the assumed pressure-broadened CO line widths; the large spread in her result largely reflects the diversity of available line-width measurements. Recent work on the 2–0 CO line widths by L. D. Tubbs and D. Williams [*J. Opt. Soc. Amer.* **62**, 423 (1972)] yields substantially larger values than those used by Young and, if included in a reanalysis of this band, will tend to give a correspondingly smaller abundance. In the interim we shall adopt $N(\mathrm{CO}) = 7.3\ (\pm 1.0)$ cm amagat.

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The Oceans: Growth and Oxygen Isotope Evolution

Abstract. *A study of the evolution of the oxygen-18/oxygen-16 ratio of the oceans suggests that this ratio is unlikely to have remained constant with time. Our models suggest that early formation of the oceans is more likely than linear growth.*

A change with time of the $\delta^{18}O$ (*1*) of chert and carbonate minerals precipitated from seawater has been suggested (*2, 3*). This change could have resulted from (i) a parallel change in the $\delta^{18}O$ of ocean water, in which case the $\delta^{18}O$ of the ocean at any time would have been about 34 per mil lower than the $\delta^{18}O$ of marine chert; (ii) a change in the temperature of the ocean, resulting in a change in the partitioning of ^{18}O between SiO_2 and water; (iii) isotope exchange during diagenesis, metamorphism, or weathering; or (iv) some combination of these possibilities. The observed increase in the $\delta^{18}O$ of chert in the last 3×10^9 years is about 15 per mil. To produce this change by mechanism ii would require that the early Precambrian ocean have a temperature of the order of 100°C. For mechanism iii to be responsible, the degree of isotope exchange would have to be roughly proportional to the age of the sediment. Although most previous workers have been skeptical that the observed $\delta^{18}O$ variations in endogenetic sedimentary rocks are primary [the arguments are summarized in (*2*) and (*3*)], several studies have supported the interpretation of a primary variation in the $\delta^{18}O$ of sedimentary rocks (*4*). Perry and Tan (*2*) concluded that the chert data are most likely to be the result of a parallel change in the $\delta^{18}O$ of ocean water (mechanism i) (*3*).

There is no a priori reason to assume that the oceans have maintained a constant oxygen isotope composition. If we assume that the 3.9×10^{22} moles of oxygen in ocean water, with $\delta^{18}O = 0$ per mil, are derived from mantle water, with $\delta^{18}O = 7$ per mil, the oceans must have become depleted in ^{18}O by 27×10^{22} per mil moles (*5*). The depletion of ocean water results from isotope exchange reactions at low temperatures between water and silicates, the reactions occurring at the earth's surface and producing large fractionations and consequent ^{18}O enrichment of sedimentary rocks. Perry and Tan (*2*) estimated that igneous (*6*) and sedimentary rocks of the crust are enriched in ^{18}O by 70×10^{22} to 112×10^{22} per mil moles with respect to the mantle material from which they were derived. The fact that the crustal enrichment and oceanic depletion do not balance suggests that we must look to the mantle for the source of much of the crustal excess. Water cycling through the mantle is the most likely exchange medium. The mantle provides an effectively infinite reservoir of oxygen, and in contrast to isotope exchange reactions at the earth's surface, water-silicate exchanges occurring at mantle temperatures are characterized by small fractionations.

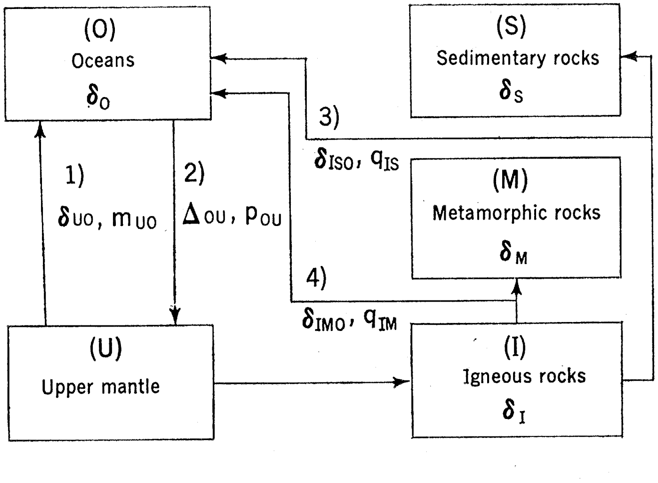

Fig. 1. Flow chart of oxygen reservoirs and isotope exchange processes. The identifying symbols for each reservoir are shown in parentheses; 1) and 2) are direct transfers between oceans and upper mantle, and 3) and 4) are indirect transfers connected with weathering and metamorphism of the surficial rock reservoirs. Symbols representing isotopic effect on oceans and rate of process are shown by each exchange path.

In order to model the oxygen isotope evolution of the oceans, we will consider the effect of four major processes (Fig. 1) on the oceanic $\delta^{18}O$. These processes are:

1) outgassing of mantle water to the oceans concurrent with volcanic and magmatic activity,

2) subduction of ocean water locked into the oceanic crust during sea-floor spreading,

3) weathering of primary igneous rocks to form sediments, and

4) metamorphism of igneous and sedimentary rocks.

All these processes involve isotopic shifts and can thus affect the $\delta^{18}O$ of the oceans. A study of our models suggests that indeed they have done so. The question of whether the volume of the oceans has grown through geologic time is tied up with the relationship between 1 and 2. If more water is being outgassed from the mantle than is supplied to it by subduction of surficial water, the oceans are growing and the mantle is becoming drier. If, however, the amount of water outgassed remains about equal to the amount subduced, the oceans must have been approximately constant in volume since magmatism and subduction processes started operating. Surprisingly, our model studies suggest that the latter case, relative constancy of oceanic volume, is more reasonable in terms of isotopic evolution.

To calculate how the $\delta^{18}O$ of seawater might have changed in the past, we need to set up a differential equation to describe the effects of processes 1 through 4 on the oceans. Let us call the isotopic composition of the oceans δ_O and say they contain M_O moles of ^{16}O. Process 1 involves oxygen being outgassed from the upper mantle as water with constant isotopic composition δ_{UO} (= 7 per mil) and entering the oceans at a rate of m_{UO} mole/year (Fig. 1). This process is direct in the sense that it represents a net transfer of material into the oceans. If it were acting alone, the change of isotopic composition of the oceans would be given exactly (7), with the time t expressed in years, by:

$$M_O d\delta_O/dt = (\delta_{UO} - \delta_O)m_{UO} \qquad (1)$$

Process 2, removal of seawater by sea-floor spreading and subduction, is a different kind of direct transfer. Here water is not entering with a constant composition independent of δ_O, but leaving with some isotopic shift Δ_{OU} relative to δ_O as a result of isotopic equilibration (Fig. 1). If this process removes p_{OU} moles of oxygen per year, the contribution to the change in δ_O of the oceanic reservoir is $\Delta_{OU}p_{OU}$ per mil moles per year. The value of p_{OU} will be negative, since the water is leaving the reservoir. We suggest that water locked into the oceanic crust during sea-floor spreading is effectively removed from contact with the oceans, and therefore that the isotopic shift Δ_{OU} is zero.

The other two processes are indirect, in that they do not change the size of the oceans, but result from the balance of isotope exchanges in other reservoirs. The physical process in 3 is weathering of surficial igneous rocks to form sediments (Fig. 1) in some kind of isotopic equilibrium with seawater. Oxygen is being transferred at rate q_{IS} from the reservoir of igneous rocks, which has isotopic composition δ_I, into the sedimentary rock reservoir, with isotopic composition δ_S. The system of the two rock reservoirs taken together gains excess ^{18}O at the rate of $(\delta_S - \delta_I)q_{IS}$ per mil moles per year by this process. Some other reservoir, in this case the oceans, must be depleted by the same amount to balance. Since the sediments are assumed to be in equilibrium with seawater, $\delta_S - \delta_O$ is a constant. If we define δ_{ISO} as $\delta_I - \delta_S + \delta_O$, this quantity will remain constant even though δ_S and δ_O change with time, since they vary together. The shift in the oceans due to the weathering process 3 is then given by $(\delta_{ISO} - \delta_O)q_{IS}$ per mil moles per year.

We will assume, as a first approximation, that isotopic changes during metamorphism affect the composition of the oceans in the same way. This requires some form of communication through groundwater exchange. The tendency to change δ_O is then $(\delta_{IMO} - \delta_O)q_{IM}$ per mil moles per year, in which the quantities are defined as above.

Now we can write the equations that govern our system's behavior. Since only direct transfers affect the mass of the oceanic reservoir,

$$M_O(t) = \int_0^t (m_{UO} + p_{OU})dt + M_O(0) \qquad (2)$$

Combining the effects of all four processes, we have

$$M_O d\delta_O/dt = (\delta_{UO}m_{UO} + \Delta_{OU}p_{OU} + \delta_{ISO}q_{IS} + \delta_{IMO}q_{IM}) - (m_{UO} + q_{IS} + q_{IM})\delta_O \qquad (3)$$

For convenience in discussion, we will abbreviate Eq. 3 as:

$$M_O d\delta_O/dt = A - B\delta_O \qquad (4)$$

We must observe two cautions in using Eq. 3 to model the oxygen isotope history of the oceans. One is that we may not have included some significant processes. The fate of oceanic sediments and their contained water upon subduction may be pertinent, but we do not know enough about this process to say how important it is. The contained water would reequilibrate with the sediments enriched in ^{18}O at moderate temperatures (8) in the upper portion of the subduction zone, and some of it could return directly to the oceans. Such enriched water might have an isotopic "pumping" effect on the oceans, mathematically similar to process 2 with a positive rate. However, if processes 1 through 4 are the dominant ones, we have a reasonable description of the behavior of our system.

The other caution is that we do not know the rates of transfer (m_{UO}, p_{OU}, q_{IS}, q_{IM}) in Eq. 3 very well, and we especially do not know how they have varied in time. In calculating models I and II (Fig. 2), we have taken estimates of these rates from Muehlenbachs (9) and Perry and Tan (2), and assumed that they have been constant since 3.3 × 10^9 years ago, to see how the oceans might behave. The actual numbers used are listed in the legend of Fig. 2. Thus, our assumptions for the first two models are: a constant rate of subduction of seawater, a constant rate of mantle outgassing, a constant rate of weathering and metamorphism, and a constant isotopic shift for each process. These assumptions also make the parameters A and B of Eq. 4 constant.

Models I and II differ only in what we assume about the history of M_O, which is proportional to the mass of the oceans. For model I, M_O is taken as constant at its present value. For model II, on the other hand, we assume that M_O has grown linearly from half its present value at 3.3 × 10^9 years ago by outgassing of primordial mantle water in excess of that carried down by subduction. Both models show exponential behavior, and neither follows the chert data (Fig. 2) particularly well, but they do demonstrate the sensitivity of the system's behavior to the history of M_O. Since we do not know the time variation of all the parameters in Eq. 3 we have selected a constant M_O for model III, and we arbitrarily vary A and B to roughly simulate the behavior of the chert data. This kind of curve fitting does not uniquely constrain the individual rates and isotopic shifts, but it does place limits on their combination expressed in A and B.

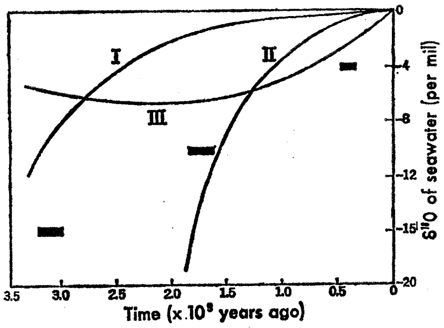

Fig. 2. The heavy bars give approximate $\delta^{18}O$ values of the oceans, based on the assumptions that the isotopic shift between cherts and seawater has remained constant at 34 per mil, and that the highest value for $\delta^{18}O$ from a suite of rocks is most likely to be primary. The data are from (2). The solid lines are the three calculated models. For all the models the present value of M_O is 3.89 × 10^{22} moles O_2, and the present isotopic composition, δ_O, is 0 per mil. In model I, $p_{OU} = -2.19 \times 10^{13}$ moles of O_2 per year (9), locked into the oceanic crust at $\Delta_{OU} = 0$ per mil, equilibrates with silicates at a high temperature during subduction and returns to the surface with an assumed equal rate of $m_{UO} = 2.19 \times 10^{13}$ mole/year and with $\delta_{UO} = +7$ per mil. For weathering of igneous rocks to sediments, $q_{IS} = 8.84 \times 10^{12}$ mole/year, and an average $\delta_{ISO} = -9.5$ per mil is estimated (2). The metamorphism of both igneous and sedimentary rocks is assumed to result in an exchange of $q_{IM} = 1.68 \times 10^{13}$ moles of O_2 per year with the oceans, depleted at $\delta_{IMO} = -3.5$ per mil. Model II differs from model I only in that water is outgassed from the mantle faster than it is subducted (causing the volume of the oceans to double linearly in 3.3 × 10^9 years); hence, it is assumed that $m_{UO} = 2.78 \times 10^{13}$ mole/year. In model III the parameter B increases linearly by 4.7 × 10^3 mole/year^2 to a present value of 1.0 × 10^{13} mole/year, and A is assumed to be equal to 25 per mil times B.

Valuable information about the possible isotopic behavior of the oceans may be obtained by direct examination of Eq. 4. For example, if A and B are constant, δ_O will approach the value A/B asymptotically as time progresses. Models I and II of Fig. 2 show this kind of behavior. It is commonly assumed that $\delta^{18}O$ of seawater has been constant in the past at its present value of zero. This requires the unlikely coincidence that A, a sum of products of mass transport rates and isotopic shifts, has remained equal to zero throughout geologic time. It is important to emphasize that there is no known buffering process, in the sense of negative feedback, that can hold the $\delta^{18}O$ of the oceans constant. Muehlenbachs (*9*) has presented a model in which the coincidence is observed that $A = 0$ at present. However, he restricted himself to oceanic processes and did not consider the crustal excess of ^{18}O mentioned above. Furthermore, to achieve a balance he had to require that greenstones in layer 2 of the oceanic crust have been depleted in ^{18}O by 0.5 per mil during metamorphism of the parent basaltic material, and that the correspondingly enriched waters have been able to circulate freely and mix back completely into the oceans. Also, the suggested isotopic shift between basalt and greenstone is not demonstrated to be statistically significant. For these reasons we conclude that the balance obtained is invalid. Thus, theoretical considerations and the chert data discussed above both lead us to the conclusion that the $\delta^{18}O$ of seawater has changed with time.

What we consider most important in Fig. 2 is the drastic effect that growth of the oceans has on the calculated $\delta^{18}O$. Model I, with constant mass, starts with a reasonable value of δ_O, -12 per mil, 3.3×10^9 years ago. The corresponding value for model II, with linear outgassing, is a quite unreasonable -519 per mil. We compared other constant-mass models with models in which the oceans grow according to various laws and found that with these paired models ocean growth greater than about 10 percent since early Precambrian results in runaway δ_O behavior. It can be seen from Eq. 4 that the effect is due to the greater sensitivity of a reservoir of small M_O to tendencies for isotopic change expressed in A and B. This limitation on the growth rate of the oceans is only applicable, therefore, if there has been a tendency to change, that is, if A and B have not been zero throughout geologic time. This is probable, so with the constraints imposed by the chert data on the oxygen isotope history of the oceans, it seems likely that their growth in volume has been limited since early Precambrian.

Fanale (*10*) has assembled many lines of evidence on rare gases and other volatiles that indicate a catastrophic early degassing of the earth and early formation of the oceans and atmosphere. Oversby and Ringwood (*11*) deduced from data on lead partitioning in appropriate core compositions that the core of the earth formed very early; this implies an initially molten earth and consequent early degassing. These conclusions are entirely consistent with the results of our models, suggesting that water can recycle through the mantle but that the current distribution between mantle and surficial water is essentially a steady-state one, and involves no significant present growth of the mass of the water in the oceans.

C. G. CHASE
EUGENE C. PERRY JR.*

Department of Geology and Geophysics, University of Minnesota, Minneapolis 55455

References and Notes

1. The quantity $\delta^{18}O$ is defined by

$$\delta^{18}O = \left\{ \frac{(^{18}O/^{16}O)_{\text{sample}}}{(^{18}O/^{16}O)_{\text{SMOW}}} - 1 \right\} \times 1000$$

where SMOW is standard mean ocean water [see H. Craig, *Science* **133**, 1833 (1961)].
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7. Equation 1 follows from these relationships: M is the number of moles of ^{16}O in the ocean; N is the number of moles of ^{18}O; $\delta_O = 10^3\,[(N/M)/R - 1]$, where R is $^{18}O/^{16}O$ in the standard; $m_{\text{ro}} = dM/dt$; and $\delta_{\text{ro}} = 10^3\{[dN/dt)/(dM/dt)]/R - 1\}$.
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* Present address: Department of Geology, Northern Illinois University, DeKalb 60115.

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Lanthanide Complexes as Nuclear Magnetic Resonance Structural Probes: Paramagnetic Anisotropy of Shift Reagent Adducts

Abstract. Magnetic anisotropy measurements on single crystals of a series of paramagnetic 8-coordinate lanthanide shift reagent adducts of the type $Ln[(CH_3)_3CCOCHCOC(CH_3)_3]_3(4\text{-}CH_3C_5H_4N)_2$ have been made for the following lanthanides: praseodymium, neodymium, samarium, europium, terbium, dysprosium, holmium, erbium, thulium, and ytterbium. The susceptibility tensors are highly anisotropic and nonaxial. Dipolar nuclear magnetic resonance shifts evaluated from the solid-state data are in satisfactory agreement with the solution results.*

The determination of the geometry and conformation of molecules in fluid solution, especially those of biological interest, is a matter of paramount importance. There has been considerable interest in the use of paramagnetic metal ions as nuclear magnetic resonance (NMR) broadening probes (*1*) and lanthanide ions in particular as both broadening and shift probes (*2*). Furthermore, the NMR shifting abilities of certain lanthanide complexes of bulky β-diketonate ligands has been exploited to a considerable extent through their use as shift reagents (SR's) (*3*) introduced by Hinckley (*4*). While it is a generally held view that isotropic NMR shifts observed for substrate protons in lanthanide systems are predominately dipolar in origin, and therefore related to substrate geometry in solution, there has been no direct, independent evidence of this prior to the research reported here.

It was pointed out by one of us (*5*), and verified by independent theoretical work (*6*), that dipolar shifts may be evaluated directly from single-crystal magnetic susceptibility data. This method has been applied to a number of transition metal systems including $Co[C_{10}H_8N_2]_3^{2+}$ (*5*), Co(CH$_3$COCH-