanic crust. From the evidence of veining in the layered gabbro section of the Samail ophiolite, and from isotopic studies (HOPSON *et al.*, 1981; GREGORY and TAYLOR, 1981; LANPHERE *et al.*, 1981; MCCULLOCH *et al.*, 1981), seawater penetrates the entire cooling oceanic crust. However, the mineralogic and isotopic effects are less pronounced with depth, and thus a conservative value of 4 km has been used as the average depth of penetration.

Continental weathering-seawater interaction

The exchange of oxygen isotopes between the continental crust and seawater is a result of the chemical weathering of the continents. Because the equilibrium oxygen isotope fractionations between minerals and water increase as temperature decreases, the weathering of low-^{18}O rocks formed at high temperature results in a net ^{18}O-depletion of the hydrosphere. If the original oceans were outgassed and equilibrated at high temperatures with the mantle, then there has been an approximately 8 per mil depletion of the $\delta^{18}O$ of the oceans to their present-day value. If this was accomplished largely by weathering igneous rocks with $\delta^{18}O$ values close to +6, then it is possible to estimate the average weathering rate provided that the bulk $\delta^{18}O$ value of sedimentary and metamorphic rocks is known. The weathering rate (Table 1) credited to MUEHLENBACHS and CLAYTON (1976) is an example of this type of calculation and as such gives a characteristic time for the seawater cycle on the order of the age of the Earth. Because of the potential for recycling sediments in subduction zones or in metamorphic terranes, the slow rate inferred from this type of analysis would be a lower limit.

Other estimates of chemical weathering rates can be inferred from the elemental fluxes carried by rivers into the oceans and from the rates of deposition of pelagic sediments. An additional constraint comes from estimates of continental growth rates. Weathering rates must not exceed the apparent continental growth rate; otherwise the continental mass would not appear to be growing with time. ARMSTRONG (1981), in his analysis of the evidence for continental crustal recycling, reports that the amount of sediment that must be recycled to justify a steady-state continental crustal volume is 1–3 km^3/yr. This range, according to ARMSTRONG's (1981) analysis, is similar to the deposition rate of pelagic sediments and to the rate of crustal accretion on the continents. By balancing the rates of accretion of new continental crust with the subduction of pelagic sediments, ARMSTRONG (1981) concludes that a steady-state model for the evolution of the continental crust is permitted by the data. This suggests that chemical weathering rates cannot exceed the long-term averages for crustal growth rates without seriously disturbing the age distribution of the continental crust. Thus, there is an additional constraint on chemical weathering rates deduced from measurement of elemental fluxes carried by rivers, provided the fluxes can be converted into volumetric rates (km^3/yr).

In order to change the contribution from conti-

Table 1. Weathering rates and time constants

Reference	Weathering rate km^3/yr	Method*	$1/k$† Ma	$\tau_{\text{continents}}$‡ Ga
Holland (1984)	7.4	1	140	1.0
Berner *et al.* (1983)	5.1	2	200	1.1
Walker and Lohmann (1989)	3.5	3	300	2.1
Gilluly (1964)	2.5	4	420	3.0
Drever *et al.* (1988)	1.9	5	550	4.0
Clarke (1924)	1.0	6	1040	7.5
Gilluly (1955)	0.2	7	5200	38
Muehlenbachs and Clayton (1976)	0.2	1	5200	38

* Methods: (1) Oxygen isotope flux due to weathering. For Holland (1984) this number is tied to Holeman's (1968) estimate for the weathering rates from river fluxes. In the case of Muehlenbachs and Clayton (1976), this is based upon the ^{18}O flux necessary to produce the observed sedimentary mass over geologic time. (2) Calcium balance. (3) Magnesium balance. (4) Speculative dissolved river load necessary to make denudation rates agree with tectonic arguments. (5) Silicon balance. (6) River flux analysis. (7) Volume of pelagic sediments.

† The mass of oxygen of the ocean divided by the weathering rate in moles of oxygen. This is the time it would take a perturbation in the δ^{18}O value of seawater to decay to $1/e$ (e is Euler's constant) of the initial value if weathering was the only process controlling the isotopic composition of seawater.

‡ Note that characteristic times for the continental crust are simply the approximate present day volume of the continental crust divided by the volumetric weathering rate.

nental weathering into a rate constant (k value), the dissolved river load or the denudation rate is converted into the number of cubic kilometers of crust dissolved or eroded; this result is then normalized for the oxygen content of rocks. Thus, for a rate of 2.5 km^3/yr, the k value for continental weathering would be 0.0024/Ma with a mean lifetime of 420 million years. Estimates for continental weathering (Table 1) vary from a low value of 0.2 km^3/yr (Gilluly, 1955; Muehlenbachs and Clayton, 1976) to a high value of >7 km^3/yr (Holeman, 1968; Holland, 1984).

For a constant continental crustal volume of 7.5×10^9 km^3 and a weathering rate of 3 km^3/yr, the inferred mean age of the continents by dimensional analysis would be 2,500 million years. Long-term weathering rates cannot be much faster than 3 km^3/yr, because then the continents would be younger than what is observed. Because continental growth rates (Gebauer and Williams, 1990) are probably less than 3 km^3/yr, it is not plausible to assume that weathering rates have been much higher than this over geologic time. Global weathering rates that are much higher than inferred continental growth rates will result in an age distribution inconsistent with what is observed. To get the characteristic times for the continental crust shown in Table 1, the entire volume of the present-day continental crust was used. For smaller volumes of continental crust, the constraint on weathering rates becomes even more prohibitive.

The mean lifetime for the multiple reservoir system is $1/\sum k_i$, and is shorter than the values for any single reservoir plus seawater. Using the values of 0.008 and 0.0024 (Ma^{-1}), the combined oceanic crust and continental weathering cycles give a mean lifetime of 96 Ma compared with 125 Ma for the oceanic crust cycle by itself. Given that these response times are ultimately controlled by tectonic processes driven by mantle convection, it is unlikely that long-term average rates would change by much more than a factor of two over Earth history. Nevertheless, it is important to understand the effect of variable rates of continental weathering and seafloor spreading rates on the steady-state δ^{18}O value of seawater and on the response time of the system.

IMPACT OF CHANGING THE RATES

Because the response times of the cycles are short ($\approx$100 Ma) compared to the age of the Earth, all of the transient terms in Eqn. (2) can be neglected. Differentiation of Eqn. (3) with respect to one of the k values results in an equation which relates the change in the δ value of seawater to the change in any one of the rate constants. For a two-rock reservoir system, integration of the resultant equation between initial and final states yields the following relationship:

$$\delta W^{\mathrm{f}} - \delta W^{0} = (\Delta_1 - \delta_1^0 - \Delta_2 + \delta_2^0) \times k_2[1/(k_1^{\mathrm{f}} + k_2) - 1/(k_1^0 + k_2)] \quad (4)$$

where the superscript f and 0 refer to the final and initial values. The first factor on the right-hand side of the equation represents the difference in the target steady-state δ values for the two reservoirs. A value of 8 per mil for the factor $(\Delta_1 - \delta_1^0 - \Delta_2 + \delta_2^0)$ and a change in the ratio of k_1/k_2 (*e.g.*, ratio of continental weathering to the mid-ocean ridge exchange rates) from 1/9 to 50/9 results in a decrease in the steady-state δ value of seawater of 6 per mil. If the initial ratio of the continental weathering contribution to the ocean ridge contribution was obtained at a global continental weathering rate of 3 km^3/yr, this 6 per mil change in the $\delta^{18}O$ of seawater would require 150 km^3/yr of continental weathering! If such weathering rates could be sustained for 15 million years, the $\delta^{18}O$ value of the oceans could change by close to 6 per mil, but only at the expense of processing about a third of the continental crust!

Alternatively, seafloor spreading could be shut off to achieve the change in the ratio of the rates. This comes at the expense of the response time, which becomes more than twenty times longer than the observed rate of the presumed seawater $\delta^{18}O$ transition (<20 Ma) observed at the Devonian-Carboniferous boundary (LOHMANN and WALKER, 1989).

In Fig. 3, the impact of changing the continental weathering rate has been enhanced by maximizing the value of the first factor on the right side of Eqn. (4). This is accomplished by setting the δ values of both rock reservoirs equal to +6 per mil. The value of the first factor changes from 8 to 14 per mil. To achieve a 6 per mil change in the $\delta^{18}O$ value of seawater still requires a twenty-fold increase in weathering rates (from 3 to 60 km^3/yr). Such an increase could not be sustained for any length of time without leaving some trace in the rock record.

In Fig. 4, the effect of increasing the global spreading rate is shown for an Earth that initially starts out with the continental and ridge oxygen fluxes equal. Once again the impact of changing the rates has been maximized by setting the two initial rock reservoir $\delta^{18}O$ values to +6. The calculation shows that approximately a ten-fold increase in spreading rates is required to generate a 6 per mil change in the $\delta^{18}O$ value of seawater. This scenario would only work if some other process besides the ridge-crest interaction contributed significantly to the steady-state value of seawater (Eqn. 3). The constraints on the cooling of the Earth and the age distribution of the continents would suggest that it would be improbable that a ten-fold increase in spreading rates could be sustained on top of the background rate that must be maintained to dissipate the internal heat of the Earth.

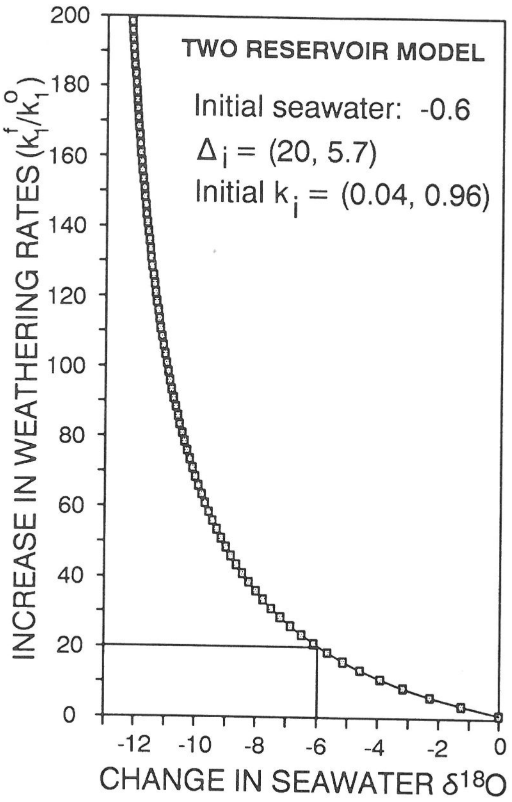

FIG. 3. The increase in weathering rates (final value divided by the initial value) necessary to change the $\delta^{18}O$ value of seawater from an initial value of −0.6 to −12 is illustrated. The bulk fractionation factor associated with continental weathering is assumed to be approximately +20, whereas the oceanic crust-seawater interaction is assigned a fractionation factor of 5.7. In order to maximize the change in the $\delta^{18}O$ value of seawater, the initial rock reservoir $\delta^{18}O$ values have been arbitrarily set to +6 for the calculations in Figs. 3 and 4. In this example, a 6 per mil change in oxygen isotopic composition of seawater comes at the expense of a 20-fold increase in weathering rates. Clearly, such an increase in weathering rates would be unsustainable for any length of time without grossly changing the age distribution of the continental crust. The values of 0.04 and 0.96 represent the initial normalized rates for the two competing processes.

The calculations represented by Figs. 3 and 4 give minimum estimates for the magnitude of the changes in the rate parameters required to produce 6 per mil changes in the $\delta^{18}O$ value of seawater. Because the average $\delta^{18}O$ value of the continental crust is certainly ^{18}O-enriched relative to the mantle and the oceanic crust, changes of only 3 per mil in the $\delta^{18}O$ value of seawater are probably more realistic. Even these more modest changes occur at the expense of very large increases in weathering rates or spreading rates. For example, a 100-fold increase in weathering rates from $\approx$1 km^3/yr only changes seawater $\delta^{18}O$ from −0.3 to −3.3 in a calculation where average continental crustal rocks

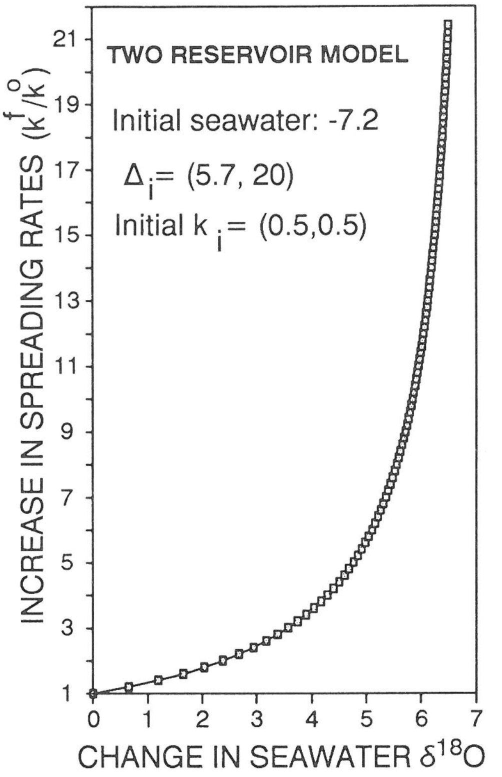

FIG. 4. The calculated curve shows the increase in global spreading rates required to change the oxygen isotopic composition of seawater by 6 per mil. In this calculation, the initial contribution from the continental weathering flux is assumed to be equal to the flux from the seawater-oceanic crustal interaction. The 6 per mil change requires a ten-fold increase in seafloor spreading rates, which is at odds with thermal models of the Earth. Also, if the oceanic crust-seawater interaction was already dominating the steady-state isotopic composition of seawater, the increase in spreading rates would not have any effect on the isotopic composition of seawater unless the bulk fractionation of the seawater-ocean crust interaction was sensitive to spreading rates. As this fractionation factor is more likely to be controlled by the contrast between the surface temperature of the Earth and the liquidus temperature of mid-ocean ridge basalts, it is not obvious that such a hypothesis could account for a spreading rate dependence of the Δ value between the seawater and the oceanic crust.

have $\delta^{18}O = +16$ and the rate constant for the ridge-crest interaction is a more robust 0.016/Ma.

In order to constrain the oxygen isotope cycle for seawater, rate constants have been used which do not intrinsically depend on the oxygen isotope parameters. By scaling the problem to the rates reported in terms of surface area or volume per unit time, the rates can be checked independently against the age distribution of the continents and ocean basins. Realistic changes in the rate constants do not produce the changes required by any objective interpretation of the sedimentary oxygen isotope record.

Strontium isotopes can be used as an independent check on the validity of the rate constants inferred from the volumetric constraints. For example, for a 3 km^3/yr continental weathering rate that affects average continental crust with a Sr content of 370 ppm (JACOBSEN and WASSERBURG, 1979), and a mass of Sr in the ocean equivalent to 1.1×10^{16} kg, the rate constant is 0.278/Ma and the mean life is ≈3.5 Ma. In contrast, if the Sr content of oceanic crust is approximately 150 ppm (LANPHERE *et al.*, 1981), the spreading rate is 3 km^2/yr, and the depth of penetration of seawater for Sr isotopes is about 2 km at a $\phi = 2$ (mass units), then the rate constant for the ridge crest–seawater interaction is 0.16 and the mean life is ≈6 Ma. This would indicate that the flux from the continental crust would dominate over the ridge-crest flux, about 64:36. If the river flux into the ocean has $^{87}Sr/^{86}Sr \approx 0.712$ (PALMER and EDMOND, 1989) and the oceanic crust is about 0.703, the present-day isotopic composition of seawater comes out to approximately 0.709, similar to the observed value (PALMER and EDMOND, 1989).

For the following reasons, the Sr isotope composition of seawater *should change* as a function of time: (1) the time constants are short, millions of years compared to 100 Ma time constants for oxygen isotopes; (2) the heterogeneity of continental crustal rocks can change the target isotopic composition of seawater, and the system can respond fast enough to reflect the changes; and (3) the ridge crest–seawater interaction has a time constant sufficiently close to the time constant for the continental weathering flux that changes in spreading rates could make a difference.

In contrast, the time constants for oxygen isotope exchange are too long to permit rapid excursions in the $\delta^{18}O$ value of seawater. In addition, as shown above, reasonable estimates of the rate constants indicate that the ridge-crest interaction is dominant. The homogeneity of the oxygen isotope composition of magmas erupted at mid-ocean ridges will militate against secular changes in seawater $\delta^{18}O$ values. Nevertheless, the parameter that may have the greatest potential for perturbing the oxygen isotopic composition of seawater may be the isotopic composition of the rocks involved in the rock cycle. Namely, is the heterogeneity of the oxygen isotope composition of the continental crust sufficient to overcome the restrictions imposed by the rate constants?

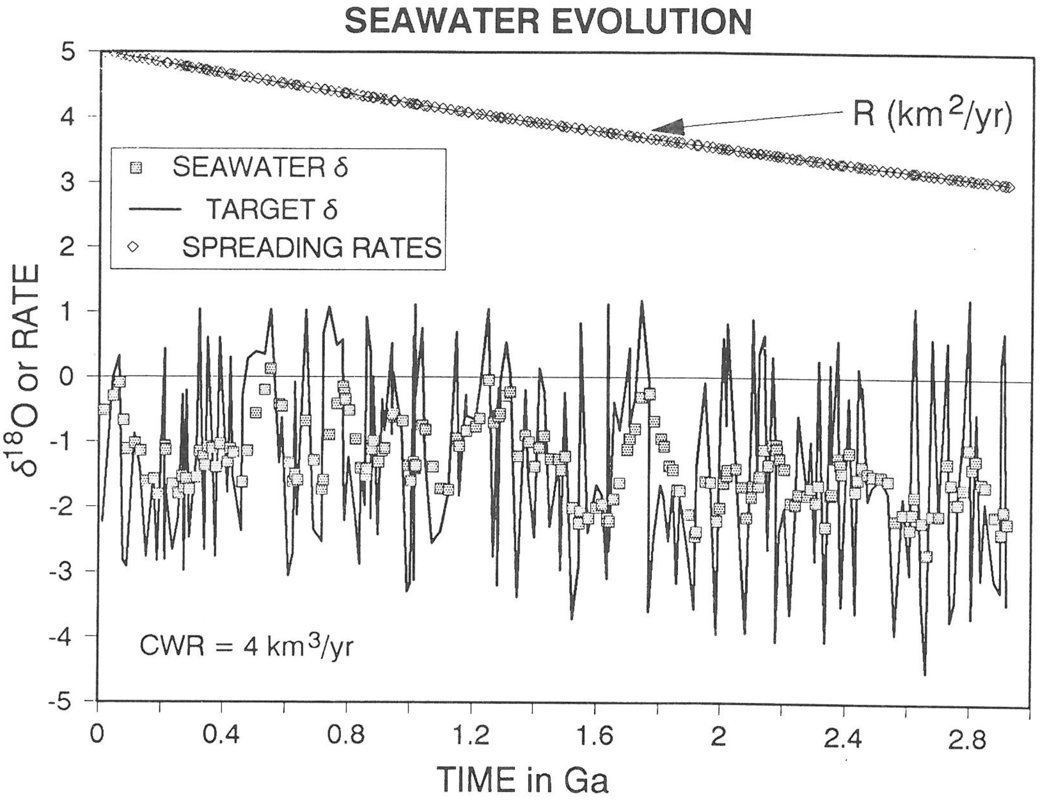

FIG. 5. A 3 Ga simulation of the ^{18}O evolution of seawater for a seafloor-spreading dominated regime where: (1) the global spreading declines at rate dictated by the decline of radioactive heat production in the mantle, (2) the continental weathering rate is fixed at an average value of 4 km^3/yr and which is allowed to fluctuate by ±25%, and (3) the range in the $\delta^{18}O$ values of continental rocks is allowed to vary by ≈20 per mil in a random fashion. The changing isotopic composition of the rocks involved in the weathering cycle is a perturbation on the system, and the parameters are fixed for random intervals not longer than 25 Ma (a time consistent with changes in plate motions). The solid thin line represents the target steady-state $\delta^{18}O$ value of seawater and the squares represent the actual value seawater achieves at the end of a time interval. In the simulation, the isotopic composition of seawater is constant to within ±1 per mil, and the most rapid change in the $\delta^{18}O$ value of seawater is ≈1 per mil/100 Ma.

IMPACT OF CHANGING THE ISOTOPIC COMPOSITION OF EXPOSED CONTINENTAL CRUST

Inspection of the steady-state term (Eqn. 3) indicates that changing the bulk $\delta^{18}O$ of the rocks participating in the weathering cycle may be an effective mechanism for changing the steady-state δ value of seawater through a long-term global cycle, because the isotopic composition of basalt is fixed by the mantle reservoir and the Δ's for the ocean crust-seawater cycle are not likely to change very much (GREGORY and TAYLOR, 1981). The change in the steady state δ value of seawater is proportional to the change in the bulk composition of the rocks involved in the cycle, weighted according to the rate constant of the process. Because continental crustal rocks do have a very large range in $\delta^{18}O$ values, >25 per mil, changes in the average $\delta^{18}O$ value of the continental crust participating in the weathering cycle could have a significant impact on the "target" steady-state value of seawater.

In Figs. 5 and 6, two simulations have been performed which illustrate the impact of changing the average $\delta^{18}O$ value of continental crustal rocks involved in the weathering cycle. Figure 5 illustrates a simulated 3 Ga isotopic history of seawater where: (1) global seafloor spreading rates (in km^2/yr) decline according to the decay of radioactive elements in the Earth's mantle; (2) the continental weathering rate averages a robust 4 km^3/yr over the entire simulation (it is allowed to randomly fluctuate within 1 km^3/yr of that value); and (3) the average $\delta^{18}O$

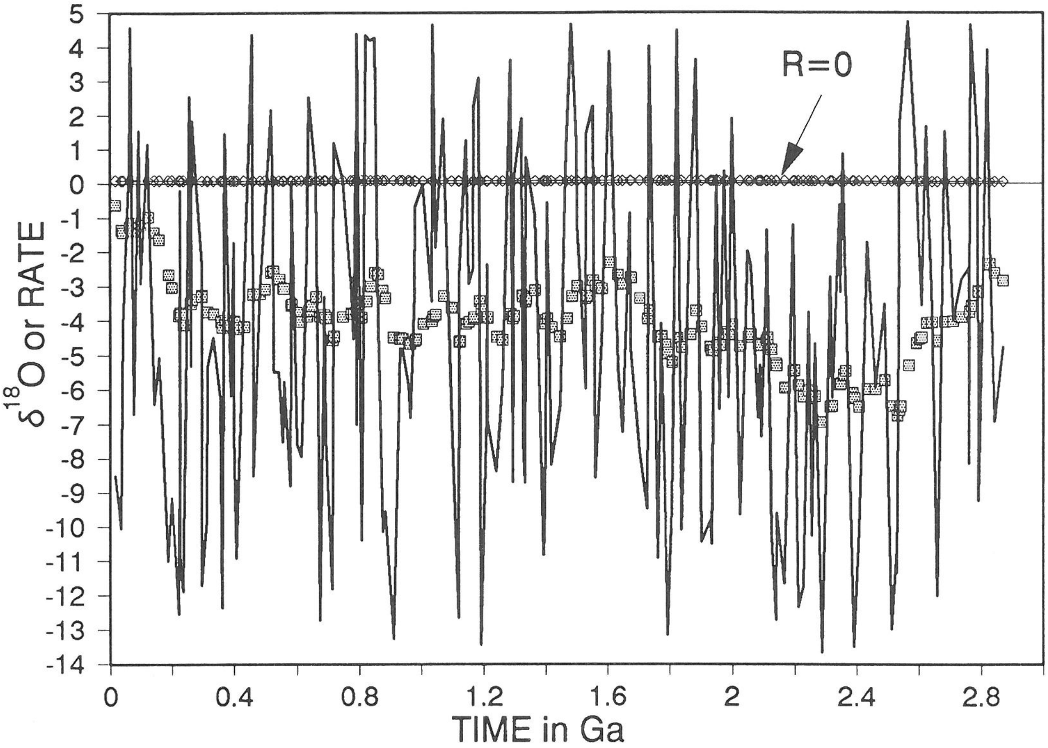

FIG. 6. In this simulation, all parameters are the same as in Fig. 5, with the exception of the global spreading rate which is now set to zero. Even though the target isotopic composition of seawater swings through extreme changes reflecting the oxygen isotope heterogeneity of the continental crust, the isotopic composition of seawater remains relatively constant over billion year intervals, and the 4 per mil excursions occur over 0.5 Ga intervals. No short time scale ($\approx$20 Ma) 3–6 per mil changes occur, because the rate constants are too slow.

value of continental crustal rocks is allowed to randomly fluctuate over a $\approx$20 per mil range in random time steps less than 25 Ma in duration. The effect of the latter is to perturb the system towards a new target steady-state value. The target steady-state values are shown by the sharply fluctuating solid curve, and the actual $\delta^{18}O$ value of seawater at the end of a time step is shown by the squares. In simulations with seafloor spreading, seawater settles in at an isotopic composition close to -1 ± 1, and no change in the oxygen isotopic composition of seawater occurs at a rate faster than about 1 per mil/100 Ma.

In Fig. 6, the effect of totally shutting-down seafloor spreading is shown with all other parameters the same as in Fig. 5. The target steady-state $\delta^{18}O$ value of seawater fluctuates over a wide range (four times greater than in Fig. 5) because buffering effect of the ridge is now eliminated. In spite of the more dramatic changes in the target steady-state δ values, the average $\delta^{18}O$ value of seawater declines slightly but still does not vary all that much. The lack of a precipitous decline in the $\delta^{18}O$ value of seawater is a consequence of the fact that the simulation allows the weathering of sediments which formed in the presence of seawater with $\delta^{18}O \approx 0$. The time constants are now much longer, so that the large changes in the target values are more than compensated by the slower response time; thus, the isotopic composition of seawater still does not change at the rates required by some interpretations of the sedimentary record.

This latter type of regime (the zero seafloor spreading case) would occur only when global seafloor spreading rates decline to and remain at levels well below their present levels of 3–4 km^2/yr, again at the expense of response time of the global cycle which becomes much longer by several hundred million years. As long as continental weathering affects rocks of all types and ages which have $^{18}O/^{16}O$ ratios covering the full diversity of $\delta^{18}O$, the time dependent variation in the $\delta^{18}O$ of seawater *should be much less* than the time dependent variation of the target "steady-state" $\delta^{18}O$ of seawater.

CONCLUSIONS

If the $\delta^{18}O$ value of seawater does change substantially on short time scales as a result of changing the proportions of the fluxes related to ridge-crest and continental weathering effects, then such changes require dramatic changes in the tectonic regime of the Earth. In the search for the interpretation of the secular variation in the $\delta^{18}O$ values of sedimentary rocks, we must recognize that the rate constants for changing the global oxygen isotope composition of the oceans appear much too slow to account for the apparent timescales of the changes observed in sedimentary rocks. Even if the latter timescales were correct, the magnitude of the tectonic changes required to shift the steady-state isotopic composition of seawater to the extremes suggested by some literal interpretations of the sedimentary data are too large to be reconciled with constraints imposed by the age distributions of the continents or the ocean crust.

At present, continental glaciation and deglaciation are the only known mechanisms that seem to operate on short enough time scales to produce rapid changes in the $\delta^{18}O$ of seawater. The oxygen isotopic changes associated with cycles of glaciation are of insufficient magnitude to explain the changes in the oxygen isotope composition of seawater that some workers have inferred from the Paleozoic sedimentary record. In the absence of other plausible explanations, the significance of the secular oxygen isotope record would appear to lie in some local (up to continent scale) environmental parameters or, alternatively, some problem with the time constants for the preservation of surface oxygen isotope signatures.

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