sphere to a change in the concentration of  $H_2O$  is of interest. For modest changes, the atmosphere readily adjusts to a new equilibrium state with a different  $CO/O_2$  mixing ratio. To first order, the concentration of OH is proportional to the concentration of  $H_2O$ , and the concentrations of O, H, and  $HO_2$  in the lower atmosphere remain constant. Only the CO concentration changes, and the change is inversely proportional to the change in  $H_2O$  concentration. To a higher level of approximation, however, consequent changes in the production of  $O_2$  must be considered. By numerical experimentation we found that if the  $H_2O$  concentration were arbitrarily reduced by a factor of 2, the CO concentration would increase by a similar factor and the  $O_2$  concentration would decrease by about 50 percent, if the eddy mixing coefficient remained constant.

It is also of interest to consider the atmospheric response to a change in the eddy mixing coefficient near 30 km. A reduction (or increase) in the eddy mixing coefficient at 30 km leads to an increase (or decrease) in  $O_2$  formation. The chemical equilibrium in the lower atmosphere is altered with a consequent increase (or decrease) in the abundance of CO and  $O_2$ . The CO/ $O_2$ mixing ratio remains relatively constant. It has been suggested that the  $O_2$  concentration varied with time in the late stages of the recent planetwide dust storm (8). This may reflect in part a change in the dynamic state of the atmosphere, in part a change in the atmospheric  $H_2O$  concentration. It is difficult to draw more quantitative conclusions. A complete analysis should allow for heterogeneous chemistry on atmospheric dust, and there are reasons to suspect that martian dust may play some role in the chemistry of atmospheric oxygen (20).

Finally, we note the central importance in the present analysis of the conservation condition (Eq. 1). The relative abundance of various forms of odd hydrogen, and the mixing ratio of odd hydrogen, are controlled by this relation in the present scheme. An increase (or decrease) in O escapeassociated, for example, with increased (or decreased) solar activity—will result in an increase (or decrease) in the amount of atmospheric CO. The concentration of HO in the lower amtosphere will change. For a fixed  $H_2O$ concentration, the concentration of  $HO_2$ will increase (or decrease) with an increase (or decrease) in O escape. The

production of  $H_2$  and escape of H will alter accordingly. The present model provides a plausible explanation of the observed relation between H and O escape and supports conclusions derived earlier (5) regarding the evolutionary history of martian  $H_2O(21)$ .

MICHAEL B. MCELROY

THOMAS M. DONAHUE\*

Center for Earth and Planetary

Physics, Harvard University,

Cambridge, Massachusetts 02138

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- hows of our hydrogen and out of  $J_1$  would be specified accordingly. We were unable to find additional important sinks for  $H_2$ . For ex-ample, the rate of loss of  $H_2$  by reaction with OH is less than  $5 \times 10^7$  cm<sup>-2</sup> sec<sup>-1</sup> at martian temperatures.

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- University of Pittsburgh. Permanent address: Department of Physics, University of Pittsburgh, Pittsburgh, Pennsylvania 15213.
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## **Detection of Molecular Oxygen on Mars**

Abstract. Molecular oxygen was detected in martian spectra near 7635 angstroms and its abundance measured both during and after the 1971 dust storm. Its column abundance in the clear martian atmosphere is about  $10.4 \pm 1.0$  centimeters amagat, giving a mixing ratio of molecular oxygen to carbon dioxide of  $1.3 \times 10^{-3}$ . The mixing ratio of molecular oxygen to carbon monoxide (1.4  $\pm$ 0.3) is quite different from the value of 0.5 that would result from the photolysis of a pure carbon dioxide atmosphere, which indicates that there is or was a net source of oxygen relative to carbon (probably water) in the martian atmosphere.

The atmospheric composition of Mars has been known (1) for several years now to be primarily  $CO_2$ , with trace amounts of CO (0.08 percent) and water vapor (approximately 0.2 percent). Upper limits have also been placed on the amounts of ozone ( $< 3 \times$  $10^{-6}$  percent), N<sub>2</sub> (< 5 percent), and  $O_2$  [< 0.26 percent (2) and < 0.19 percent (3)]. The measurements we report here yield 0.13 percent for the  $O_2$ abundance.

Knowledge of the  $O_2$  abundance, in addition to its intrinsic interest, provides us with another clue to a puzzle

concerning the photochemistry of  $CO_2$ atmospheres. A number of investigators (4, 5) have noted that in a period of about 2000 years most of the CO<sub>2</sub> on Mars should be decomposed by sunlight (at wavelengths below 2270 Å) into CO and O<sub>2</sub>, according to laboratory measurements of the rates of the reactions  $CO_2 + h\nu \rightarrow CO + O$ ,  $O + O + M \rightarrow O_2 + M$ , and  $O + CO + M \rightarrow CO_2 + M$ , where M is a third body. By including transport terms in the rate equations, Mc-Elroy and McConnell (4) were able to account for the small amounts of

observed CO and O in the martian upper atmosphere, although they required an unexpectedly large amount of vertical mixing, about 100 times that observed on the earth. Even this, however, was insufficient to account for the observed amount of CO in the lower atmosphere; in this case it is also necessary to increase the expected rate of recombination of O and CO by a very large factor (6). This may be done by invoking catalytic schemes involving minor constituents, which have been discussed by various authors (5). The O<sub>2</sub> concentration is an important boundary condition on this problem.

Our observations were made with a Pepsios spectrometer (7), which essentially consists of three Fabry-Perot etalons in series (see Fig. 1), and the 60-inch (152-cm) telescope of the Smithsonian Astrophysical Observatory, located at an altitude of 2320 m on Mt. Hopkins, south of Tucson, Arizona. The method of observation is similar to that employed by Belton and Hunten (2) and consists of observing two lines in the "forbidden" electronic band of  $O_2$  near 7635 Å, at times when the Doppler shift of the martian lines is 0.3 Å or more, so that they can be distinguished from the strongly saturated telluric lines. Since we expect the martian  $O_2$  lines to have full widths of about 15 mÅ, owing to thermal (Doppler) broadening, we chose the instrumental width to be close to this value, to maximize the detectability of a line.

We analyze each scan by first removing the effects of the telluric  $O_2$  lines (see Fig. 2); the data are fitted (by using an iterative, nonlinear, least-squares computer program) by a profile of the form

$$I(\lambda)/I_0 = \exp[-AF(\lambda)] + b \qquad (1)$$

where  $I_0$  is the continuum intensity and  $I(\lambda)$  is the intensity in the absorption lines, and

$$F(\lambda) = \frac{S_{\varrho}\delta/\pi}{\delta^2 + (\lambda - \lambda_{\varrho})^2} + \frac{S_{\rho}\delta/\pi}{\delta^2 + (\lambda - \lambda_{\rho})^2}$$
(2)

is the expected pressure-broadened profile. The line strengths S of the oxygen  ${}^{P}Q(9)$  and  ${}^{P}P(9)$  lines were calculated from the band strength  $S_v = 4.09 \text{ cm}^{-1}$ .  $g^{-1} \text{ cm}^2$  (or 340 A km<sup>-1</sup> amagat<sup>-1</sup>) found by Burch and Gryvnak (8); however, the Hönl-London factors calculated by Schlapp (9) were used. The unit centimeter amagat (centimeter atmospheres at STP.) is equal to 2.687  $\times$  $10^{19}$  molecules cm<sup>-2</sup>. The line-of-sight

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Fig. 1. Block diagram of the Pepsios interferometer and data-handling system.

abundance A is the number density of  $O_2$  in the earth's atmosphere above the observing site, multipled by the secant of the zenith angle. The pressurebroadened width (8)  $\delta = 13$  mÅ refers to an average terrestrial pressure, according to the Curtis-Godson approximation (10). These values for  $S_{y}$  and δ provide accurate predictions ( $\pm$  5 percent) of the intensities of the telluric O<sub>2</sub> lines and also of the same lines observed over a short path length in our laboratory. In comparison, a similar calculation of intensities with the values of  $S_v$  and  $\delta$  obtained by Miller *et al.* 

(11) yields a poorer match with our data, unless the product  $S_{\rm v}\delta$  is increased by about 47 percent and  $S_v$  by about 13 percent. The background level b measures the unwanted transmission by the instrument of light well outside the instrumental passband and has a value of about 3 percent of the continuum intensity in this work. By comparing the observed positions of the P(9) line formed on Mars (effective pressure approximately 3 mb) with those of the P(9) line formed in the earth's atmosphere ( $p_{\rm eff}$  approximately 360 mb), and allowing for the Doppler shifts due to orbital and spin motions, we find a small difference (about 5 mÅ) that could be due to a pressure shift of the line with magnitude  $+14 (\pm 7)$ mÅ/atm.

The summed scans for each day are shown in Fig. 3, and the data derived from them are listed in Table 1. We derive martian O2 column abundances, N, from the observed equivalent widths, W, by using the equation  $W' = \rho W =$  $\eta NS$ , where  $\rho$  is a saturation correction (typically about 10 percent),  $\eta$  a planetary air-mass factor, and S the line strength. We calculate  $\eta$  by assuming that Mars has a clear atmosphere with a constant surface pressure (that is, no topographical features are included). If the surface brightness of the observed disk is uniform (no limb darkening), then

 $\eta = \frac{8(1-i/\pi)}{(1+\cos i)}$ 

where *i* is the phase angle. For the November, February, and April observations,  $\eta = 3.52$ , 3.53, and 3.58,

Table 1. Observed equivalent width W of the martian  ${}^{P}P(9)$  and  ${}^{P}Q(9)$  oxygen lines from the daily summed scans shown in Fig. 2. The total line-of-sight abundance  $\eta N$  and the corresponding column abundance N are also listed (see text for the air-mass factors  $\eta$ ). An averaged abundance N is calculated for those observations that were made under similar conditions in the martian atmosphere, as estimated from Mariner 9 data and earth-based observations on  $CO_2$  lines; the uncertainties in the averages are derived from the corresponding numbers for individual scans and do not reflect the scatter in points.

Abundances (cm amagat)		
(±1 S.D.)	Comments	
6.8 ± 0.3	Extensively dusty atmosphere	
9.0 ± 0.8	Partially dusty atmosphere	
$7.4 \pm 1.0$	"Clear" atmosphere	
$11.8\pm0.8$	"Clear" atmosphere	
	N. Hemisphere S. Hemisphere*	

989

respectively. The question of topography is discussed below; our observations are normalized to the geometrical air mass because of incomplete knowledge of the topography. We take the effective spectroscopic temperature of the clear atmosphere to be 203°K (12) and the dust-storm temperature to be 230°K, as estimated from S-band occultation measurements by Mariner 9 (13). The P(9) line strengths,  $S_{\rm P}$ , are 0.138 and 0.136 mÅ  $cm^{-1}$  amagat<sup>-1</sup> for 203° and 230°K, respectively. Table 1 also shows an averaged abundance  $\overline{N}$  for those observations that were made under similar conditions in the martian atmosphere, as discussed below. The uncertainties in all cases are  $\pm 1$ S.D., estimated from the noise level on constituent scans, and do not reflect systematic effects such as variations of brightness across the disk, topographical relief, or variable dust obscuration.

The abundances derived from the ob-

servations of November and December 1971 are particularly difficult to interpret, because the dust coverage was regionally variable and had begun to clear during this period (14). In addition, the south polar region was relatively clear, according to the Mariner 9 ultraviolet experiment (15). Thus, the air-mass factor is ill defined for the whole planetary disk, and the apparent  $O_2$  abundance that we measured in November (0.66 of the amount measured later on the clear planet) is an average over the variably covered surface. By comparison, on 25 November 1971, Parkinson and Hunten (16) measured an apparent  $CO_2$  abundance that was 0.36 of the value for a clear atmosphere. Unifortunately, the experiments are not immediately comparable, since the CO<sub>2</sub> data were obtained over about the central 25 percent of the area of the disk and did not include the clearer south polar region, as did the  $O_2$  observations. We repeated our measurements in February and April 1972, having learned meanwhile that the dust had essentially settled by 10 December 1971 (16). In February, in order to explore possible seasonal variations in  $O_2$ , we made separate measurements of the northern and southern hemispheres. To the accuracy achieved, which was not very great, we could see no difference between the two hemispheres (see Table 1).

We obtain the estimated  $O_2$  column abundance of  $10.4 \pm 1.0$  cm amagat from a statistically weighted average of the February and April 1972 data. We believe that the disparity in abundance between these last two dates is simply a result of the longitudinal variations in martian topography (17). Both radar studies (18) and direct spectroscopic observations of CO<sub>2</sub> abundance variations (19) show large-scale relief, of the order of 8 km, while the atmo-



Fig. 2 (left). Typical single scan of the entire disk of Mars, obtained on 27 November 1971. In the lower trace, the prominent features are the  ${}^{P}Q(9)$  and  ${}^{P}P(9)$  lines of  ${}^{16}O_{2}$ , as well as the  ${}^{P}Q(11)$  line of  ${}^{16}O^{18}O$ , with the weaker  ${}^{P}P(10)$  line of  ${}^{16}O^{17}O$  just beginning to appear off the right-hand end of the scan. Doppler-shifted lines of martian  ${}^{16}O_2$  are marginally visible in the wings of the corresponding telluric lines. The upper trace is obtained from the lower by dividing through with a theoretical profile (see text); the vertical scale applies to this trace only. An average scan, such as this one, was recorded in about 15 minutes, with an average signal level of roughly 1700 photoelectrons per second. Fig. 3 (right). Summed spectra for each day's observations of Mars and a sum over several days for the moon are shown. Each Mars spectrum is a composite of a number of individual scans (see Fig. 2), aligned with respect to the expected position of the martian P(9) line, which is measured from the observed center of the telluric P(9) line with the appropriate Doppler



shift included. In short scans the telluric line center is poorly determined, and the resulting spectra are somewhat smeared. The Mars-Earth Doppler shift increased substantially between November and February, and the extra displacement of the telluric "blackout" region is apparent. Scans of the northern and southern martian hemispheres in February 1972 show little difference in line strength, and are especially noisy owing both to the decreased brightness of the planet and to the difficulty in holding exactly half the planet's image on the spectrometer aperture. Observations in April were made over an especially short spectral range in order to make best use of the available time. A comparison spectrum of the moon is shown, but shifted to make the telluric absorptions approximately coincident with those above. There are no features in the region of the martian lines. A weak Fraunhofer line can be seen between the telluric Q and P lines in the lunar spectrum; on the Mars spectra this feature will be shifted to higher wavelengths and entirely masked by the P(9) line in the earth's atmosphere.

spheric scale height is about 11 km. A direct comparison of the areas of Mars that were observed (17) with a midlatitude topographic map (19) indicates that the measured variation could well be due entirely to these geometrical effects. To derive completely well defined column abundances (and thus to compare these two measurements accurately), we should generate correct averages over the real topography, weighted by the surface brightness. Since the large-scale topography is not yet known for the polar regions, we cannot do this really correctly, and therefore simply give this average value, derived from the geometrical air mass. For a CO<sub>2</sub> abundance of 78  $\pm$ 11 m atm (1), we get a mixing ratio  $O_2/CO_2$  of  $1.3 (\pm 0.3) \times 10^{-3}$ 

We should also ask whether we might expect the O2 abundance either to change as a result of the dust storm, or to vary seasonally as the  $H_2O$  abundance does. The main photochemical cycle, of CO<sub>2</sub> dissociation and effective recombination of O and CO, has a time constant that is still fairly long on this time scale, although it is very short on the geological scale. For instance, at the average photodissociation rate calculated by McElroy and Mc-Connell (4),  $2.5 \times 10^{12}$  O atoms are produced per square-centimeter column per second, so that to make 1 cm amagat of  $O_2$  requires  $2.2 \times 10^7$ seconds, or 250 days. If minor constituents are responsible for catalyzing the effective recombination, then a sudden increase in their concentration might produce a decrease in  $O_2$  and CO concentrations.

By strict analogy with  $H_2O$ , we should explore whether oxygen itself may be "frozen out" [in the form of condensed ozone in the polar caps (20)] and then released into the atmosphere by sublimation. The Mariner 9 ultraviolet spectrometer revealed a small amount of ozone (0.0015 cm amagat) in the northern hemisphere of Mars (21), although on the average the ozone abundance is less than  $10^{-4}$ cm amagat. McElroy and Hunten (22) give a photodissociation rate of ozone (at zero optical depth) of 4.2  $\times$  10<sup>-3</sup>  $sec^{-1}$ , which is effectively reduced by a factor of 250, because ozone reforms many times by the reaction  $O + O_2 +$  $M \rightarrow O_3 + M$  before the reaction  $O + O_3 \rightarrow 2O_2$  finally stabilizes the odd oxygen. Thus, the observed amount of ozone, if maintained locally by evaporation, would generate  $O_2$  at a

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rate of 1 cm amagat in about 2.5  $\times$ 107 seconds, or 290 days. This rate is large enough so that there might conceivably be some variation in the  $O_2$  abundance from this process, as well as some possible variation in the catalytic effects accompanying the changes of  $H_2O$  concentration. The rough equality of our measurements in the northern and southern hemispheres in February 1972 precludes any drastic north-south variation at that time.

It is of interest to compare the  $O_{2}$ abundance with that of CO, which we take to be  $7.3 \pm 1.0$  cm amagat (23). In a steady state, an initially pure CO<sub>2</sub> atmosphere will yield an  $O_2/CO$  ratio of 0.5, if one neglects all sources and sinks of carbon and oxygen atoms, whereas we find  $O_2/CO = 10.4/7.3 =$  $1.4 \pm 0.3$ . McElroy (24) has calculated that oxygen atoms escape from the martian atmosphere at a rate of about  $6 \times 10^7$  cm<sup>-2</sup> sec<sup>-1</sup> and carbon atoms at a rate of about  $1 \times 10^6$  cm<sup>-2</sup>  $sec^{-1}$ , chiefly on account of energy imparted during dissociative recombination of  $O_2^+$ ,  $CO^+$ , and  $CO_2^+$  ions in the upper ionosphere. These numbers may be compared to the rate of photolysis of  $CO_2$  into CO + O, which is about  $10^{12}$  cm<sup>-2</sup> sec<sup>-1</sup>, on the average, and which must be very nearly balanced by the rate of effective recombination of O and CO. Thus, all oxygen and carbon atoms must pass many times through this cycle during their lifetime in the martian atmosphere. The time required, for instance, to evaporate all the oxygen atoms currently in the atmosphere as  $CO_2$  (about  $4 \times 10^{23}$  cm<sup>-2</sup>) is about  $6 \times 10^{15}$ seconds or about  $2 \times 10^8$  years. The larger loss rate of oxygen atoms, compared to carbon atoms, suggests a deficiency of oxygen rather than the excess that we measure. This in turn suggests the existence of a source of oxygen in the martian atmosphere, other than  $CO_2$  and greater than any other source of carbon. If the evolution of gases from the interior of the planet is like that on the earth, we expect that water will furnish such a source, since water evolves on the earth at a much greater rate than  $CO_2$  (25). As McElroy (24) has shown, such an evolution on Mars could be expected to supply both oxygen and hydrogen at an appropriate rate to keep up with the estimated exospheric escape of these elements.

In summary, we have measured

 $10.4 \pm 1.0$  cm amagat of  $O_2$  in the martian atmosphere, which is consistent with earlier lower limits of detectability and in agreement with the recent results of Barker (26), who obtains  $9.5 \pm 0.6$  cm amagat. This result, along with the estimated CO abundance and exospheric loss rates, indicates that oxygen must have entered or must be entering the martian atmosphere in some form other than  $CO_2$ , with  $H_2O$ being a likely candidate.

> N. P. CARLETON W. A. TRAUB

Smithsonian Astrophysical Observatory and Harvard University, Cambridge, Massachusetts 02138

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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(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  $\delta^{18}O(l)$ 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 18O between SiO., 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  $3 \times 10^9$  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  $3.9 \times 10^{22}$  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  $27 \times 10^{22}$  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 <sup>18</sup>O en-

> 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.

richment of sedimentary rocks. Perry and Tan (2) estimated that igneous (6) and sedimentary rocks of the crust are enriched in <sup>18</sup>O by  $70 \times 10^{22}$  to  $112 \times$ 10<sup>22</sup> 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.

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  $\delta_{\Omega}$  and say they contain  $M_{\Omega}$  moles of <sup>16</sup>O. Process 1 involves oxygen being outgassed from the upper mantle