

WHY THE OXYGEN ISOTOPIC COMPOSITION OF SEA WATER CHANGES WITH TIME

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Abstract. The oxygen isotopic composition of sea water is determined by interactions with fresh, silicate rocks. Interactions at high temperature, principally hydrothermal interactions on the sea floor, make sea water isotopically heavier. Interactions at low temperature, including sea floor weathering but principally weathering of fresh, crystalline rocks on the continents, make sea water isotopically lighter. Any change in the relative rates of these high and low temperature interactions will cause a change in the composition of sea water. Extreme limits might be -15 per mil relative to SMOW to +4 per mil. Possible rates of change appear to be quite slow, perhaps 1 per mil in 10^8 years, because of the large size of the oceanic reservoir. Evolution in tectonic style over the course of earth history may have caused a change in the oxygen isotopic composition of sea water as fresh crystalline rocks have been increasingly blanketed by weathered sediments and as deepening oceans have increasingly flooded the places where earth's internal heat is released at the surface.

Introduction

The paper by Lohmann and Walker in this issue presents evidence for a change during the course of earth history in the isotopic composition of the oxygen in chemical sediments. Do these and other data that show a similar pattern (Popp et al., 1986) indicate that the isotopic composition of sea water oxygen has changed with time? Controversy over this question has continued for some time (Anderson and Arthur, 1983; Hoefs, 1980). Some papers argue that the oxygen isotopic composition of the ocean has not changed significantly during the course of earth history (Hoffman et al., 1986). Others even argue that the oxygen isotopic composition can not change, that it is fixed at close to its present value. This paper explores these questions by looking at the budget of sea water oxygen isotopes and the processes that control isotopic composition. Possible causes of change in isotopic composition are considered.

Interactions Affecting Isotopic Composition

Most of earth's oxygen is combined in silicate minerals of the mantle and the crust. The oxygen isotopic composition of the ocean depends ultimately on interactions with the large silicate reservoir. A key element of these interactions is the equilibrium isotopic fractionation between

oxygen in minerals and oxygen in water. This equilibrium fractionation is a strong function of temperature varying, for many minerals, from about 30 per mil (parts per thousand) at earth surface temperatures to values as small as 1 per mil at temperatures of 300-400°C (Friedman and O'Neil, 1977). Typically, the mineral is isotopically heavier (richer in ^{18}O) than the water. This qualitative description of the equilibrium fractionation applies not only to interactions between water and silicate minerals but also to equilibria between water and carbonate minerals and water and chert. This temperature dependence of the equilibrium fractionation means that interactions at low temperature drive water strongly negative in isotopic composition with respect to the rock. Interactions at high temperature cause the water to approach the rock in isotopic composition.

Figure 1 provides a cartoon representation of the most important loci of interaction between the hydrosphere and previously unweathered crystalline rock. Weathering of fresh igneous rock on the continents occurs at low temperatures and produces isotopically heavy weathered rock along with isotopically light water. Weathering reactions with previously weathered rocks and old sediments have little effect on the isotopic composition of the water because these rocks are already isotopically heavy, having achieved approximately the equilibrium fractionation with respect to the ocean on a previous weathering cycle. Interactions on the sea floor occur at both low and high temperatures (Bowers and Taylor, 1985). At shallow levels in the sea floor temperatures are low and interactions between water and rock yield heavy rock and light water. At greater depth, temperatures are high and hydrothermal interaction yields little difference in isotopic composition

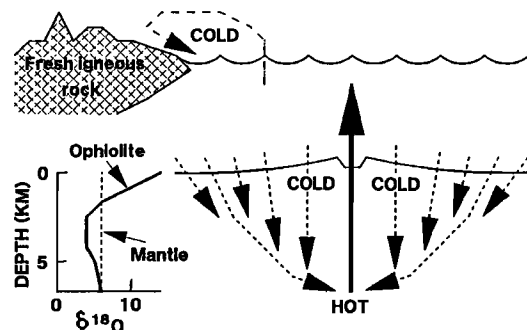


Fig. 1. The isotopic composition of sea water is determined by oxygen exchange reactions with unweathered crystalline rocks. Fractionation depends on the temperature of the interaction. Cold interactions occur during the course of continental weathering. Hydrothermal interactions on the sea floor are hot at depth and cold near the top. The panel at the bottom left is a schematic illustration of the oxygen isotopic composition of ophiolites, which reflects the sea floor exchange.

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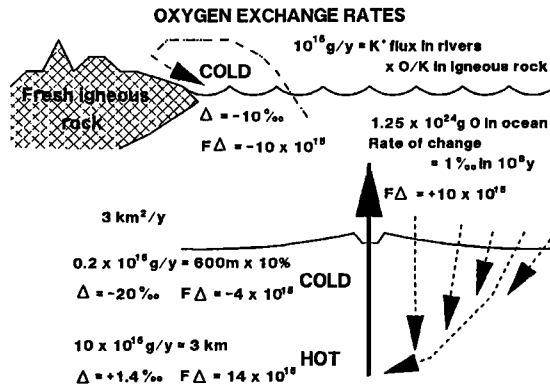


Fig. 2. Oxygen exchange rates estimated for continental weathering and for the hot and cold components separately of sea floor hydrothermal interactions. The elements of the calculation are described in the text. The quantity $F\Delta$, expressed in g per mil/y, is the product of oxygen exchange flux and the associated change in isotope ratio.

of water and rock. The impact of hydrothermal interactions on the isotopic composition of the oceanic crust is sketched in the lower left corner of Figure 1, which presents a simplified view of ophiolite data (Gregory and Taylor, 1981). The dashed line indicates the isotopic composition of mantle rocks, about +5.7 per mil on the SMOW scale. The rocks close to the top of the crust have interacted at low temperatures with water at $\delta = 0$ to become isotopically heavy with respect to the initial, mantle value. At greater depths the hot interactions have yielded isotopic compositions intermediate between the initial rock and the initial water values. Thus the rocks have become lighter and the water has become heavier.

It has been suggested (Muehlenbachs and Clayton, 1976; Gregory and Taylor, 1981) that the total change in the isotopic composition of the rocks, integrated over the depth in the sea floor, is zero, implying that high and low temperature interactions balance so that sea water isotopic composition is not changed by interaction with the sea floor. The ophiolite data are derived from several outcrops of uncertain correlation. It is not clear that they represent a complete section without repetition. Therefore, these data do not test the suggestion of no change.

Budget of Oxygen Isotopes

Conservation of matter requires that the mass of ¹⁸O added to a rock must just balance the mass of ¹⁸O removed from water and vice versa. We can therefore use ophiolite data to estimate the fluxes associated with sea floor interactions. The same approach was used by Muehlenbachs and Clayton (1976) and by Holland (1984).

The calculation is summarized in Figure 2. We assume that new sea floor is produced at the rate of 3 km²/y (Chase, 1972). We assume that low temperature weathering occurs to a depth of 600 meters and affects 10% of the rock (Muehlenbachs and Clayton, 1976). The mass of oxygen exchanged is therefore 0.2 x 10¹⁵ g/y. The fractionation involved in this exchange is 20 per mil, positive for the rock and negative for the water so the product of oxygen flux and

isotope change is

$$F\Delta = -4 \times 10^{15} \text{ g per mil/y} \quad (1)$$

Hot hydrothermal interactions are assumed to extend through a 3 km thickness of the sea floor to yield an oxygen exchange flux of 10 x 10¹⁵ g/y. This interaction results in change in isotopic composition of the whole rock of -1.4 per mil, with the opposite sign for the water. The isotope flux is therefore

$$F\Delta = 14 \times 10^{15} \text{ g per mil/y} \quad (2)$$

In this analysis the combined flux of hot and cold interactions in the sea floor is

$$F\Delta = +10 \times 10^{15} \text{ g per mil/y} \quad (3)$$

The thickness of sea floor undergoing hot hydrothermal interactions has been adjusted in this calculation to yield an overall balance in the oxygen isotope budget. The data are not sufficiently precise to determine whether or not the budget is at present balanced. Our estimates here indicate that sea floor interactions tend to drive sea water isotopic composition positive because these numbers yield more hot exchange than cold exchange. In this we agree with Holland (1984). Muehlenbachs and Clayton (1976), on the other hand, concluded that hot and cold exchange on the sea floor were approximately equally important as did Gregory and Taylor (1981); we do not know enough about the extent of hydrothermal alteration of the sea floor to reach firm conclusions on this point. Specifically, the ophiolite data do not establish the relative contributions of hot and cold interactions because of uncertainty about the completeness and representativeness of the measured section.

To estimate the contribution of continental weathering to the oxygen isotopic budget of sea water we use the flux of dissolved potassium ions in rivers 48 x 10¹² g/y, as an indicator of the rate of weathering of fresh silicate minerals, because dissolved potassium is nearly all derived from silicate weathering (Meybeck, 1979). The flux we use has been reduced by about 10% from present data to correct for anthropogenic contributions (Meybeck, 1979). This flux is multiplied by the ratio of oxygen to potassium in average igneous rocks, 20 to 1 by weight (Taylor and McLennan, 1985), to obtain an estimate of the rate at which oxygen becomes available for exchange with water as a result of the dissolution of silicate minerals. The estimated oxygen exchange rate is 10¹⁵ g/y. The average change in the whole rock isotopic composition is +10 per mil from an average of +8 per mil for continental crystalline rocks to an average of +18 per mil for continental sedimentary rocks (Perry and Tan, 1972). As already noted, subsequent weathering of these sedimentary rocks causes little further change in oxygen isotopes. These values yield a continental isotope flux of

$$F\Delta = -10 \times 10^{15} \text{ g per mil/y} \quad (4)$$

The sea floor calculations were adjusted to yield a sea floor flux just big enough to balance this continental flux, which we regard as much better

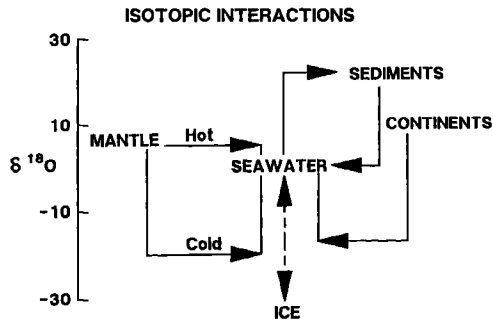


Fig. 3. Sea water composition is determined by the relative rates of hot and cold interactions with mantle rocks and weathering reactions with fresh igneous rocks on the continents. The composition of sedimentary rocks is determined by sea water composition. The deposition and weathering of sedimentary rocks has little effect on sea water composition. Small variations in sea water composition can result from growth or decay of the isotopically light ice reservoir.

constrained by the data on the composition of river water and of crustal rocks than the sea floor estimate, based largely on ophiolite data, where the thickness of the various layers in the ophiolite is not well constrained. The main uncertainty in the continental calculation concerns the ratio of oxygen exchanged to potassium dissolved. Holland's (1984) estimate of the continental flux based on data of Holeman (1968), is larger than ours by a factor of nearly 2.

An estimate of the potential rate at which the isotopic composition of sea water oxygen might change is obtained by dividing one or another of these fluxes by the mass of oxygen in the ocean, 1.25×10^{24} g. As indicated in the middle on the right of Figure 2 the potential rate of change is approximately 1 per mil in 10^8 y, slow because of the very large size of the oceanic reservoir.

According to the budget summarized in Figure 2, the isotopic composition of sea water oxygen depends on the relative rates of cold interactions, which occur mostly on the continents but include sea floor weathering, and hot interactions associated with sea floor hydrothermal systems. Changes in the rates of continental weathering or of sea floor spreading, to take two examples, can be expected to cause changes in the oxygen isotopic composition of sea water. The oxygen isotope system is therefore similar, in some respects, to the strontium or neodymium isotope systems, where sea water composition also depends on the relative rates of continental weathering and of sea floor hydrothermal interactions (McCulloch et al., 1981; Albarede et al., 1981; Hess et al., 1986).

Muehlenbachs and Clayton (1976) estimated the continental contribution to the oxygen isotope budget by dividing the mass of sediments by the age of the earth. The procedure neglects the destruction of sediments by metamorphism or subduction (Holland, 1984), yielding an underestimate of the continental flux by a factor of approximately 4. These authors were therefore able to conclude that the system is dominated by sea floor interactions and is not susceptible to change by changes in the relative rates of sea floor spreading and continental weathering.

Controlling Processes

Figure 3 summarizes these isotopic interactions. The composition of sea water is fixed by interactions with the large reservoirs of mantle oxygen at $\delta = +5.7$ per mil and continental oxygen at $\delta = +8$ per mil. Hot interactions make sea water heavier; cold interactions make it lighter. On short time scales the transfer of water into and out of an isotopically light reservoir of ice can shift sea water composition by as much as 1 per mil.

The composition of sea water, in turn, determines the composition of sedimentary rocks. The weathering of sedimentary rocks has little effect on the isotopic composition of sea water because these rocks have already achieved approximately the equilibrium fractionation with respect to sea water.

Figure 3 illustrates possible limits on sea water isotopic composition. If there were circumstances that would eliminate cold interactions completely the sea water composition would move close to the mantle, say $\delta = +4$ per mil on the SMOW scale. Alternatively, if there were no hot interactions at all the oceans would achieve isotopic values lighter than silicates by perhaps 20 per mil. The limit of no hot interactions would be achieved if fresh basalt erupted on land rather than beneath the sea. The composition of sea water might then be $\delta = -15$ per mil. Are there circumstances in which the ocean might approach one or another of these limits closely?

The Archean Ocean

Imagine an earth on which most of the crystalline basement is covered with a blanket of sedimentary rocks. The effect of this blanket is to diminish the rate of cold interactions between hydrosphere and fresh crystalline rocks. This imaginary earth resembles the modern earth with its extensive sedimentary cover.

Alternatively, imagine an earth on which the ocean was so shallow that mid-ocean ridge axes of sea floor spreading were largely above sea level. Such an earth might get rid of its internal heat by subaerial cooling or volcanism without the hydrothermal interaction that is a consequence of modern, deep oceans. Oxygen isotopic composition of the ocean on such an earth might therefore be close to the cold limit illustrated in Figure 3.

The Archean ocean may have been shallow, and Archean sediments are isotopically light compared with Phanerozoic sediments. The change has been interpreted to result from a general decrease in global average temperature (Knauth and Lowe, 1978), or as a change in the oxygen isotopic composition of sea water (Perry and Ahmad, 1983). Here we suggest that just such a secular change in the oxygen isotopic composition of sea water might be expected to result from the tectonic evolution of the earth, particularly the development of stable continental platforms with thick sedimentary cover and the concomitant increase in oceanic depth.

The Devonian-Carboniferous Change

In this sense the increase in oxygen isotopic composition at the end of the Devonian could be seen as just another manifestation of the long

term evolution that began in the Archean. The shift at the end of the Devonian is, however, much too rapid to be interpreted in just this way. In the discussion of the isotope budget, illustrated by Figure 2, we estimated the possible rate of change of sea water isotopic composition as 1 per mil in 10^8 years. The shift at the end of the Devonian was clearly much faster than this (Lohmann and Walker, this issue), perhaps 4 per mil in 10 million years. The paper by Lohmann and Walker considers possible interpretations of the data. Perhaps the change represents a combination of marked change in climate combined with the fastest possible change in the isotopic composition of sea water, a fortuitous combination of circumstances.

Summary

The isotopic composition of sea water depends on the relative rates of hot and cold interactions with the large reservoir of unweathered silicate minerals in the crust and mantle. On the modern earth cold interactions occur mostly as a result of subaerial weathering but include sea floor weathering, while hot interactions occur in sea floor hydrothermal systems. Changes in the oxygen isotopic composition of sea water can be expected in response to changes in sea floor spreading rates or in continental weathering rates. In this the oxygen isotopic system resembles strontium and neodymium isotopic systems.

The large size of the oceanic reservoir of oxygen implies that the rate of change of isotopic composition is generally slow. There is therefore no reason to suppose that changing interactions with silicate minerals would have had any impact on deductions concerning Pleistocene paleoclimate. The long term sedimentary record of a steady increase in sea water isotope ratio is consistent with the presumed change in global tectonic style. On the Archean Earth the instability of much of the basement prevented accumulation of extensive sedimentary cover. The areas of fresh crystalline rock exposed to low temperature interactions with sea water were larger than they are today. At the same time, some of the spreading and volcanic activity that today occurs underwater in association with hydrothermal systems may have been subaerial on the Archean Earth, where ocean depths were presumably less.

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