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Oxygen isotope study of mid-ocean ridge hydrothermal fluids: Implication for the oxygen-18 budget of the oceans

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Abstract—New data are reported for the ^{18}O composition of hot hydrothermal fluids from various sites with different tectonic settings. The measured $\delta^{18}O$, in the range 0.53–2.3‰ confirm earlier data suggesting that mid-ocean ridge hydrothermal vents are a major source of ^{18}O to the ocean. In light of this new data, we attempt to re-evaluate the marine ^{18}O budget from direct quantification of the main sources and sinks of oceanic oxygen-18. Within the uncertainty of the flux estimates, ^{18}O inputs and outputs are found to balance each other, showing that oceanic ^{18}O is presently at a steady-state. Using these present fluxes, we examine the past evolution of the ^{18}O composition of the ocean and speculate that the initial ^{18}O oceanic content may have evolved rapidly towards its present value. This suggests, as already pointed out in previous studies, that ocean water may have had a rather constant ^{18}O composition over most of the Earth's history and that $\delta^{18}O$ measurements in ancient cherts and carbonates may primarily record the evolution of the ocean temperature. *Copyright © 1997 Elsevier Science Ltd*

1. INTRODUCTION

Several studies have focused on understanding the ^{18}O economy of the main terrestrial reservoirs and their interactions, including ocean, mantle, sediments, igneous and metamorphic rocks (Chase and Perry, 1972; Perry and Tan, 1972; Muehlenbachs and Clayton, 1976; Holland, 1984), with the objective of determining the past evolution of oceanic ^{18}O. This problem bears directly on the interpretation of the $\delta^{18}O$ record in ancient chert and carbonate minerals which shows increasing $\delta^{18}O$ values from 3 Gyr to the present (Perry, 1967; Perry and Tan, 1972; Knauth and Epstein, 1976; Savin, 1977; Perry et al., 1978; Knauth and Lowe, 1978; Ahmad and Perry, 1980; Burdett et al., 1990; Das Sharma et al., 1994). This trend may have resulted from a progressive decrease of climatic temperatures from around 70°C for the Archean ocean to present values, due to temperature control on ^{18}O fractionation between water and mineral phases. Alternatively, it may simply indicate a long-term evolution of oceanic $\delta^{18}O$.

The ^{18}O composition of the ocean results mainly from the balance of two independent processes: (1) high temperature alteration concurrent with hydrothermal processes at mid-ocean ridges, which produces ^{18}O enrichment of seawater (Bowers and Taylor, 1985); (2) low temperature rock weathering (Gregory and Taylor, 1981; Bowers and Taylor, 1985; Savin, 1986) and sediments formation (Savin, 1986), accompanied by isotope exchange reactions which produce ^{18}O depletion of seawater. In the past decade, our knowledge of these processes has significantly increased: spectacular manifestations of deep-sea hydrothermal high temperature circulation at spreading centers were discovered in 1977 (Corliss et al., 1979). Since then, the characteristics of these fluids in terms of chemical composition and volatile content have been studied extensively. ^{18}O composition of hydrothermal hot fluids was determined for several venting sites of the East Pacific Rise, north of 9°N (Table 1). We report here new isotopic data from a wider range of sites of different geological and tectonic settings, going from ultra-fast spreading ridges on the southern EPR to low spreading centers on the Mid-Atlantic Ridge and also including sites in the back-arc environment. These hydrothermal fluids are all enriched in ^{18}O relative to ambient seawater, between 0.5 and 2.3‰, and fully confirm that the seawater-basalt interaction at high temperature is a source of ^{18}O to the ocean. The flux of the hydrothermal fluids into the deep ocean was also determined with some confidence from magmatic heat flux and chemical element budget studies (Sleep et al., 1983; Mottl, 1983; Thompson, 1983; Mottl and Wheat, 1994; Kadko et al., 1995) as well as from the oceanic ^{3}He budget (Clarke et al., 1969; Craig et al., 1975; Jean-Baptiste, 1992) and the average ^{3}He concentration in hydrothermal fluids. Also, the fate of particulate matter in the ocean and the burial rate of deep-sea sediments have been the focus of extensive investigations in studies of global ocean fluxes, aimed primarily at assessing the global carbon cycle and the fate of anthropogenic CO_2 emissions.

Here, we attempt to re-evaluate the ^{18}O balance of the oceans in the light of these improved data. Although this endeavor is not strictly original, since several studies have been published in the past which deal with the oxygen isotope composition and evolution of seawater, we think that the present updating could be instructive, for the following two reasons: (1) Previous studies were carried out mostly in the 1970s, several of them before the discovery in 1977 of the widespread phenomenon of hot hydrothermal fluids venting at the seafloor of spreading centers. Hence, these studies deal mostly with the ^{18}O oceanic composition from the viewpoint of the ^{18}O budget of the main geological reservoirs (sedimentary, metamorphic, and igneous rocks) exchanging with the ocean, with considerable uncertainty in the mass of material involved or in the relative proportion of these rocks, and to a lesser extent, in their ^{18}O shift in the alteration process. Some of these reservoirs are depleted in ^{18}O as others are enriched, and the total effect on the $\delta^{18}O$

Table 1. ^{18}O endmember composition of hot submarine hydrothermal fluids from various tectonic environments.

Hydrothermal sites	Sample number	δ^{18}O‰ end-member	Mean δ^{18}O‰	References
MAR 23°N/Snake Pit	HS-88-5-1	2.30	2.30	this work
			2.37	Campbell et al., 1988
MAR 26°N/TAG	2581/Ti6	1.54	1.57 ± 0.06	this work
	2583/Ti6	1.63		this work
	2594/Ti8	1.53		this work
MAR 37°N/Lucky Strike/Menez Gwen	DV1-01-D3	1.24	1.17 ± 0.06	this work
	DV1-09-D1	1.07		this work
	DV1-09-D3	1.15		this work
	DV1-14-D3	1.25		this work
	DV1-17-G1	1.14		this work
	LS-93-2607	1.19		this work
	LS-93-2608	1.18		this work
EPR/17-19°S	ND-03G	0.49	0.53 ± 0.06	this work
	ND-08G	0.60		this work
	ND-17D	0.49		this work
EPR/9-10°N			0.6-1.9	Shanks et al., 1991
EPR/13°N			0.38-0.65	Merlivat et al., 1984; 1987
EPR/21°N			1.6	Craig et al., 1980
Gorda Ridge			0.43 ± 0.06	Böhlke and Shanks, 1994
S Juan de Fuca			0.6-0.8	Shanks & Seyfried, 1987
Juan de Fuca			0.7-1.1	Massoth et al., 1989
Lau Basin	LAU-20-G2	0.90	0.85 ± 0.07	this work
	LAU-22-G2	0.80		this work

of the ocean is obtained by adding up the various depletions and enrichments. In contrast to this, the present approach is from the viewpoint of the ocean and is based as much as possible on the direct determination of the oceanic input and output fluxes of ^{18}O that are made possible by the significant advances achieved by the marine geosciences in the past two decades. We think that comparing these two different approaches could be very informative with respect to the as yet unresolved problem of whether the oceanic ^{18}O budget is balanced or not. (2) Past oceanic ^{18}O budget studies indeed have produced conflicting results and led to opposite conclusions regarding the question of the possible present steady-state of the oceanic ^{18}O composition. Li (1972) showed that conversion of the igneous rocks into sedimentary rocks could admirably match the isotopic decrease of δ^{18}O of the ocean from its initial magmatic value (≈7.5%) to its present value (≈0%), hence first suggesting that oceanic ^{18}O was at a steady-state. Unfortunately, as pointed out by others (Perry and Tan, 1972; Holland, 1984), the Li (1972) balance calculation was in error, as it did not take into account the metamorphic rocks reservoir. Chase and Perry (1972) modeled the oxygen isotope evolution of the oceans considering the main rocks reservoirs involved in the oxygen exchange with water, based on the Perry and Tan (1972) data and came to the conclusion that the ^{18}O oceanic budget was not balanced and that δ^{18}O of seawater had not remained constant throughout most of the ocean's history. Their model was challenged by Becker (1973) and again by Muelhenbachs and Clayton (1976) who re-estimated the ^{18}O budget of the main rock reservoirs and concluded that the δ^{18}O value of seawater is most likely balanced at its present value (with a sum of all the fluxes being 0.0 ± 2.8 δ^{18}O per-mil/10^9 years). Their calculation was re-evaluated by Holland (1984) based on revised data for the mass of material involved. His new estimated fluxes differ significantly, with a resulting ^{18}O flux of 9 ± 12, hence pointing to the problem of the large error bars inherent in this approach.

Using a more direct approach, made possible by the increased database for ^{18}O oceanic fluxes, we show in the following that, although the accuracy of the different fluxes still need further improvement, the ^{18}O hydrothermal input cancels out ^{18}O removal through weathering and sedimentary processes, so that the present ^{18}O composition of the ocean appears to be close to a steady-state.

2. ^{18}O COMPOSITION OF SUBMARINE HYDROTHERMAL WATERS

2.1. Studied Hydrothermal Sites Geological Settings

We have measured the ^{18}O composition of hot vent fluids in a variety of tectonic contexts in order to extend further the database for oxygen isotopes in hydrothermal fluids and to provide additional information for comparison among hydrothermal sites in various tectonic and geological environments, including slow spreading centers on the Mid-Atlantic ridge (Snake Pit site at 23°N, TAG site at 26°N, Lucky Strike/Menez Gwen sites, respectively, at 37°15-37°50N), an ultra-fast spreading ridge (EPR, 18°S) and a back-arc spreading center (Lau basin). All the analyzed fluids come from hot temperature vents and were sampled using 0.75 L titanium syringes operated from a submersible. They were selected on the basis of their high quality, i.e., their low dilution by ambient seawater, as indicated by their low magnesium content, making the calculation of the pure hydrothermal endmember more accurate.

Three hydrothermal sites are located on the MAR, from 23°N to 37°50N. The discovery of the TAG site (MAR, 26°N) in 1985 (Rona, 1986) was the first direct evidence for high temperature venting on a slow spreading ridge. The hydrothermal field lies in the central part of a 40-km long ridge segment. The TAG samples were taken during the 1993 diving cruise in the Black Smokers Complex located on the massive sulfide Mound at a depth between 3625 m and 3670 m, near the base of the eastern wall of the rift. The sampled hydrothermal fluids show a chemical composition (Charlou et al., 1996a) similar to that reported by Campbell et al. (1988) and remarkably similar to those already observed on the East Pacific Rise at 13°N and 21°N. Vents exit temperatures are in the range 320–364°C.

The Snake Pit site, at 23°22N, 44°57W on the MAR, is on an elongated dome which is part of an axial neovolcanic ridge, at 3450 m depth (Thompson et al., 1988). The Snake Pit fluids have almost the same temperatures (330–345°C) and chemical composition (Campbell et al., 1988; Jean-Baptiste et al., 1991) as those of the TAG area.

The third Atlantic field comprises two hydrothermal sites, Lucky Strike and Menez Gwen, located close to each other further north, respectively at 37°17N and 37°50N, in the southern part of the Azores domain (Fouquet et al., 1995). The samples were obtained by the Alvin in 1993 and by the Nautile in 1994 as part of the Diva cruise. The Lucky Strike black smokers are at 1700 m depth around a lava lake and have temperatures up to 320°C. The Menez Gwen site, only 840 m deep, has somewhat cooler fluids (265–280°C). Fluids analyses at both sites show low metal concentrations and high gas contents (Charlou et al., 1995), typical of phase separation processes.

The southern EPR fluids were sampled during the Naudur cruise (1993) with the Nautile between 17°S and 19°S. This portion of the EPR has an exceptionally high spreading rate, above 14 cm/yr and displays intense hydrothermal circulation associated with widespread magmatic and tectonic activity. High temperature vents (in the range 300–340°C) were sampled between 2573 and 2669 m depth. The chemical composition of the fluids (Charlou et al., 1996b) indicates that they underwent phase separation. However, no ^{18}O shift among the fluids originating from both separated phases could be detected, in agreement with the low predicted water-vapor ^{18}O fractionation factor (Bottinga and Craig, 1968) at very high temperatures (the boiling point at 260 bars, i.e., at the depth of the site, is $T = 392°C$).

The last set of samples was obtained in the Lau Basin during the Nautilau cruise with the Nautile in 1988. The Lau basin is a typical example of an active back-arc basin. Hot fluids (up to 334°C) were sampled on the Valu Fa ridge, between 21° and 23°S, at depths from 1700 m to 2000 m. The chemical composition of some of the minor species (trace metals) differs from other MOR hydrothermal fluids (Fouquet et al., 1991), this is explained by the different geology of the basement rocks in this back-arc environment.

2.2. Analytical Method and ^{18}O Results

Waters for ^{18}O measurements were stored in 15 cm^3 Pyrex flasks. The $^{18}O/^{16}O$ isotopes ratio was determined at Saclay with a MAT 252 mass spectrometer using the CO_2 equilibration technique first developed by Epstein and Mayeda (1953). The principle is to isotopically equilibrate the water sample with a CO_2 gas phase. The equilibrium isotopic shift between CO_2 and H_2O is temperature dependent and to keep it constant, equilibration of all samples and standards is carried out at the same controlled temperature (20°C). After six hours of equilibration, the CO_2 samples are successively directed to the mass spectrometer for $^{18}O/^{16}O$ determination. The overall accuracy for the $\delta^{18}O$, determined from the measurements of several replicates of selected samples is $\pm 0.1‰$ (2σ). Table 1 displays the ^{18}O hydrothermal endmember for each sample based on the rate of dilution given by the magnesium concentration. Also indicated are the mean value and its sigma at each site. For each hydrothermal site, the measurements give rather uniform results, but show significant differences from site to site, with a range of values going from 0.5‰ to 2.3‰. The literature data, mostly from the northern EPR and the MAR, are also displayed in Table 1 for comparison. These data are quite consistent with our present measurements. The main result of this ^{18}O compilation is that hydrothermal hot fluids show a systematic ^{18}O enrichment relative to the initial ambient seawater, whatever their tectonic environment. This result is consistent with the mineral-H_2O equilibrium fractionation curves for oxygen isotopes (Friedman and O'Neil, 1977) which characterize the seawater-basalt high temperature interaction in axial mid-ocean ridge systems: the hydrothermal circulation is accompanied by widespread seawater-basalt interactions and results in large chemical modifications of the initial water entering the system as well as $\delta^{18}O$ isotopic change of the water. The initial water entering the hydrothermal system has a fairly uniform $\delta^{18}O$ ($\approx 0‰$ vs. SMOW) and in addition, the main rock types involved in the reaction, including MORB and gabbros, have relatively uniform ^{18}O composition with fairly constant ^{18}O in typical fresh MORB ($\delta^{18}O \approx 5.7‰$, Muehlenbachs and Clayton, 1972b). Because of ^{18}O fractionation temperature dependence, seawater reacting with basalt will be enriched in ^{18}O at temperatures above around 200°C but will be depleted in ^{18}O at lower temperatures. As a consequence, the ^{18}O composition of the vents fluids represents the integrated effect of the water-rock reaction along the whole plumbing system, going from the penetration of cold ambient deep seawater in the fissured crust of the recharge areas, to its progressive heating as it proceeds downwards toward higher temperatures and to its final return to the seafloor. The evolution of seawater $\delta^{18}O$ along this whole circulating loop has been modeled in detail by Bowers and Taylor (1985) (see also Bölke and Shanks, 1994) along with its chemical evolution and the mineralogical transformations of the reacting rocks. The result of this calculation shows that at lower temperatures, the $\delta^{18}O$ of the solution first decreases slightly, reaching a minimum value of $-0.2‰$ at 150°C. Beyond 250°C the $\delta^{18}O$ starts increasing and further reaction with basalt at 300–350°C results in a significant enrichment in the $\delta^{18}O$ up to about 2‰ (with a water-rock ratio $W/R = 0.5$ in the high temperature zone). As shown above, oxygen-18 data for hydrothermal fluids support this theoretical approach and show that the net effect of the sea-rock interaction at the ridge axis is a slight ^{18}O enrichment of the high temperature vents. These sea-rock interactions are also complemented by and consistent with studies of the ^{18}O composition of the altered crust (Muehlenbachs and Clayton, 1972a, 1972b, 1976; Stakes and O'Neil, 1982; Taylor, 1983; Alt et al., 1986) and data for the ^{18}O vertical profiles of ophiolites sections (Gregory and Taylor, 1981; Cocker et al., 1982). Both types of data obtained either for fluids or rocks provide a quite coherent picture of the hydrothermal circulation with respect to oxygen isotopes.

We have seen above that the ^{18}O composition of the deep submarine hydrothermal hot springs is consistently enriched relative to normal seawater, with an average $\delta^{18}O$ of 1.1‰ according to existing measurements. Therefore, some ^{18}O is continuously added to the world ocean. This raises the question of whether this ^{18}O input is counter-balanced by some concurrent processes removing ^{18}O from water, a situation which could lead to a steady-state ^{18}O composition of the ocean, or whether the oceanic ^{18}O is continuously evolving with time. To address this question, we examine in the following the different possible sources and sinks of oceanic ^{18}O with the objective of quantifying and comparing their respective contribution to the global marine ^{18}O budget.

3. THE PRESENT-DAY ^{18}O BUDGET OF THE OCEAN

3.1. High Temperature Hydrothermal Alteration

Beyond short-term variations of the $\delta^{18}O$ occurring during the growth or retreat of continental glaciers and polar ice caps due to climatic changes, the ^{18}O input due to high temperature hydrothermal alteration of the mid-ocean ridge basalts (MORB) is the only major steady source of oxygen-18 to the ocean. This was first recognized from the study of oceanic basalts (Muehlenbachs and Clayton, 1976), although the estimation of the ^{18}O fluxes involved in this process was difficult to assess with the required precision from these geological observations. The mass of seawater that cycles annually through mid-ocean ridges and emerges at high temperatures can be obtained rather easily from the helium-3 oceanic budget, in the range 3 ± 1 ^3He atoms/cm^2/s (Clarke et al., 1969; Craig et al., 1975; Jean-Baptiste, 1992), and from the average ^3He concentration in the hydrothermal fluids, of the order of $3.6 \pm 1.5 \times 10^{-10}$ cm^3 STP/g (Jean-Baptiste et al., 1991). This helium-3 budget leads to a global hydrothermal mass flow of around $2 \pm 1 \times 10^9$ g/s, leading to a turnover rate of the ocean through the newly formed crust at the spreading axis every 15 to 45 million years. This figure corresponds to a heat flux evacuated by the hydrothermal waters at ≈300°C of the order of 2.6×10^{19} cal/yr. This value is in reasonable agreement with thermal models of the crust (Sleep et al., 1983; Mottl, 1983; Thompson, 1983; Mottl and Wheat, 1994), although on the upper side of heat flux estimates. It is also consistent with the magnesium cycle (Mackenzie and Garrels, 1966; Drever, 1974), which is one of the simplest with respect to hydrothermal circulation since hot fluids are totally magnesium free: taking a magnesium concentration in seawater of 54.2×10^{-6} mole/g and a river discharge rate of 5.5×10^{12} mole/yr (Garrels and Mackenzie, 1971) the hydrothermal mass flow determined above corresponds to a Mg removal rate of 62% of the river inputs. With regards to ^{18}O input to the deep ocean, the hydrothermal flux of $2 \pm 1 \times 10^9$ g/s corresponds to a net gain of ^{18}O by the ocean of 240 ± 120 ^{18}O mol/s, due to high temperature alteration processes. This continuous addition of ^{18}O is counter-balanced by two main processes which remove ^{18}O from the ocean, (1) low-temperature alteration processes (a) of the oceanic crust away from the ridges and (b) of the continental rocks and (2) precipitation and sedimentation processes in the ocean.

3.2. Low Temperature Submarine Alteration

In agreement with water-rock isotopic fractionation curves mentioned above, ^{18}O analyses of weathered basalts show that moderate and low temperatures reactions result in an enrichment of the rock in ^{18}O and a subsequent depletion of the water (Lawrence et al., 1975; Muehlenbachs and Clayton, 1976; Stakes and O'Neil, 1982; Taylor, 1983; Savin, 1986; Lawrence, 1986). As stated, extensive sampling has shown that all unaltered basalts have $\delta^{18}O$ values near 5.7‰ relative to SMOW (Muehlenbachs and Clayton, 1972b; 1976). Muelhenbachs and Clayton (1972b) have shown that basalts recovered by dredging mid-ocean ridges increase progressively in $\delta^{18}O$ by weathering at a rate of 0.25‰/M year. Likewise, all the basalts recovered by the DSDP drillings are weathered ($\delta^{18}O$ = 6–9‰), showing that seawater percolates through the oceanic crust to depths of hundreds of meters (Muelhenbachs and Clayton, 1976) and interacts with it. Further evidence for weathering of the oceanic crust by seawater can be found in the study of porewaters of sediments from the ocean floor. Oxygen isotope analyses have been reported for pore fluids of numerous DSDP sites (Lawrence and Gieskes, 1981) that show a decrease of the $^{18}O/^{16}O$ ratio with increasing depth, corresponding to a $\delta^{18}O$ gradient of −0.36‰/100 m. This feature is interpreted as being the result of the progressive consumption of oxygen-18 by low temperature alteration of basalts, controlled by diffusion through the sedimentary cover (Lawrence et al., 1975; Lawrence, 1986). From this, a flux of ^{18}O out of the ocean can be calculated using the average ^{18}O concentration gradient (−0.36‰/100 m) and the appropriate value of the diffusion coefficient for interstitial waters. Using data by Li and Gregory (1974) for diffusion of ions in deep-sea sediments (6×10^{-6} cm^2/s), Lawrence and Gieskes (1981) calculated a global sink of ^{18}O into the crust of 2.3×10^{15} moles of ^{18}O per million years for the total area of the deep ocean, i.e., 73 mol/s. As said above, this flux is mainly the results of ^{18}O consumption by low temperature alteration of basalts to smectites and zeolites. However, because of its calculation method, it also includes additional alteration processes in the sediment layer itself.

One potential problem with the above calculation is that it ignores the possible contribution of convection on ridge flanks. Heat flow studies definitely shows that a large fraction of the heat corresponding to the cooling of the newly formed crust is removed by water circulation through the ridge flanks. Chemical fluxes associated with this phenomenon are poorly known, as it involves large volumes with only minute compositional changes. However, while cellular convection can be active in the crust over a long period, the lower permeability of the sediment might cause convection to cease much earlier in the sedimentary cover (Zoback and Anderson, 1983) which acts as an hydraulic lid. In the region of ridge flanks where convection does nevertheless take place in the sediment blanket, the ^{18}O composition of the exiting fluids is not known precisely, thus making ^{18}O fluxes highly uncertain. Fortunately, however, the temperature range over which water and crust interact encompasses the $\Delta^{18}O_{\text{rock-water}}$ inversion temperature where water either gains or loses ^{18}O, so that the ridge flank contribution to the ^{18}O oceanic budget is likely to remain marginal.

Finally, an additional term to consider is the volume of porewater expelled from the subducted sediments (dewatering process) and which is returned to the ocean with a mean $\delta^{18}O$ value (−2 ± 1‰) lower than ambient ocean waters (Lawrence et al., 1975; Lawrence, 1986). The volume of fluid concerned is roughly estimated at 1 km^3/yr (Von Huene and Scholl, 1987), leading to an additional removal of around 10 mol ^{18}O/s.

3.3. Continental Weathering

Reactions of meteoric waters with continental rocks during weathering also enriched the rocks in ^{18}O (Lawrence and Taylor, 1972; Perry and Tan, 1972; Taylor, 1974, 1983; Savin, 1986) and cause a corresponding decrease of the $\delta^{18}O$ of the waters returning to the sea via groundwaters or river run-offs, relative to precipitations. Due to the short time constant of this hydrological cycling, however, the corresponding $\delta^{18}O$ shift of the waters may not be detectable analytically. Indeed, as far as water stable isotopes (D and

^{18}O) are concerned, run-off waters and groundwaters are almost always characterized by the local meteoric water line that links the two isotopic species (Craig, 1961; Craig and Gordon, 1965), hence showing no detectable isotopic shift due to low temperature alteration. However, due to the large water fluxes associated with the hydrological cycle on land (river run-offs = 10^6 m^3/s), even a minute ^{18}O shift could be important in the global oceanic budget. Therefore, in this particular case, the only way to obtain a broad estimate of the ^{18}O shift is to evaluate the global ^{18}O sink related to the global mass of the igneous and metamorphic rocks on continents and to divide it by the age of the earth, as suggested by Muelhenbachs and Clayton (1976), Perry and Tan (1972), and Holland (1984): metamorphic and crustal igneous rocks are enriched in ^{18}O with respect to the mantle rocks. Using the Ronov and Yaroshevsky (1969, 1976) estimate of the composition of the crust, Perry and Tan (1972) and more recently Holland (1984) attempted to calculate the most probable value of the ^{18}O sink due to continental weathering. The Holland (1984) best estimate approaches 120×10^{22} mil-mole, which represents the sum of the ^{18}O excess (expressed in Δ^{18}O‰ × mole of oxygen) between each rock type and the mantle δ^{18}O value. We calculate that this corresponds to an average flux of 17 mol ^{18}O/s over the age of the earth. Obviously, this figure is rather uncertain, but it suggests that the continental weathering, although within an order of magnitude of that for the submarine weathering of basalts, is of lesser importance. This result seems quite reasonable if one keeps in mind that the oceans are by far the largest part of the hydrosphere.

3.4. Sedimentation

The last important contribution to the ^{18}O budget of the ocean is the biogenic sedimentation resulting from fixation of mineral phases in the formation of the hard parts of marine organisms as well as the in situ formation of authigenic sediments, produced by alteration or chemical precipitation in the marine environment. Both processes are accompanied by large ^{18}O fractionation, ^{18}O/^{16}O being enriched in the minerals at the expense of seawater and, therefore, are a major sink of oceanic ^{18}O. In fact, the greater proportion of the products of erosion enter the sea in particulate form. They are dropped by the winds to the sea surface or discharged by rivers in coastal areas. This category of lithogenic sediments of continental origin is of the so-called detrital type. They consist of rock fragments and soil residues which are chemically quite inert and, therefore, should not be considered here. Biogenic sediments can be divided into two subcategories: calcereous and siliceous. The oxygen isotopes fractionation curves between calcium carbonate and water, and between silica and water, are well established at usual seawater temperatures (Epstein et al., 1953; Vinot-Bertouille and Duplessy, 1973; Labeyrie, 1974; Savin, 1986; Bowen, 1991). The isotopic shift is more pronounced for silica than for calcium carbonate, with δ^{18}O values vs. SMOW in the range 37 ± 3‰ and 30 ± 3‰, respectively, in the temperature interval of oceanic interest. Likewise, if we turn to the formation of genuine authigenic sediments, fractionation factors for clay minerals-water systems, inferred from the isotopic composition of natural samples, are the same order of magnitude (Savin and Epstein, 1970a,b; Lawrence and Taylor, 1972) with values in the range 20 ± 5‰. However, this type of sediments, that chemically precipitate from seawater, represents only a tiny fraction relative to biogenic type and will be neglected in the following.

The fate of particulate matter in the ocean and its burial rate as deep-sea sediments have been extensively studied over the past twenty years with the central objective of understanding and quantifying the main marine bio-geochemical cycles and their role in climate dynamics. Only a very small portion of the particulate material (calcareous or siliceous) formed at the surface of the ocean is eventually preserved as sediment. Most of it is redissolved on its way down to the ocean floor and also after the particles have reached the seafloor. Li et al. (1969) and Broecker and Peng (1982) estimate that only 20% and 14%, respectively, of the calcium carbonate fixed in the surface waters is deposited as sediment, due to dissolution in the water column and at the sediment-water interface. Similarly, Heath (1974), Broecker and Peng (1982) and Nelson et al. (1995) estimate that only 2–5% of silica fixed in surface waters is eventually incorporated in the sediments. Global carbonate burial rates have been estimated in numerous studies (see for example the data compilation of Sunquist, 1985). The most probable value is around 0.3 ± 0.15 Gt of carbon/y, precipitated as calcium carbonate ($CaCO_3$), corresponding to a flux of 7.9 $\times 10^5$ mol $CaCO_3$/s. Using the average δ^{18}O for $CaCO_3$ of 30 ± 3‰ discussed above, this leads to an ^{18}O sink of 142 ± 70 mol ^{18}O/s. Similarly, marine silica budget data (DeMaster, 1981; Treguer et al., 1995) give a total removal rate of 7.1 ± 1.8 $\times 10^{12}$ mol SiO_2/yr, which leads to an additional ^{18}O sink of 33 ± 10 mol ^{18}O/s using a mean δ^{18}O value of 37‰.

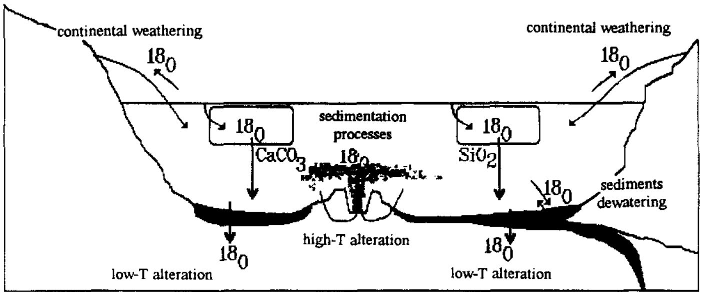

Fig. 1. The ^{18}O cycle in the oceans.

Table 2. Estimated ^{18}O budget of the oceans.

^{18}O inputs (mol ^{18}O/s)		^{18}O outputs (mol ^{18}O/s)	
Submarine high temperature hydrothermalism	240 ± 120	submarine low-temperature weathering	73 ± 35
		sediments dewatering	10 ± 5
		continental weathering	17 ± 10
		sedimentation:	
		biogenic carbonates	142 ± 70
		biogenic silicates	33 ± 10
TOTAL:	240 ± 120	TOTAL:	275 ± 130

The main ^{18}O oceanic inputs and outputs discussed above are shown in Fig. 1 and their best estimates are summarized in Table 2. The uncertainty in both the flux in and the fluxes out is around ±50%, due to the cumulative effect of the accuracies in the magnitude of the various processes involved in the ^{18}O exchange and the uncertainty in the various average ^{18}O fractionations. This definitely represents an improvement relative to previous results based on rock reservoirs budgeting. However, there is clearly room for further progress. Comparison of the sources and sinks columns of Table 2 shows that, within the existing uncertainties of present ^{18}O fluxes, the oceanic oxygen-18 budget is balanced and points to the likely stability of the present ^{18}O oceanic composition: the ^{18}O input by high temperature hydrothermal processes cancels out ^{18}O removal by low temperature continental and marine alteration and by sedimentation.

4. SPECULATIONS ON THE PAST ^{18}O OCEANIC COMPOSITION

The fact that the present ^{18}O oceanic budget may be close to a steady-state is not particularly informative about the possible past evolution of the oceanic ^{18}O composition and about the interpretation of the ^{18}O record of ancient cherts. The evolution of the ^{18}O composition of seawater over the age of the world ocean has been the subject of an intense debate since Perry (1967) on the isotopic composition of oxygen in ancient cherts, showing that recent cherts are isotopically heavier than older deposits. Numerous additional studies of cherts of various ages have confirmed this trend. However, there is little consensus concerning the interpretation of these measurements. It is still unclear to what extent the $\delta^{18}O$ values reflect the origin of these cherts, the $\delta^{18}O$ value and temperature of the waters in which they formed, and/or the post-effects of diagenesis. In our view however, studies coupling both oxygen and deuterium isotopes like those of Knauth and Epstein (1976) put additional constraints on the stable isotope geochemistry of the cherts and give convincing arguments in favor of the climatic interpretation of the trend in opposition to the secular changes in the $\delta^{18}O$ value of seawater favored by Perry (1967) and Perry et al. (1978). If the lower $\delta^{18}O$ values of the ancient cherts are entirely due to the temperature effect on the isotopic fractionation factor, the $\delta^{18}O$ shift over geological times corresponds to a decreasing trend in ocean temperature of the order of 50–70°C (Knauth and Lowe, 1978) over 3.4 Gy. Conversely, an explanation based on the change of the ^{18}O composition of seawater with time requires a progressive increase in oceanic ^{18}O concentration. Since there is little doubt that the starting value of the $\delta^{18}O$ of ocean waters was rather close to mantle values, $\delta^{18}O$ = 7–8‰ (Silverman, 1951; Chase and Perry, 1972), that is clearly above the present-day value ($\delta^{18}O \approx$ 0‰), a positive oceanic $\delta^{18}O$ trend would require an initial dramatic drop in the oceanic $\delta^{18}O$ below the present value, followed by a recovery trend towards 0‰. We do not see in the geological trend of the main sources and sinks of oceanic ^{18}O any arguments in favor of such dramatic changes. Cores recovered by the DSDP have provided much information about deep-sea sediments: the estimated difference in sedimentation rates between times of low and high rates of sediment deposition is the order of a factor of 2–3 in general (Whitman and Davies, 1979; Barron and Whitmann, 1981) with a typical timescale of the order of 10 My, presumably due to variation in climate and continental weathering and/or variations in land/sea ratio. On the other hand, studies concerned with the past intensity of the oceanic crust production and the subsequent intensity of water cycling at spreading axis, using various methodological approaches (Larson, 1991a,b; Gaffin, 1987; Kaiho and Saito, 1994) suggest that oceanic crust production could have fluctuate by no more than a factor of 2, on a

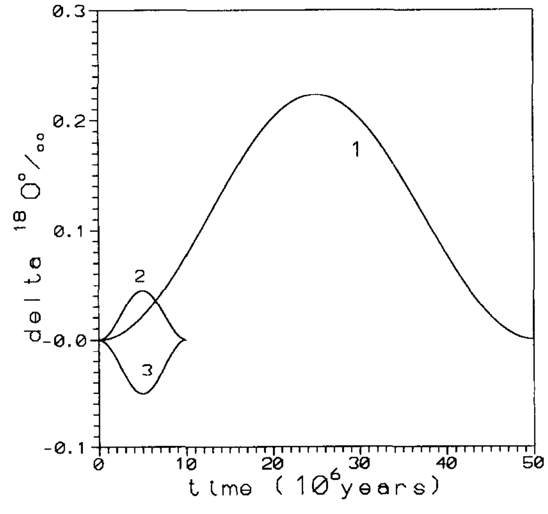

Fig. 2. Oceanic $\delta^{18}O$ response to sinusoidal transients of input or output fluxes: *Curve 1:* High temperature hydrothermal flux transient: $F_{hy} = F_{hy_0} + 0.3 \times F_{hy_0} \times \sin(2\pi t/\tau)$, with $\tau = 50$ Myear. *Curve 2:* High temperature hydrothermal flux transient: $F_{hy} = F_{hy_0} + 0.3 \times F_{hy_0} \times \sin(2\pi t/\tau)$, with $\tau = 10$ Myear. *Curve 3:* Sedimentation rate transient: $F_{sed} = F_{sed_0} + 0.6 \times F_{sed_0} \times \sin(2\pi t/\tau)$, with $\tau = 10$ Myear.

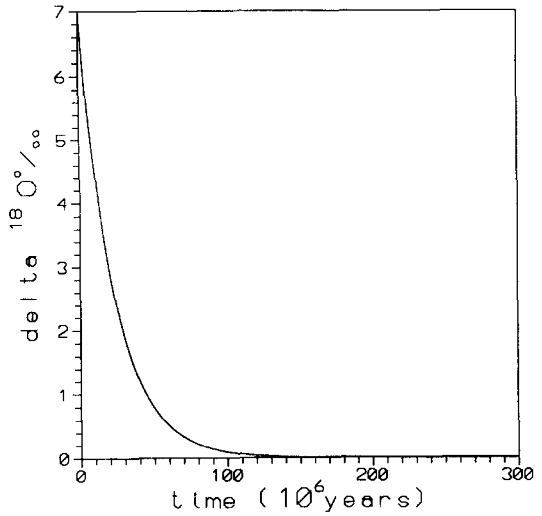

Fig. 3. $\delta^{18}O$ evolution of the ocean vs. time with an initial value around 7‰ and with the present ^{18}O fluxes and fractionation factors.

timescale of the order of 10–50 My. Furthermore, the lithium content of ancient shales (Cameron and Garrels, 1980), which is a good tracer of high temperature sea-rock interactions, is consistent with only limited variations in the intensity of these high temperature water-rock reactions. Translated in terms of ocean $\delta^{18}O$ variations by solving the mass balance equation of the oceanic ^{18}O, we calculate that these fluctuations in the intensity of both sources and sinks of ^{18}O produce only limited changes (<0.3‰) in the $\delta^{18}O$ composition of the ocean (Fig. 2). This suggests that the $\delta^{18}O$ of the ocean may have experienced only limited fluctuations through geological times, in agreement with the conclusions drawn by Muehlenbachs and Clayton (1976) and Gregory and Taylor (1981) who postulated that ocean waters had a rather constant $\delta^{18}O$ value during almost all of the Earth's history. Using again the ^{18}O mass balance equation, Fig. 3 shows the calculation of what would be the $\delta^{18}O$ evolution of the ocean vs. time, with an initial value around 7‰ and with the present ^{18}O fluxes and fractionation factors. Higher temperatures of the water-rock reactions and crust production rate in the past, as well as increased ocean temperatures (implying reduced isotopic fractionation) may have slowed the pace of the ^{18}O drop with time. Nevertheless, this crude calculation again supports previous suggestions, based on rock ^{18}O data (Muehlenbachs and Clayton, 1976; Gregory and Taylor, 1981), that the initial ^{18}O content of the ocean may have evolved rather quickly, in a matter of a few hundreds of million years, from its initial magmatic value to the present equilibrium, with only limited variations thereafter.

5. CONCLUSION

New measurements of the ^{18}O composition of hydrothermal fluids from a wider range of geological and tectonic settings show that hydrothermal hot waters are consistently enriched in ^{18}O relative to seawater whatever the spreading rate or the tectonic environment and, therefore, are a major source of ^{18}O to the ocean. Study of the marine ^{18}O budget based upon updated data of the direct inputs and outputs of ^{18}O to the ocean, leads to the conclusion that the sources and sinks of oceanic ^{18}O globally balance each other, and that the ^{18}O oceanic composition is presently close to a steady-state. This new budget estimate obtained using an approach different from previous studies, reaches the same basic conclusion as Muelhenbachs and Clayton (1976) based on the budget of rock reservoirs. Although their result was challenged by Holland (1984) who, using an approach identical to theirs but with revised geological data, came to significantly different figures, we think that these diverging results emphasize above all the large uncertainty of the method. Therefore, we think that the claim for the present steady-state of the oceanic ^{18}O composition is correct. Extrapolation to the past ^{18}O evolution of the ocean is far more speculative. It suggests, however, that the ^{18}O composition of the ocean may have reached its present value quite rapidly and has been rather constant over most of the earth's history. This implies that $\delta^{18}O$ measurements in ancient cherts and carbonates may primarily record the past evolution of the ocean temperature and the global earth climate evolution.

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