assumption is questionable.

39. The abundance of water *a* in reservoir two does not vary in this model. Integration of the appropriate differential equation results in

$$\frac{(D/H)_{\text{Mars}}}{(D/H)_{\text{Earth}}} = \frac{1}{f} - \left(\frac{1}{f} - 1\right) e^{-\frac{a_e}{a} f} \qquad (6)$$

for constant escape flux and a more complicated expression for variable flux; $f = 0.79 F$. However, the result is rather insensitive to the adopted temporal dependence of escape flux. Our calculation was made for $\phi(t) = 25\ e^{-t/\tau}$ m per billion years, where $\tau = 1.25$ billion years (Gyr). This relation fits the current escape flux of 1.2 m Gyr^{-1} and the total escape a_e = 30 m. Our model differs from the model (*12*) in which reservoir two is disconnected from reservoir one and gradually shrinks from 3.6 to 0.2 m.

40. Reservoir two may be a part of the polar cap water, which is estimated at 15 m by B. M. Jakosky [*J. Geophys. Res.* **95**, 1475 (1990)]. It should also include some crustal water.

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Atmosphere-Surface Interactions on Mars: $\Delta^{17}O$ Measurements of Carbonate from ALH 84001

James Farquhar, Mark H. Thiemens, Teresa Jackson

Oxygen isotope measurements of carbonate from martian meteorite ALH 84001 ($\delta^{18}O$ = 18.3 ± 0.4 per mil, $\delta^{17}O$ = 10.3 ± 0.2 per mil, and $\Delta^{17}O$ = 0.8 ± 0.05 per mil) are fractionated with respect to those of silicate minerals. These measurements support the existence of two oxygen isotope reservoirs (the atmosphere and the silicate planet) on Mars at the time of carbonate growth. The cause of the atmospheric oxygen isotope anomaly may be exchange between CO_2 and $O(^1D)$ produced by the photodecomposition of ozone. Atmospheric oxygen isotope compositions may be transferred to carbonate minerals by CO_2-H_2O exchange and mineral growth. A sink of ^{17}O-depleted oxygen, as required by mass balance, may exist in the planetary regolith.

Chemical and isotopic measurements of the present-day martian atmosphere indicate that many elements and isotopes are fractionated from their initial compositions (*1*). Modeling suggests that the composition of the martian atmosphere has evolved on planetary time scales as a result of escape processes, impact erosion, outgassing, and photochemical reactions (*2–6*). Morphologic evidence points to times early in martian history when greenhouse heating supported warmer climates and liquid water shaped Mars's surface (*7, 8*). Measurements of trapped gases and mineral phases in martian meteorites indicate that atmospheric evolution occurred before the excavation of these meteorites from the martian surface (*9–15*).

The present martian atmosphere interacts with the hydrosphere and regolith through diurnal, seasonal, and longer term exchange of water between the atmosphere and regolith (*16, 17*). In the past, liquid water acted as a medium for atmosphere-surface exchange and new mineral precipitation. High rates of oxygen exchange between H_2O and CO_2 facilitated the transfer of atmospheric oxygen isotopic characteristics to H_2O and to minerals that precipitated from it. Because oxygen is present in CO_2, H_2O, dust, and other atmospheric constituents such as O_2, CO, and O_3, the oxygen isotope compositions of minerals formed in the regolith serves as a tracer for atmospheric chemistry and evolution and its interactions with the martian surface. Here we report measurements (*18*) of ^{16}O, ^{17}O, and ^{18}O in carbonate minerals from martian meteorite ALH 84001 [$\delta^{18}O$ = 18.3 ± 0.4‰, $\delta^{17}O$ = 10.3 ± 0.2‰, and $\Delta^{17}O$ = 0.8 ± 0.05‰ (*23*)]. High-temperature silicate phases in ALH 84001 give $\delta^{18}O$ = 4.53 to 4.64‰, $\delta^{17}O$ = 2.58 to 2.74‰, and $\Delta^{17}O$ = 0.22 to 0.327‰ (*12*). Secondary ion mass spectrometry analysis of SiO_2 yielded $\delta^{18}O$ = 20.4 ± 0.9‰ (*24*), and analyses of carbonate have yielded $\delta^{18}O$ = –9 to 26‰. The mean of these measurements is 15 ± 5‰ (one 3σ outlier is omitted) (*15, 24–26*). Our $\delta^{18}O$ measurements fall within the range of previous measurements for carbonates but differ from the $\Delta^{17}O$ of the high-temperature silicate phases.

Karlsson *et al.* (*27*) extracted H_2O from six martian meteorites by stepwise pyrolysis and found that the $\Delta^{17}O$ of this water ranged from 0.1 to 0.9‰. H_2O extracted from Nakhla, Lafayette, Chassigny, and Zagami meteorites during 600° and 1000°C pyrolysis steps ($\Delta^{17}O$ = 0.4 to 0.9‰) was fractionated relative to martian meteorite silicates [$\Delta^{17}O \sim 0.3$‰ (*12*)]. The same pyrolysis steps for Shergotty produced H_2O unfractionated with respect to martian meteorite silicates, and for meteorite EETA 79001 they produced H_2O with $\Delta^{17}O$ = 0.1‰, which is intermediate between terrestrial waters ($\Delta^{17}O$ = 0) (*11*) and martian meteorite silicates. These results (*27*) were interpreted to indicate that H_2O extracted from Nakhla, Lafayette, Chassigny, Zagami, and Shergotty had a martian origin and that H_2O extracted from EETA 79001 was a mixture of martian and terrestrial waters. Because water extracted from Nakhla, Lafayette, Chassigny, and Zagami was not in oxygen isotopic equilibrium with martian meteorite silicate minerals, two distinct oxygen reservoirs were inferred to be present on Mars—the silicate planet (the crust and mantle) and the atmosphere (including H_2O that exchanged oxygen with it).

Our measurements of carbonates ($\Delta^{17}O$ = 0.8‰) are fractionated relative to measurements of martian meteorite silicates and indicate that ALH 84001 also preserves evidence of oxygen isotope disequilibrium between the atmosphere and the silicate planet. Carbonate nodules in ALH 84001 preserve chemical and isotopic gradients (*24, 25, 28*) that would have been homogenized by diffusion and exchange if post-growth reequilibration occurred. Our oxygen isotope data therefore indicate that the atmosphere and lithosphere were out of isotopic equilibrium at the time of carbonate growth.

On Earth, plate tectonics facilitates oxygen exchange between the hydrosphere and lithosphere through global-scale hydrothermal circulation systems at plate margins. Because the amount of oxygen in the silicate Earth is greater than that in the hydrosphere and atmosphere, this exchange buffers the oxygen isotope composition of the hydrosphere (*29*). The oxygen isotope composition of water in Earth's oceans is buffered to a steady-state value on a time scale with a mean life (1/rate constant) of ~100 to 250 million years (*29*). The lack of plate tectonics on Mars is seen as a means of maintaining an atmosphere that is isotopically distinct from the solid planet (*27*). It is unclear whether other types of hydrothermal activity may have caused sufficient atmosphere-surface oxygen exchange to affect atmospheric $\delta^{18}O$, $\delta^{17}O$, and $\Delta^{17}O$. Massive hydrothermal systems have been invoked to explain surface features associated with the Oceanus Borealis and spectroscopic features in the Valles Marineris canyon system (*7, 30*) and also as a means of generating catastrophic floods and release of CO_2 of sufficient quantity to stabilize episodic, greenhouse-state, atmospheric conditions with higher CO_2 pressure (*7*). If these

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Department of Chemistry, University of California San Diego, 92093-0356, USA. E-mail: jfarquha@ucsd.edu (J.F.), mht@ucsd.edu (M.H.T.), tjackson@ucsd.edu (T.J.)

processes released CO_2 and H_2O with juvenile composition in amounts comparable to the atmospheric burden, they might affect the oxygen isotopic composition of the atmosphere.

Hydrothermal interactions have been invoked to explain differences between the $\Delta^{17}O$ data of (*27*) and the H/D data of martian meteorite waters extracted in a second set of pyrolysis experiments (*14*). It has been suggested that hydrogen and oxygen isotope systematics may have been decoupled during martian hydrothermal interactions in the same way that they are decoupled in meteoric hydrothermal systems (*14, 31*). Because the relative H/O ratio of hydrothermal fluids is much greater than the H/O ratio in silicate rock, the hydrothermal fluid $\Delta^{17}O$ will approach the value of the rock for much lower fluid/rock than does the fluid D/H ratio. For a ^{17}O- and D-enriched atmosphere, these interactions should produce positively correlated D/H ratios and $\Delta^{17}O$ for both fluid and rock. The pyrolysis data (*14, 27*) form a negatively correlated array with a low-D/H, high-$\Delta^{17}O$ end member and a high-D/H, low-$\Delta^{17}O$ end member (Fig. 1). Although hydrothermal decoupling of D/H from $\Delta^{17}O$ is an inevitable consequence of martian hyrothermal interactions, the negatively correlated array cannot be interpreted solely in this context. We suggest that this negatively correlated array reflects the operation of additional processes—secular changes that occurred in martian atmospheric D/H and $\Delta^{17}O$ as a result of the mixing of evolved and juvenile oxygen-bearing and hydrogen-bearing reservoirs.

Yung and others (*2*) have modeled the evolution of the D/H ratio by Jeans escape. The present atmospheric burden of H_2O is sufficiently low to accommodate evolution from D/H ~ 0 to the present atmospheric D/H in $\sim 10^5$ years (*2*). To extend this time scale to the 4.5-billion-year planetary time scale requires an initial column of 3.6 m and a present column of 0.2 m of exchangeable water (*2*), an amount that is less than the total water budget inferred on the basis of geomorphological features (*7, 8, 17*). The amount of exchangeable water has changed on planetary time scales (*7, 8*) and may change episodically on time scales of 10^5 to 10^7 years as a result of orbital changes and concomitant mobilization of water trapped in the polar caps and of injection of juvenile waters by floods and volcanic activity (*32*). The atmospheric D/H ratio would undergo secular variations if the size of the exchangeable H_2O reservoir changed by an equal or greater amount than itself on time scales $<10^5$ years. Because there is more oxygen in the atmosphere than hydrogen, atmospheric $\Delta^{17}O$ is more difficult to change than the D/H ratio but may also have been influenced by changes in the size of the exchangeable oxygen-bearing reservoir.

Suggestions to explain the evolution of atmospheric $\Delta^{17}O$ include an atmosphere that originated as a late cometary or meteoritic veneer (heterogeneous accretion), an atmosphere whose composition evolved as a result of escape processes, and an atmosphere that evolved as a result of photochemical reactions (*5, 6, 27*). No direct tests exist to support the possibility that atmospheric $\Delta^{17}O$ was produced by heterogeneous accretion.

Oxygen isotope fractionations produced by gravitational separation above the homopause, followed by escape at the exobase, raise atmospheric $\delta^{18}O$, $\delta^{17}O$, and $\Delta^{17}O$ (*5*). Given the range of atmospheric parameters determined for Mars (*1, 5*), isotopic fractionations produced by this process predict an increase in $\delta^{18}O$ of ~15 to 50‰ for a $\Delta^{17}O$ enrichment of 0.5‰. The $\delta^{18}O$ of H_2O and carbonates in ALH 84001 do not support an enrichment of ~50‰ in atmospheric CO_2. Smaller $\delta^{18}O$ enrichments are not supported unless the balance of exchangeable H_2O is much smaller than even the H_2O/CO_2 ratio in the present-day martian atmosphere and polar caps, because H_2O-CO_2 exchange can account for the $\delta^{18}O$ enrichments observed in ALH 84001 carbonates.

Oxygen isotope fractionations produced by atmospheric gas-phase mass-independent chemistry on Earth produce positive $\Delta^{17}O$ values in stratospheric CO_2 (*6, 33*). For the martian atmosphere, the requirements for production of positive $\Delta^{17}O$ values are the presence of ultraviolet (UV) radiation, O_3 chemistry, CO_2-$O(^1D)$ chemistry, and a negative $\Delta^{17}O$ sink. Because of the thinness of the martian atmosphere, UV radiation has been sufficient to cause O_3 chemistry throughout the martian atmospheric column throughout martian history. CO_2-$O(^1D)$ chemistry follows from photodecomposition of O_3 and CO_2, with net production of ^{17}O-enriched CO_2 and ^{17}O-depleted O_2.

Many reactions may have contributed to the observed $\Delta^{17}O$ values of martian meteorite waters and carbonates. We suggest that the predominant reactions responsible for producing the observed anomaly are as follows: a1: $CO_2 + h\upsilon \rightarrow CO + O(^3P)$, wavelength ($\lambda$) < 227.5 nm; a2: $\rightarrow CO + O(^1D)$, $\lambda < 167$ nm; b1: $O(^3P) + O(^3P) + M \rightarrow M + O_2$; b2: $O(^3P) + OH \rightarrow H + O_2$; b3: $O(^3P) + NO_2 \rightarrow NO + O_2$; c: $O_2 + O(^3P) + M \rightarrow O^{\#}_3 + M$; d: $O^{\#}_3 + h\upsilon \rightarrow O^{\#}(^1D) + O_2$, $\lambda < 310$ nm; e: $O^{\#}(^1D) + CO_2 \leftrightharpoons CO^{\#*}_3 \leftrightharpoons CO^{\#}_2 + O(^3P)$, exchange reaction; f: $CO^{\#}_2 + H_2O \leftrightharpoons H_2CO^{\#}_3 \leftrightharpoons CO_2 + H_2O^{\#}$, exchange reaction, where $h\upsilon$ denotes the energy of a

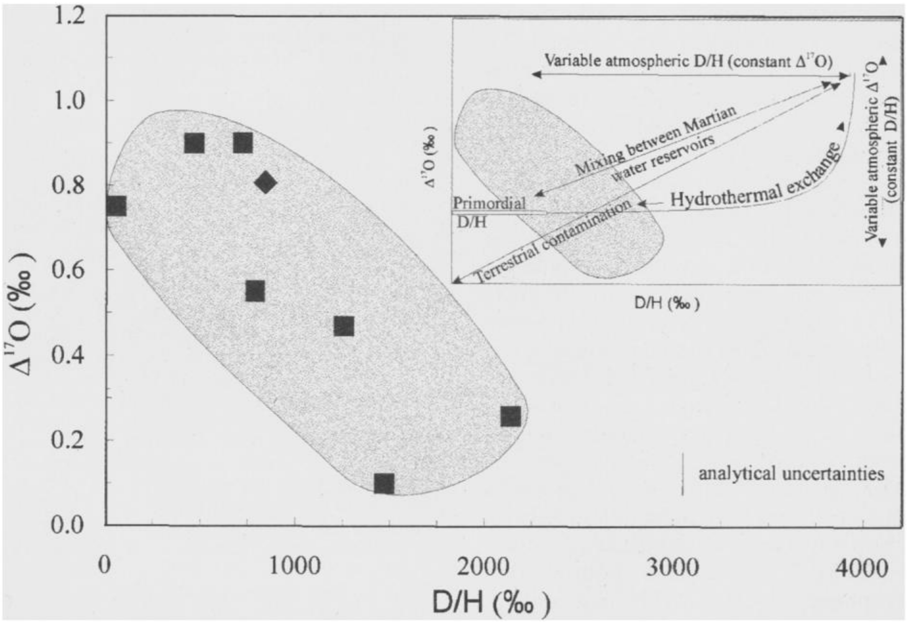

Fig. 1. Plot of maximum values of D/H versus $\Delta^{17}O$ for martian meteorite H_2O (■) extracted by pyrolysis (*14, 27*) and carbonate (◆) $\Delta^{17}O$ data versus pyrolysis D/H data from (*14*). Note that D/H and $\Delta^{17}O$ were collected in different sets of experiments. The H_2O and the carbonate data form a negatively sloped array. Assuming the martian atmosphere has elevated D/H and $\Delta^{17}O$, positively sloped arrays would be predicted by simple mixing with terrestrial waters (terrestrial contamination arrays), hydrothermal exchange, or mixing of juvenile and evolved martian reservoirs. Variable atmospheric D/H ratios would produce horizontal arrays, and variable atmospheric $\Delta^{17}O$ would produce vertical arrays. The primordial D/H field is from (*13*).

photon of frequency υ, # denotes isotopically anomalous oxygen, and * denotes electronically excited states. Reactions a1 and a2 are CO_2 photodissociation reactions. Reactions b1 through b3 are responsible for production of O_2 in the martian atmosphere. Reaction c, an ozone formation reaction, has an associated mass-independent fractionation of ~100‰ in $\delta^{17}O$ and $\delta^{18}O$. Reaction d, an ozone photodissociation reaction, may transfer this mass-independent anomaly to $O(^1D)$. Reaction e is the exchange reaction between $O(^1D)$ and CO_2 but may have a mass-independent fractionation associated with the CO^*_3 transition state, which would only require the presence of $O(^1D)$, such as in reaction a2. Reaction f is the CO_2-H_2O oxygen exchange reaction. Two possible sources of the isotopic anomaly in CO_2 include the combined action of reactions c and d, or a2, and reaction e.

Photochemical production of $O(^1D)$ by ozone or CO_2 photolysis and subsequent exchange with CO_2 provides a mechanism for generating a 0.5‰ increase in $\Delta^{17}O$ in the martian atmosphere with only a ~1‰ increase in $\delta^{18}O$. A requirement of this model is that there be a corresponding sink for a negative $\Delta^{17}O$ atmosphere-surface system. O_2 is the atmospheric species that acquires negative $\Delta^{17}O$, but in the martian atmosphere there is only sufficient O_2 to accommodate a $\Delta^{17}O$ enrichment of 0.1‰ (assuming a CO_2-O_2 exchange value for $\Delta^{17}O$ of ~50‰). Another possibility is that a sink for O_2 with negative $\Delta^{17}O$ exists. An oxidized sink of ~100 mg/cm^2 in the martian regolith (ferric? oxides and hydroxides) with $\Delta^{17}O \sim -0.5$‰ would accommodate atmospheric $\Delta^{17}O$ of ~ 0.5‰.

We suggest that mass-independent chemistry and oxidation of the martian regolith may be the principal reason for the positive $\Delta^{17}O$ of the martian atmosphere at the time of carbonate growth in ALH 84001. A 0.5‰ contribution to positive atmospheric $\Delta^{17}O$ by escape processes is not supported by the $\delta^{18}O$ of ALH 84001 carbonates. Models that explain positive atmospheric $\Delta^{17}O$ by heterogeneous accretion are not required and cannot be tested directly. Operation of the former processes permits temporal variations of atmospheric $\Delta^{17}O$ if the size of exchangeable O reservoirs varied. Temporal changes in martian atmospheric $\Delta^{17}O$ and D/H may explain the negative correlation between the D/H ratio and $\Delta^{17}O$ of martian meteorite carbonate and H_2O extracted by (*14*, *27*). Tests of these hypotheses include oxygen isotope and D/H analyses of additional secondary phases in martian meteorites and samples of atmosphere, soil, and ice to be returned from Mars.

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18. One hundred ninety-three milligrams of coarsely ground ALH 84001.137 was loaded into a reaction vessel containing 10 ml of 100% H_3PO_4 (density ρ = 1.932 g/cc). The sample was outgassed at 25°C for 7 days and reacted at 25.1°C for 24 hours to remove $CaCO_3$ according to a procedure similar to that in (*19*). One micromole of condensible gas was evolved. The sample was subsequently heated to 150°C in an oil bath for 3 hours while connected online to a liquid N_2-chilled trap; 6.5 mmol of condensible gas evolved in this reaction were purified at –80°C. This 6.5-mmol sample of CO_2 was purified by gas chromatography, using a Varian 3600 gas chromatograph equipped with a packed Alltech Hayesep Q column 8 inches long with an inside diameter of 1/8 inch. The sample was then transferred to a Ni reaction tube along with an excess amount (1000 times) of precooked (for 120 min at 800°C) BrF_5. The mixture was reacted for 45 hours at 800°C (*20*). O_2 and CF_4 were separated in a U-Trap filled with molecular sieve 13X (60/80 mesh) at –116.5°C for 68 min. $\delta^{18}O$ and $\delta^{17}O$ were measured with a Finnigan MAT 251 mass spectrometer. Isotopic compositions are reported relative to standard mean ocean water (SMOW), assuming the fractionation factors of (*21*). Our collection scheme was slightly different from (*21*), which may introduce a small change to the $\delta^{18}O$ value. The fractionation factor for ^{17}O was assumed to be $a^{0.52}$. Three measurements of 5- to 18-μmol samples of calcite SRM NBS-18 yielded $\delta^{18}O = 6.8 \pm 0.4$‰, $\Delta^{17}O = 3.6 \pm 0.2$‰, and $\Delta^{17}O = 0.05 \pm 0.03$‰. The accepted value of SRM NBS-18 is 7.20‰. (*22*). Procedural blanks are difficult to determine. Estimates of the contribution of blank are equal to or less than 0.1 mmol of CO_2 for the acidification and gas purification steps and less than 0.2 μmol for the fluorination procedure (determined from the final oxygen yield).
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