The oxygen isotopic composition of the oceans, sediments and the seafloor

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Abstract

The oxygen isotope history of seawater remains controversial despite decades of study. Isotopic data from fossils and chemical sediments generally indicate significantly ^{18}O-depleted seas during the Paleozoic and earlier, whereas the isotopic composition of contemporaneous ophiolites imply an ocean indistinguishable from today's. Uncertainty in $\delta^{18}O$ of seawater limits the usefulness of oxygen isotope geothermometry as well as challenges current paradigms of plate tectonics. This paper reviews the controversy and revises earlier estimates on the ^{18}O-balance within the hydrosphere. The conclusion is that the $\delta^{18}O$ of seawater is mainly buffered by hydrothermal and weathering processes at mid-ocean ridges to a $\delta^{18}O$ value of about 0‰ (SMOW). At values other than 0 ± 2‰, a large countervailing flux of ^{18}O would return seawater to near 0‰. The $\delta^{18}O$ of Paleozoic, Proterozoic and Archean ophiolites support the above model. The discrepancy in $\delta^{18}O$ between most (but not all) post-Mississippian fossils and chemical sediments and ophiolites must be explained as a combination of: (1) loss of integrity of $\delta^{18}O$ in sediments and fossils; (2) warmer paleoenvironments that lead to the precipitation of lower $\delta^{18}O$ exogenic products; (3) isotopically distinct water masses in inland seas that host the fossils but which are not well mixed with the open ocean that alters the seafloor. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Almost all geological processes, directly or indirectly, affect the composition of seawater. Knowledge of what controls seawater composition over geologic time is fundamental to understanding the functioning of our planet. This paper concerns itself solely with the controversial topic (cf. exchange by Land, 1995; Veizer, 1995), of the oxygen isotopic composition of seawater ($\delta^{18}O_{sw}$). Starting with De-

gens and Epstein (1962) hundreds of studies have found most Paleozoic and older fossils, as well as carbonate, chert and phosphate sediments, to be lower in $\delta^{18}O$ than modern analogs. Depletions of 3–12‰ in ancient vs. modern samples, are usual and these are frequently interpreted to reflect a low $\delta^{18}O$ ocean, implying a secular change in $\delta^{18}O_{sw}$ (Perry, 1967; Veizer et al., 1986; Lohmann and Walker, 1989; and many others). However, ancient ophiolites and ore deposits are indistinguishable in $\delta^{18}O$ from modern equivalents indicating no major (0 ± 2‰) change in $\delta^{18}O_{sw}$ (cf. Muehlenbachs, 1986; Lecuyer and Fourcade, 1991; De Wit and Hart, 1993; Holm-

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den and Muehlenbachs, 1993a; Lecuyer et al., 1995; Muehlenbachs et al., 1997). However, some fossils and sediments are as high in $\delta^{18}O$ as modern examples, indicating no secular change in $\delta^{18}O_{sw}$ or at least a periodic return to 0‰. All clay stones (Land and Lynch, 1996), some Devonian carbonates (Bates and Brand, 1991; Gao, 1993), Ordovician terrestrial iron formations (Yapp, 1993), Proterozoic carbonates (Tucker, 1982) and Archean cherts (Sharma et al., 1994) imply a $\delta^{18}O_{sw}$ of 0‰.

Uncertainty of $\delta^{18}O_{sw}$ value of ancient oceans limits both practical and theoretical applications of geochemistry. Correct paleotemperatures from oxygen isotope geothermometry of fossils and chemical sediments can only be obtained if the contemporary $\delta^{18}O_{sw}$ is precisely known. All too often such exercises have used circular reasoning. Studies attempting to evaluate paleoclimates, temperatures of diagenesis, or sediment burial depths from the isotopic compositions of Paleozoic fossils and sediments frequently assume a depleted $\delta^{18}O_{sw}$ (usually -3 to -7‰). A low value for $\delta^{18}O_{sw}$ is chosen such that the $\delta^{18}O$ of common Paleozoic fossils give temperatures similar to today's. The assumed $\delta^{18}O_{sw}$ is then used to calculate a 'temperature' which is used to evaluate burial depths, paleo-environments etc., without realizing that the 'calculated' temperatures of interest only reflect the assumed temperature chosen to calculate $\delta^{18}O_{sw}$ in the first place (e.g. Mountjoy and Halim-Dihardja, 1991).

A more abstract consequence of disagreement over ancient $\delta^{18}O_{sw}$ is an implicit challenge to our current paradigm of plate tectonics. The current $\delta^{18}O_{sw}$ of 0‰ reflects a balance of plate tectonic driven water/rock interactions. If $\delta^{18}O_{sw}$ were different by more than ± 2‰ in times past, or more dramatically, changed 3‰ or more over short periods of time then the mechanism of seafloor spreading must operate in ways that are as of yet unknown. Nevertheless, a sharp 3 to 6‰ change in $\delta^{18}O_{sw}$ at the end of the Devonian has been suggested based on $\delta^{18}O$ in brachiopods, carbonate cements and conodonts (Veizer et al., 1986; Lohmann and Walker, 1989; Carpenter et al., 1991; O'Neil et al., 1996).

I will review the history of the debate over $\delta^{18}O_{sw}$ and present an updated inventory of the oxygen isotope fluxes between seawater, sediments, continents and mantle. Recently, Frank and Sigwarth

(1997) suggested on the basis of satellite observations, that the Earth is subjected to a 'cosmic rain' of water because of bombardment by numerous small comets. They suggest a very large annual net addition of extraterrestrial water by this mechanism. Robert et al. (1992) examined the $\delta^{17}O$ and $\delta^{18}O$ systematics in Archean to Holocene cherts and found no measurable influx of extraterrestrial water, assuming that cometary water would be unlike the Earth in $\delta^{17}O/\delta^{18}O$. In the following discussions I will not invoke an extraterrestrial source of water.

2. Review

Present-day seawater is relatively well mixed and uniform with a $\delta^{18}O_{sw}$ value of 0 ± 0.5‰ except in polar regions of mixing with melt waters or in tropical zones of extensive evaporation (Craig and Gordon, 1965). The volume of continental ice affects both the $\delta^{18}O_{sw}$ and sealevel. If all the ice melted the ocean would stand several tens of meters higher with a $\delta^{18}O_{sw}$ of about -1‰. At the time of maximum continental glaciation, the $\delta^{18}O_{sw}$ could be $+1$ to $+2$‰ with a much lower sealevel. Such cyclic variations of sealevel and $\delta^{18}O_{sw}$ occurred over 10^4–10^5 years during the Pleistocene. The causal mechanisms presumably are Milankovich astronomical cycles and the $\delta^{18}O_{sw}$ record is routinely cited as primary evidence by climate modelers as well as sequence stratigraphers.

There is much less unanimity on possible variations of $\delta^{18}O_{sw}$ over the age of the whole Earth. First principle arguments led Silverman (1951) to suggest that the initial $\delta^{18}O_{sw}$ of the primordial ocean was near $+7$‰ if, as seems likely, it was volcanically outgassed from the Earth and in high-temperature equilibrium with the mantle. The present day value of 0‰ would reflect the removal of ^{18}O from the hydrosphere as a result of the formation of low-temperature weathering and diagenetic products (all higher in $\delta^{18}O$ than the mantle-derived precursors). This, the simplest model suggests a progressive lowering of $\delta^{18}O_{sw}$ from $+7$‰ to 0‰ over time.

Early isotopic studies found ancient carbonate and siliceous sediments to be depleted, not enriched in

^{18}O compared to modern equivalents (cf. Degens and Epstein, 1962). Perry (1967) found ancient cherts to be extraordinarily ^{18}O-depleted and suggested that the Archean ocean may have been as low as -12 to -18‰. Most subsequent isotopic studies have found lower δ^{18}O values for ancient fossils and chemical sediments than in modern analogs. Degens and Epstein (1962) attributed the temporal trend in isotopic compositions as reflecting progressive loss of isotopic integrity due to exchange with groundwaters etc. but many authors believe that the low-δ^{18}O chemical sediments record an ^{18}O-depleted ocean prior to the Mississippian (Veizer et al., 1986; Lohmann and Walker, 1989; Wadleigh and Veizer, 1992; for only a few of many examples). Several authors have attempted to model ^{18}O-depletion of the early ocean. Chase and Perry (1973) suggested the primordial ocean was small in volume and very reactive such that weathering reactions would extraordinarily deplete the Archean seawater of ^{18}O. Ocean growth by volcanic outgassing would bring over time the δ^{18}O$_{sw}$ up to its present value. Walker and Lohmann (1989) suggested the early sealevel was so low as to have been beneath the crests of the spreading ridges, precluding the hydrothermal activity to be discussed below. Becker (1973) found errors in the model of Chase and Perry, whereas geological field evidence, e.g. the presence of subaqueous basalt pillows in earliest greenstone belts, points to a relatively high sealevel in the Archean. Also, alteration studies of volcanic systems on Iceland indicate that subaerial volcanic alteration is more efficient than submarine alteration, in transferring ^{18}O to the hydrosphere (Gautason and Muehlenbachs, this issue). Irrespective of a particular ocean growth history, both Perry and Tan (1972) and Li (1972) argued that the observed, present-day inventory of ^{18}O-enriched chemical sediment could account for the expected 7‰ depletion of the ocean over the age of the earth. Such arguments were reasonable at the time but neglected to consider consequences of plate tectonics.

Muehlenbachs and Clayton (1976) noted that the sediments removed by subduction or the consequences of weathering and hydrothermal alteration of the seafloor dykes and gabbros of oceanic layer 3 were not included in the earlier ^{18}O-inventories or models. Muehlenbachs and Clayton (1972a,b) found

that seawater reacts with the seafloor (δ^{18}O$_{MORB}$ = $+5.8 \pm 0.3$‰) during its formation and aging. Cold seawater loses ^{18}O to MORB, whereas hot hydrothermal fluids extract ^{18}O from the oceanic crust. They suggested that these competing processes, as well as continental weathering and recycling of subducted seawater, buffer δ^{18}O$_{sw}$ to 0 ± 2‰. When δ^{18}O$_{sw}$ is near 0‰ there is no net gain or loss of ^{18}O to the hydrosphere. They argued that if δ^{18}O$_{sw}$ were higher or lower than 0‰, a counterbalancing flux of ^{18}O will return δ^{18}O$_{sw}$ to 0 ± 2‰ in 15 to 60 m.y. (Gregory, 1991). The predicted and observed value for δ^{18}O$_{sw}$ of 0‰ is not coincidental, but is a consequence of the prevalent 250 to 350°C hydrothermal alteration at the mid-ocean ridges whose equilibrium ^{18}O-fractionation between basalt and water is near 6 ± 2‰ while the seafloor is continually derived from the mantle (δ^{18}O ≈ 6‰) whose volume is too great to change in δ^{18}O. Holland (1984) calculated that the model of Muehlenbachs and Clayton (1976) would hold at all times when seafloor spreading was greater than one half of the present rate.

The imprint of excess seawater on the isotopic composition of the oceanic crust was proven in ophiolites of Miocene (Cocker et al., 1982), Cretaceous (Heaton and Sheppard, 1977) and Jurassic (Stern et al., 1976) age. Gregory and Taylor (1981) and Stakes and Taylor (1992) tested the model of Muehlenbachs and Clayton (1976) for ^{18}O-mass balance on exposures of Cretaceous Somail Ophiolite. In the Ibra area the ^{18}O-enrichments in upper pillow parts of the ophiolite equaled the ^{18}O-depletions in the lower dykes and gabbros. Other sections did not display such an exact ^{18}O-balance but do show the imprint of alteration by excess seawater. All the various sections imply that seawater/seafloor interactions in the Cretaceous set δ^{18}O$_{sw}$ to the present value. Gregory (1991) tested the robustness of this conclusion by modeling the effect on δ^{18}O$_{sw}$ of possible changes in reservoir sizes, seafloor spreading and weathering rates. Gregory concluded that as long as plate tectonics is operating δ^{18}O$_{sw}$ can not differ from near 0 ± 2‰ for extended times under any conditions. Studies of ophiolites of all ages confirm that their pillow piles (6 to 10‰) are enriched in ^{18}O in contrast to ^{18}O-depletions observed in the gabbros and dikes (3 to 5‰). No secular trend

is observed and the isotopic compositions of the ophiolites requires that $\delta^{18}O_{sw}$ was near 0‰ (Hoffman et al., 1986; Lecuyer and Fourcade, 1991; Holmden and Muehlenbachs, 1993a; De Wit and Hart, 1993; Lecuyer et al., 1995; Muehlenbachs et al., 1997).

One must also consider the meaning of the overwhelming preponderance of low $\delta^{18}O$ Paleozoic and older chemical sediments and fossils that imply a proportionally low $\delta^{18}O_{sw}$. Three explanations to this enigma have been offered: (1) loss of marine isotopic signal; (2) higher environmental temperatures; (3) biased sampling. The first explanation questions the integrity of the isotopic record (first offered by Degens and Epstein, 1962; see also the discussions of Land and Lynch, 1996, and Land, 1995, vs. Qing and Veizer, 1994, and Veizer, 1995). Significantly, a few ancient undepleted carbonate or chert sediments have been reported. Some deep water Devonian brachiopods and carbonates (Bates and Brand, 1991; Gao, 1993), an Ordovician iron formation (Yapp, 1993), Proterozoic dolomites at Beck Springs (Tucker, 1982) and Archean cherts in S. India (Sharma et al., 1994) show no evidence of an ^{18}O depleted ocean. Knauth and Epstein (1976) and Knauth and Lowe (1978) argued that only the highest $\delta^{18}O$ fossils and chemical sediments of any given age should be considered in discussions of secular trends of ancient seawater, because almost all imaginable alteration processes will lead to a diminution of $\delta^{18}O$. One should note in this context that the $\delta^{18}O$ of Paleozoic brachiopds of a given age, chosen to be least altered on trace element and thermal luminescence criteria, still may vary by over 10‰ (Wadleigh and Veizer, 1992), whereas the total variation in $\delta^{18}O$ for Cretaceous marine fossils is far smaller. However, the number of pre-Mississippian high-^{18}O carbonates and cherts is very small when compared to the many low-^{18}O ones, and Veizer (1995) argues not all carbonates have been altered.

A second explanation of the low-^{18}O sediments is that some may reflect a higher environmental temperature in the past (Knauth and Lowe, 1978; Karhu and Epstein, 1985). Carpenter et al. (1991) and many others, argue that such an interpretation leads to unreasonably high temperatures inamicable to life as we know it today and contrary to the evidence of contemporary ice ages.

A third possibility has been suggested by Holmden and Muehlenbachs (1993b) that much of the argument *re* the Paleozoic $\delta^{18}O_{sw}$ is an artifact of sampling as all the Paleozoic fossils and sediments are of necessity samples from epicontinental seas and shelves because of subduction of pelagic sediments. Water in the Paleozoic shallow seas may not be equivalent to deep ocean water for it may have locally evolved to low but variable $\delta^{18}O$ values by dilution with meteoric waters as well as concentration by evaporation (Holmden et al., 1997). The salt content of the inland seas could be decoupled from $\delta^{18}O$ if transport of water across the submerged continent is faster as vapor through the atmosphere than by physical mixing due to currents in the shallow seas. Unaltered Paleozoic fossils and chemical sediments consequently, may record the isotopic compositions of local seawaters which are isotopically variable and distinct from the $\delta^{18}O_{sw}$ for open ocean water. Deep ocean water of $\delta^{18}O_{sw}$ of 0 ± 2‰ is recorded by ophiolites of Silurian (Lecuyer and Fourcade, 1991), Ordovician (Lecuyer et al., 1995; Muehlenbachs et al., 1997) and Cambrian age (Bay of Islands Ophiolite, cited in Gregory and Taylor, 1981; Muehlenbachs, 1986).

Considering the vigorous arguments over the secular history of $\delta^{18}O_{sw}$ there is surprisingly little controversy surrounding the processes that remove or add ^{18}O to the oceans today.

3. ^{18}O-fluxes to the oceans

This section will discuss and tabulate the five major geological processes that affect the $\delta^{18}O$ balance of the oceans through reactions between the hydrosphere and lithosphere. Table 1 presents revisions and an addition to the ^{18}O-inventory compiled by Muehlenbachs and Clayton (1976). To assess the effect each process has on $\delta^{18}O_{sw}$, one needs to estimate both the amount of oxygen exchanged per year (volume × density × % oxygen) between the oceans and a given rock reservoir as well as the magnitude of the $\delta^{18}O$ difference in the rocks before and after the reaction with the hydrosphere (Δ^{*}). Also, it is very instructive to estimate these factors for times when $\delta^{18}O_{sw}$ may have differed from today's value (Table 2).

Table 1
Oxygen isotope inventory of interactions between the present-day hydrosphere and lithospere

Process	Volume, km^3/yr (a)	ρ, g/cm^3 (b)	Oxygen, % (c)	Oxygen exchanged $\times 10^{-15}$ g/yr (d)	[(O-process/yr)/ O-ocean] $\times 10^9$ (e)	Δ^* (f)	Normalized flux to ocean δ^{18}O/10^9 yr, (e) $\times$ (f)
Continental weathering	8	2.5	50	10	8.0	−1.8	−14.4
Submarine weathering	1.8	2.7	45	2.2	1.7	−3.8	−6.6
Continental growth	1.1	2.7	50	1.5	1.2	−2	−2.4
Hydrothermal alteration	14.5	2.8	45	18.3	14.6	+1.4	+20.4
Water recycling	0.9	1	89	0.8	0.64	+4.5	+2.9
TOTAL							−0.1

$\Delta^* = \delta^{18}$O(starting reservoir) $- \delta^{18}$O(altered reservoir).

3.1. Continental weathering

First consider the weathering and diagenetic processes that remove ^{18}O from the hydrosphere. Oxygen isotope fractionation factors between rock forming minerals and water at ambient near Earth surface temperatures are large (1000 ln $\alpha \approx +15$ to $+35$‰). If water is in excess, as is usual in weathering and diagenetic reactions, there will be a net transfer of ^{18}O from hydrosphere to crust. For example, a unit of crust with an igneous value δ^{18}O of $+7$‰ if weathered by excess water of δ^{18}O of -3‰ will produce an equivalent unit of shale with a δ^{18}O of $+17$‰ (1000ln $\alpha \approx \delta^{18}O_{clay} - \delta^{18}O_{water} \approx +20$‰), removing, 17‰ -7‰ $= 10$‰ equivalents of ^{18}O from the hydrosphere. Precipitation of chert and carbonate are even more effective in removing ^{18}O from water because the 1000 ln α for them is larger ($\approx +30$ to $+35$‰). If the initial seawater were $+7$‰, then proportionally ^{18}O-richer sediments would have been produced that would even more

effectively lower δ^{18}O$_{sw}$ of the early ocean (assuming the same ambient temperature). Note in this example, that if the water were less than -13‰ (e.g. the Archean ocean of Perry, 1967), then the resultant shale would have δ^{18}O of 7‰ or less, and hence weathering would have *enriched* the hydrosphere in ^{18}O, not depleted it (Becker, 1973).

To determine the effect of weathering on δ^{18}O$_{sw}$ one needs to know not only the isotopic fractionation factors but also the amount of chemical sediment and rock altered by surface waters in the geological inventory, their initial and final isotopic compositions as well as the volume and initial δ^{18}O$_{sw}$. The present-day volume of seawater is well known at 1.4×10^9 km^3 and in this discussion I assume its volume has not changed and have normalized the estimated annual fluxes in Tables 1 and 2 to the amount of oxygen in the ocean. It is not easy to estimate the total amount of chemical sediment formed and rock diagenetically altered. Ronov and Yaroshevsky (1976) estimated the inventory of the

Table 2
Oxygen isotope fluxes to the hydrosphere as a function of isotopic composition of the ocean

Process	[(O-process/yr)/O-ocean] $\times 10^9$ (e)	Δ^* (f)	Normalized flux δ^{18}O/10^9 yr (e) $\times$ (f)
Continental weathering	8.0	$-(0.25\delta^{18}$O$_{sw} + 1.8$‰)	$-2\delta^{18}$O$_{sw} - 14.4$‰
Submarine weathering	1.7	$-(0.2\,\delta^{18}$O$_{sw} + 3.8$‰)	$-0.34\delta^{18}$O$_{sw} - 6.6$‰
Continental growth	1.2	$-(0.1\,\delta^{18}$O$_{sw} + 2.0$‰)	$-0.12\delta^{18}$O$_{sw} - 2.4$‰
Hydrothermal alteration	14.6	$-(\delta^{18}$O$_{sw} - 1.4$‰)	$-14.6\delta^{18}$O$_{sw} + 20.4$‰
Water recycling	0.64	$-(\delta^{18}$O$_{sw} - 4.5$‰)	$-0.64\delta^{18}$O$_{sw} + 2.9$‰
TOTAL			$-17.7\delta^{18}$O$_{sw} - 0.1$‰

$\Delta^* = \delta^{18}$O(starting reservoir) $- \delta^{18}$O(altered reservoir).

Earth's continental sediments from geological maps and geophysical observations but such estimates do not include higher-grade meta-sediments nor subducted altered oceanic crust and sediments. Garrels and Mackenzie (1971) derived an approximately two times larger estimate of chemical sediment mass (3.2×10^{24} g) based on acid and chloride ion balance due to weathering over the whole history of the Earth. Muehlenbachs and Clayton (1976) used the estimate of Garrels and Mackenzie to calculate the ^{18}O-flux due to continental weathering. Such an estimate is a minimum for the mass of chemical sediment because chloride is not completely conservative as assumed in their calculation and consequently some sediment will not have been counted due to subduction of chloride or its incorporation into metamorphic minerals. Holland (1984) estimated an ^{18}O-flux due weathering based on the present river load of sediment, of 20×10^{15} g/year. But since the river load is 75% recycled sediment, he used a proportionately smaller shift in oxygen isotope ratio in the calculation of flux.

The estimate in Table 1 for the ^{18}O-flux resulting from continental weathering follows Holland's (1984) suggestion that it be based on river load. River load is 75% recycled sediment which will not contribute to an ^{18}O-flux. Holland suggested that of the remaining sediment, 12.5% is derived from igneous and 12.5% from high-grade metamorphic rocks, with a net δ^{18}O difference between precursor and river sediment (Δ^{*}_{cw}) of about -1.8‰. The estimate in Table 1 of net ^{18}O loss from the hydrosphere is 7 times larger than that of Muehlenbachs and Clayton (1976). If δ^{18}O$_{sw}$ were not 0‰ (Table 2) as at present, the isotopic shift upon continental weathering, Δ^{*}_{cw}, would be (following Holland, 1984):

$$-\Delta^{*}_{cw} = (0.75 \times 0‰) + 0.125(\delta^{18}O_{sw} + 10‰)$$
$$+ 0.125(\delta^{18}O_{sw} + 5‰)$$
$$= (0.25 \delta^{18}O_{sw} + 1.8‰) \qquad (1)$$

3.2. Weathering of seafloor basalt

Low temperature weathering of the continually extruded basalts at mid-ocean ridges is an additional large sink for ^{18}O from the hydrosphere. Based on dredged basalts from mid ocean ridges, Muehlenbachs and Clayton (1976) estimated that the δ^{18}O of the mature basalt pillow pile was raised from the primary value of 5.8‰ to 8‰ due to weathering. That shift in δ^{18}O corresponds to about 10% of the glass and groundmass of basalt being weathered to clay (δ^{18}O$_{clay} \approx 25‰$, Muehlenbachs and Clayton, 1972a). This is an underestimate because low-temperature alteration of basalt continues off axis. To account for low-δ^{18}O pore waters in deep-sea sediments, Lawrence and Gieskes (1981) postulated a nearly equivalent amount of sub-sediment basalt weathering. A more realistic estimate of the degree of weathering of the pillow pile over the life time of the seafloor is therefore 20%, or to a final δ^{18}O of about 9.6‰. This ^{18}O-enriched section of the oceanic crust (layer 2) is ultimately subducted but the counterbalancing ^{18}O-depleted seawater and pore water remains for the most part in the hydrosphere. Table 1 includes a revised estimate of the ^{18}O-flux due to seafloor weathering based on 3 km^2 of seafloor being formed each year and that a 0.6 km thick section of basalt is 20% weathered. The isotopic shift between the fresh MORB and altered pillows (Δ^{*}_{sfw}) is 5.8‰ − 9.6‰ or −3.8‰. If δ^{18}O$_{sw}$ (Table 2) was not 0‰ then Δ^{*}_{sfw}:

$$\Delta^{*}_{sfw} = 5.8‰ - \left[0.2(\delta^{18}O_{sw} + 25‰) + 0.8(5.8‰)\right]$$
$$= -(0.2\delta^{18}O_{sw} + 3.8)‰ \qquad (2)$$

3.3. Recycling of sediment by crustal growth

More difficult to estimate is the mass of ^{18}O-rich sediment that has been remelted and assimilated into the continental crust during mountain building and other tectonic events. Silverman (1951) recognized that continental igneous and high-grade metamorphic rocks are richer in ^{18}O than the mantle and asked if this implied sediment assimilation, anticipating the suggestions of Campbell and Taylor (1985) that the origin of continental rocks is intimately linked to the oceans. We now know that the ^{18}O-enrichment of continental basement rocks with respect to the mantle (from 2 to 5‰) is too high to be accounted for by igneous differentiation (Muehlenbachs and Byerly, 1982) and reflects sediment assimilation (O'Neil and Chappell, 1977). These observations do not lead to a simple estimate of the inventory for ^{18}O of the putative assimilated sediment because the continental crust is highly heterogeneous (see review by Rudnick and Fountain, 1995).

Reymer and Schubert (1984) estimated an average island arc accretion rate of 1.1 km³ per year. A reasonable estimate of the $\delta^{18}O$ of the accreted crust is near +8‰ (cf. Taylor, 1968), indicating that 10% of its oxygen may be from sediments, if the $\delta^{18}O$ were +26‰, typical of deep-sea sediment. The ^{18}O-flux from sediments to the continental crystalline crust may have varied with time. Longstaffe and Gower (1983) observed that Archean granitoids have lower, mantle-like, $\delta^{18}O$ in contrast to Proterozoic and younger igneous rocks and suggested that ^{18}O-rich sediments were not available in the Archean to be assimilated into the crust. Table 1 gives an estimate of the ^{18}O-flux from the hydrosphere to the growing continental crystalline crust based on the mechanism of subduction of sediment. The island arc accretion rate is taken as 1.1 km³/yr (Reymer and Schubert, 1984) and the new continental crust as having a $\delta^{18}O$ of 8‰. The new crust is mantle-derived but is about 10% contaminated by deep-sea sediment (26‰). Δ^*_{cg} for continental growth is $\delta^{18}O_{mantle} - \delta^{18}O_{crust} \approx -2‰$. If $\delta^{18}O_{sw}$ (Table 2) was not 0‰ then Δ^*_{cg}:

$$\Delta^*_{cg} = 6‰ - \left[0.1\left(\delta^{18}O_{sw} + 26‰\right) + 0.9(6‰)\right]$$

$$= -\left(0.1\,\delta^{18}O_{sw} + 2‰\right) \qquad (3)$$

It is clear from evaluating some or all of the above ^{18}O-depleting mechanisms (Perry and Tan, 1972) that many times over, more ^{18}O has been removed from the hydrosphere than can be balanced by lowering the primordial ocean of $\delta^{18}O_{sw} \approx +7‰$ to the present-day value of 0‰. If only the above mechanisms were operating the present-day $\delta^{18}O_{sw}$ would be near −12‰. Countervailing mechanisms must operate that efficiently return ^{18}O from rocks to the hydrosphere and oceans.

3.4. Hydrothermal alteration of the seafloor

Fluxes that increase $\delta^{18}O_{sw}$ can be found in the hydrothermal alteration of the seafloor and the recycling of subducted water. Hydrothermal alteration of the dykes and gabbros of the seafloor is key in controlling $\delta^{18}O_{sw}$ in both Muehlenbachs and Clayton's (1976) and Gregory and Taylor's (1981) models. Oxygen isotope fractionations decrease in magnitude with increasing temperature. At temperatures of 250–350°C, fractionation factors between minerals and water range from about 10‰ (quartz) to 1‰ (chlorite). Modal mineral assemblages in MOR pillows, dykes and gabbros that have been hydrothermally altered by excess seawater at temperatures of 250–350°C are such that the resultant greenstones have $\delta^{18}O$ near 4 or 5‰, measurably depleted relative to unaltered MORB $(5.8 \pm 0.3‰)$ (Muehlenbachs and Clayton, 1972b). Calculations (Bowers and Taylor, 1985) and field data (Merlivat et al., 1984; Shanks and Seyfried, 1987) show that the ^{18}O lost by hydrothermally altered seafloor is returned to the oceans by exiting black smoker fluids enriched in ^{18}O by 1 to 2‰. It should be noted that if at any time in the past $\delta^{18}O_{sw}$ were different, the size and the direction of the ^{18}O-flux would differ from the present one, even if the seafloor spreading rate remains the same. If $\delta^{18}O_{sw}$ were +7‰, then the $\delta^{18}O$ of hydrothermally altered basalt would be near +12‰, and the resultant ^{18}O-transfer $(5.8‰_{MORB} - 12‰_{greenstone})$ would not only be in the opposite direction as today's $(5.8‰ - 4.5‰)$, but also 5 times greater. If as is often suggested, the $\delta^{18}O_{sw}$ of the Paleozoic ocean was −7‰, then the hydrothermally altered dykes and gabbros of the Paleozoic oceanic crust (layer 3) would be approximately −2‰. The resultant ^{18}O-addition to the Paleozoic ocean would be $(5.8‰ - [-2‰])$, or about 6 times greater in magnitude even if seafloor spreading rates were the same as today.

Muehlenbachs and Clayton (1976) estimated that in addition to the 0.6 km of the basaltic oceanic crust altered by low-temperature weathering, hot seawater reacts with a further 1 to 5 km of the crust. If 3 km² of new floor are created each year than 3 to 15 km³ of basalt are altered at high temperature by ≈ 350°C seawater per annum at mid-ocean ridges. Field studies on ophiolites indicate that the higher volume for ^{18}O-depleted rock is more likely to be correct (Gregory and Taylor, 1981). Table 1 assumes 5 km penetration of hot seawater into the oceanic crust. Based on limited data, Muehlenbachs and Clayton (1976) suggested that the current hydrothermally altered crust that is altered by 250 to 350°C seawater, has a $\delta^{18}O$ of approximately 4.5‰. Recent, unpublished, analyses of 21 composite samples designed to average the composition of oceanic layer 3 which was recovered by DSDP hole 735B ranged from 2.0

to 5.8‰ but yielded an average $\delta^{18}O$ of 4.4 ± 1.0‰. The isotopic shift, Δ^*_{ha}, in Table 1 reflects the new data (5.8‰ − 4.4‰ = +1.4‰). As will be shown, the most important ^{18}O-flux in the isotopic inventory is the effect of hydrothermal alteration. The general value of Δ^*_{ha} for hydrothermal alteration is (Table 2):

$$\Delta^*_{ha} = 5.8‰ - \left(\delta^{18}O_{sw} + 4.4‰\right)$$

$$= -\left(\delta^{18}O_{sw} - 1.4‰\right) \qquad (4)$$

3.5. Recycling subducted water

Recycling of subducted seawater may return ^{18}O to the hydrosphere (Chase and Perry, 1973). A precise ^{18}O-inventory of recycled water is difficult to establish. Water in pores as well as chemically bound in subducted sediments and the altered seafloor may affect the ^{18}O-flux. About 1 km^3 of water is carried by sediment to the trenches each year but 50 to 90% is thought to be expelled by compaction (Von Huene and Scholl, 1987). The $\delta^{18}O$ of the recycled water will depend on the return path. If connate water is simply expelled from sediments at an accretionary wedge, there would be no $\delta^{18}O$ change due to dewatering. On the other hand, connate water which participates in tectonic activity associated with accretion wedges could become heated, exchange with sediment and thus become very high in $\delta^{18}O$ and then return to the hydrosphere. Such a flux would lower the $\delta^{18}O$ of sediment and must be large, but it has already been accounted for in the budget on weathering (Table 1). As discussed above, ancient sediments are significantly depleted of ^{18}O compared to present-day ones, but the lower $\delta^{18}O$ values of the ancient ones are used to calculate the continental weathering ^{18}O-flux.

Water of hydration within the altered oceanic crust that is subducted to some depth would upon release and outgassing achieve a $\delta^{18}O$ in equilibrium with the mantle. Muehlenbachs and Clayton (1976) estimated the amount of subducted water that carries ^{18}O back to the hydrosphere to be about 2% (wt) of the subducted altered oceanic crust (both oceanic layers 2 and 3). That is sufficient volume to make up the oceans in about 10^9 years and is nearly the same as the amount of pore water carried into the trenches by sediment (Rea and Ruff, 1996). The

resulting transfer of ^{18}O is more difficult to ascertain. The $\delta^{18}O$ of mineral-bound water being subducted is no longer that of seawater nor that of the bulk oceanic crust because the $\delta^{18}O$ of hydroxyl groups are lower than the silicate of the minerals. In illite at 350°C, hydroxyl water could be 3.8‰ lower than the silicate portion (Bechtel and Hoernes, 1990). Experimental data do not exist for hydroxyl/silicate fractionation for chlorite, epidote or amphibole but using illite as a guide I assume a 3‰ difference between subducted oceanic crust and hydroxyl water. The pillows, dykes and gabbros of bulk subducted crust have a $\delta^{18}O$ of ≈ +6‰, thus the subducted hydroxyls would be +3‰. The isotopic shift from seawater (0‰) to that of bound water (3‰) is already inventoried in the budget for alteration of the oceanic crust (Table 1). Upon degassing this water reenters the hydrosphere with $\delta^{18}O$ of +7.5‰, Δ^*_r is then 7.5‰ − 3‰ or 4.5‰. Table 1 carries over the original volume estimate of Muehlenbachs and Clayton (1976) that the combined water content of the subducted layers 1 and 2 is 2%. Again, note that if the $\delta^{18}O_{sw}$ were different then $\delta^{18}O$ of subducted water would be different and the consequent ^{18}O-flux back to the oceans would also be different. At different $\delta^{18}O_{sw}$, Δ^*_r (Table 2) is:

$$\Delta^*_r = 7.5‰ - \left(\delta^{18}O_{sw} + 3‰\right)$$

$$= -\left(\delta^{18}O_{sw} - 4.5‰\right). \qquad (5)$$

The weighted sum of the fluxes in Table 1 reveals that at present there is only a trivial net contribution of ^{18}O to the ocean of −0.1‰ per 10^9 years. Table 2 sums the processes with $\delta^{18}O_{sw}$ included as a variable. A zero net flux between the hydrosphere and lithosphere will occur when $\delta^{18}O_{sw}$ is −0.006‰. However, Table 2 shows that large fluxes would result if for some reason $\delta^{18}O_{sw}$ were significantly different from 0‰. The direction of the putative ^{18}O-flux would be to return $\delta^{18}O_{sw}$ to 0‰. Whereas a loss of ^{18}O from seawater results if $\delta^{18}O_{sw} > 0‰$, seawater gains ^{18}O when $\delta^{18}O_{sw} < 0‰$. The magnitude of the flux of ^{18}O to the ocean per 10^9 years is plotted vs. $\delta^{18}O_{sw}$ in Fig. 1.

Errors have not been explicitly listed on the estimates of reservoir size nor their isotopic differences. The errors are undoubtedly large but the uncertainty on the predicted, 'buffered', $\delta^{18}O_{sw}$ is likely to be
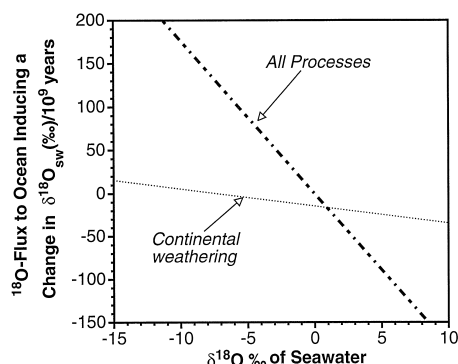
Fig. 1. The flux of ^{18}O from the lithosphere to the ocean vs. the δ^{18}O of seawater. The units are normalized by the oxygen content of the current ocean and are in ‰-change of δ^{18}O per 10^9 years. The heavy dashed line represents the sum of all processes (Table 2) whereas the thin dotted line is only for continental weathering. Note that when δ^{18}O of seawater is negative, the flux is positive, and vice versa.

within the ± 2‰ claimed by Muehlenbachs and Clayton (1976). The ^{18}O-fractionation between rock altered at mid-ocean ridges and water at hydrothermal temperatures (250 to 350°C) is $0 \leq \pm 2$‰. The oxygen isotopic composition of seawater will be held to those bounds as long as seafloor spreading continues at rates at least one half of today's (Holland, 1984), and MORB has δ^{18}O of 5.8 ± 0.3‰.

The last column of Table 2 compares the relative importance of the various processes as sinks or sources of ^{18}O to the ocean. The two largest are hydrothermal alteration of the oceanic crust and continental weathering (Fig. 1). Hydrothermal alteration of the seafloor dominates the budget by a factor of 7 over that of weathering for two reasons: (1) a huge amount of seafloor is created and altered every year; and (2) the effect of changing δ^{18}O$_{sw}$ is directly proportional to the ^{18}O-flux, whereas that effect is modulated by a factor of 0.2 and 0.25 in the weathering processes. The consequences of this observation is that if seafloor spreading ceased, a slow decline of δ^{18}O$_{sw}$ would follow (14.4‰ per 10^9 years), but upon restarting, a 7 times more rapid increase back to 0‰ would result. At first glance this appears consistent with the postulated rapid jump from $(-6$‰, or -3‰ to 0‰) in δ^{18}O$_{sw}$ at the end of the Devonian (cf. Carpenter et al., 1991) but geological history does not indicate early Paleozoic plate tectonic quiescence nor do older Paleozoic ophiolites

record the hypothesized low δ^{18}O$_{sw}$ (Lecuyer and Fourcade, 1991; Lecuyer et al., 1995; Muehlenbachs et al., 1997).

4. Conclusions

A detailed budget of oxygen isotope fluxes between the hydrosphere / ocean and the lithosphere indicates that at present there is no net ^{18}O-transfer despite massive oxygen exchange caused by weathering, hydrothermal activity, continent growth and subduction related recycling. The δ^{18}O$_{sw}$ is 'buffered' to the present value of 0 ± 2‰. Hydrothermal alteration of the oceanic crust dominates the budget and the present δ^{18}O$_{sw}$ of 0‰ results because it is in approximate isotopic equilibrium between MORB (5.8‰) and water at the prevalent hydrothermal conditions excess seawater reacting with mantle-derived rock at 250 to 350°C.

This model predicts that ancient oceans must have had the same δ^{18}O$_{sw}$ as today's if seafloor spreading and plate tectonics were operating. Isotopic analyses of Miocene to Archean ophiolites prove that this indeed was the case. The secular trends frequently observed in low δ^{18}O of fossils and chemical sediments must reflect a combination of (1) diagenetic or later re-equilibration of the carbonates etc. with pore waters, (2) warmer surface temperatures than current prejudice allows, or (3) biased sampling. The innumerable studies of Paleozoic and older fossils and sediments all have sampled continental shelves and seas. These may be water bodies whose δ^{18}O is only tenuously linked to δ^{18}O$_{sw}$ of the of the deep ocean.

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