Reports

Water in SNC Meteorites: Evidence for a Martian Hydrosphere

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The Shergotty-Nakhla-Chassigny (SNC) meteorites, purportedly of martian origin, contain 0.04 to 0.4 percent water by weight. Oxygen isotopic analysis can be used to determine whether this water is extraterrestrial or terrestrial. Such analysis reveals that a portion of the water is extraterrestrial and furthermore was not in oxygen isotopic equilibrium with the host rock. Lack of equilibrium between water and host rock implies that the lithosphere and hydrosphere of the SNC parent body formed two distinct oxygen isotopic reservoirs. If Mars was the parent body, the maintenance of two distinct reservoirs may result from the absence of plate tectonics on the planet.

RECENT EVIDENCE SUGGESTS THAT the planet Mars once had a water-rich atmosphere and flowing water on its surface. However, at some stage in its history, most of the water vanished, so that the surface of the planet is now devoid of liquid water and the atmosphere contains only minute amounts of water vapor (*1–3*). Because water plays a pivotal role in most geological processes, it is important to obtain further information about this ancient water for a better understanding of the geological history of Mars.

To shed further light on the nature of water on Mars, we have measured the oxygen isotopic composition of water extracted from six meteorites of the SNC group. Many lines of evidence, such as their young crystallization ages compared to that of other meteorites and compositions of trapped volatiles that match those of the martian atmosphere, suggest that these objects came from Mars (*4–6*). Earlier stable isotopic studies of water from SNCs have concentrated on measuring D/H ratios, but results are conflicting and researchers have not been able to show whether the water is extraterrestrial (*7–10*). In this work, we studied the isotopic composition of oxygen because the systematics of its three isotopes can be used to identify unequivocally extraterrestrial material.

We extracted water from six SNC meteorites, using vacuum pyrolysis. Samples of each meteorite, ranging from 2.0 to 3.4 g, were ground in a sapphire mortar under air and loaded into a reaction tube made of low-water fused silica. A fresh reaction tube was used for each run. The charged tube was attached to a high-vacuum line, evacuated overnight at room temperature, and then heated stepwise to 150°, 350°, 600°, and 1000°C. The charges were held at each temperature for 1 hour. Volatiles evolved in each heating step were condensed in a cold trap at liquid nitrogen temperature. Water was cryogenically separated from other volatiles and converted quantitatively to oxygen with the use of BrF_5 (*11*). The isotopic composition of this oxygen was determined on a double-collecting isotope ratio mass spectrometer to yield $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios (*12*). Isotopic results are displayed in δ-notation (*13*). Data are summarized in Table 1 and Figs. 1 through 3.

The shergottites (EETA-79001A, Shergotty, and Zagami) contain less water than the nakhlites (Lafayette and Nakhla) or Chassigny (Table 1). In all, 70 to 80% of the water was evolved in the first two steps, 15 to 25% in the third step, and 5 to 15% in the final step. Water from SNC meteorites may have several sources: (i) adsorbed H_2O on grain surfaces and boundaries, (ii) hydrated minerals, and (iii) water dissolved in small pockets of interstitial glass. Two kinds of hydrous minerals have been observed: low-temperature alteration products such as gypsum and iddingsite and high-temperature igneous minerals such as amphibole and mica (*14–18*). Amphibole and gypsum have been detected in all the SNCs, iddingsite in the nakhlites only, and mica in Chassigny. During heating, the water that is most loosely bonded and thus most readily exchanged with external water comes off in the lower temperature fractions; the most strongly bonded and least readily exchangeable water comes off in the higher temperature steps. Most adsorbed water is released during the room-temperature outgassing and in the 150°C step. Water from the breakdown of minerals is produced over a wide range of temperatures, depending on the mineral. Gypsum dehydrates up to 230°C (*19*). The iddingsite appears to be a mixture of clays, iron oxides (*20*), and possibly chlorite. Clay minerals lose their interlayer water at low temperatures and then lose structural hydroxyl at temperatures ≥600°C (*21*). Amphiboles, most chlorites, and micas also lose their water (dehydroxylate) at temperatures ≥600°C (*21, 22*). Glass dehydrates above 600°C. In terms of abundance, the high-temperature hydrous phases are sparse compared to the low-temperature phases. Most of the water, especially in the nakhlites and Chassigny, is therefore probably derived from alteration minerals rather than from high-temperature phases.

Clayton and Mayeda (*12*) showed that oxygen isotope ratios of SNC whole rocks lie on a mass fractionation line parallel to the terrestrial line on a three-isotope plot, with an average $\Delta^{17}O$ excess ($\Delta^{17}O = \delta^{17}O - 0.52\delta^{18}O$) of +0.3 per mil relative to that of Earth (Fig. 1). Our ability to resolve sam-

Table 1. SNC sample sizes and water abundances (percent by weight) as a function of temperature.

Sample	Weight (g)	Water content (%)				
		150°C	350°C	600°C	1000°C	Total
EETA-79001A	3.06	0.026	0.024	0.009	0.005	0.064
Shergotty	3.09	0.016	0.022	0.015	0.011	0.064
Zagami-1	2.93	0.014	0.015	0.007	0.006	0.042
Zagami-2	3.43	0.012	0.015	0.008	0.008	0.043
Nakhla	2.09	0.042	0.045	0.023	0.003	0.114
Lafayette	2.99	0.136	0.131	0.091	0.029	0.387
Chassigny	2.07	0.030	0.036	0.028	0.007	0.102

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ples from the terrestrial line is ±0.1 per mil (2σ).

The $\delta^{18}O$ values of the SNC waters change as a function of pyrolysis temperature (Fig. 2). Overall, the waters have a much wider range of $\delta^{18}O$ values than the bulk rocks (whole rock: 3.9 to 5.6 per mil), and there is a wide variation among waters from individual meteorites. The two replicate Zagami samples show that the reproducibility of our method is good. One might expect that with increasing temperature the waters extracted would approach isotopic equilibrium with the host rock and thus have values close to that of the bulk rock ($\sim+5$ per mil). Clearly, such was not the case. Except for Lafayette, the waters extracted in the 600° to 1000°C fraction are not in isotopic equilibrium with the host rock. The nonequilibrium effects must be related to the pyrolysis process because similar data were also obtained for a terrestrial control sample (Fig. 2B). The dehydration process evidently has a large kinetic isotope effect favoring light isotopes in the evolved water. Thus the $\delta^{18}O$ of martian water reservoirs cannot be determined from our data. These dehydration effects follow a mass-dependent fractionation pattern and therefore do not alter the $\Delta^{17}O$ excess of original hydroxyl or water. In spite of possible kinetic isotope effects, EETA-79001A is clearly set apart from the other samples by its overall lower $\delta^{18}O$ values in all water fractions (Fig. 2A). Inasmuch as this meteorite was in contact with Antarctic ice [$\delta^{18}O = \sim-40$ per mil (*23*)] for at least tens of thousands of years before it was collected (*24, 25*), it is plausible that the original $\delta^{18}O$ values have been lowered by terrestrial weathering.

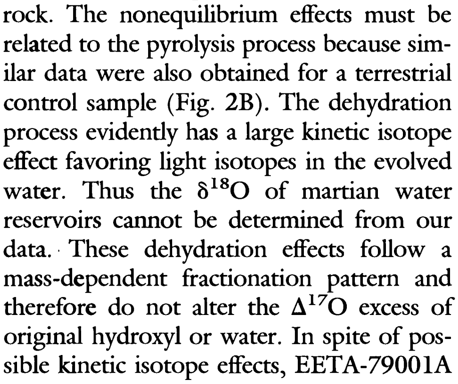

Fig. 1. Oxygen three-isotope graph showing whole-rock SNC samples. Each SNC meteorite is denoted by its initial letter. "A" or "B" enclosed in parentheses next to letter E refers to lithology A or B of EETA-79001. The whole-rock data lie significantly above the line defined by terrestrial materials. The solid line marked "SNC (Mars?)" drawn through the whole rocks is parallel to the "Earth" line but shifted by 0.3 per mil to higher $\delta^{17}O$ values.

Different behavior on the $\Delta^{17}O$ plot (Fig. 3) is expected for the different possible sources of water in each meteorite. Adsorbed water, readily exchanged with terrestrial water, should have $\Delta^{17}O = 0$, as is seen for the data from most of the low-temperature extractions and for the terrestrial control sample (Fig. 3B). Magmatic water derived from dehydration of primary high-temperature minerals or glass from SNC meteorites should have $\Delta^{17}O$ of 0.3 ± 0.1 per mil, the value found for the igneous silicates. The data that conform most closely to this pattern are those from Zagami (Fig. 3A). Terrestrial weathering products of meteoritic minerals should yield water with $\Delta^{17}O$ between 0.0 and 0.3 per mil, as is seen for the data from Shergotty and EETA-79001A (Fig. 3A). The most surprising and interesting data are those in which the evolved water has $\Delta^{17}O > 0.4$ per mil (Chassigny, Nakhla, Lafayette, and possibly Zagami). These data imply that some water was contributed from an additional extraterrestrial reservoir that was not in isotopic equilibrium with the rock material of the SNC parent body. The plausible choices are either the impactor that ejected the meteoroids from their parent or a parent-body surface reservoir (atmosphere or hydrosphere) that had evolved independently of the lithosphere. Because Nakhla, the meteorite that showed the largest ^{17}O excess, contains abundant iddingsite as a weathering product that formed at low temperature (*20*), it is probable that all the ^{17}O excesses observed in water from SNCs are derived from a martian surface reservoir.

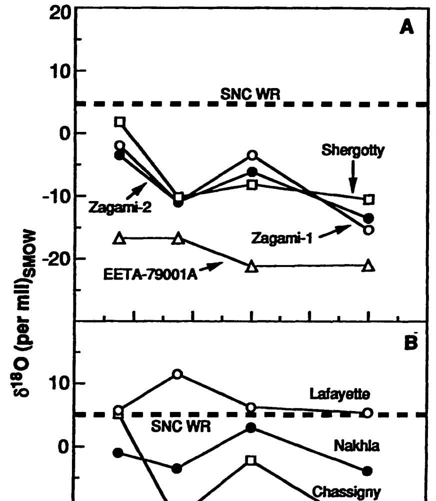

Fig. 2. $\delta^{18}O$ of SNC waters and control sample waters as a function of pyrolysis temperature. The dotted line in both panels shows the composition of whole-rock SNC samples. (**A**) Shergottites. (**B**) Nakhlites, Chassigny, and a terrestrial control.

The presence of an ^{17}O excess in some of the SNC meteorites implies that there were at least two distinct oxygen isotopic reservoirs on the SNC parent body (Mars). This isotopic difference may have arisen during accretion of the parent body or after accretion during the evolution of the atmosphere. The most likely source of the ^{17}O excess is the hydrosphere because water in the SNCs is mostly in the form of aqueous alteration products. Two scenarios arise. The hydrosphere and the lithosphere could have evolved separately from isotopically distinct reservoirs during accretion and remained decoupled thereafter. Many proposals for planetary accretion require separate volatile-poor and volatile-rich components. Such components are likely to have differed in

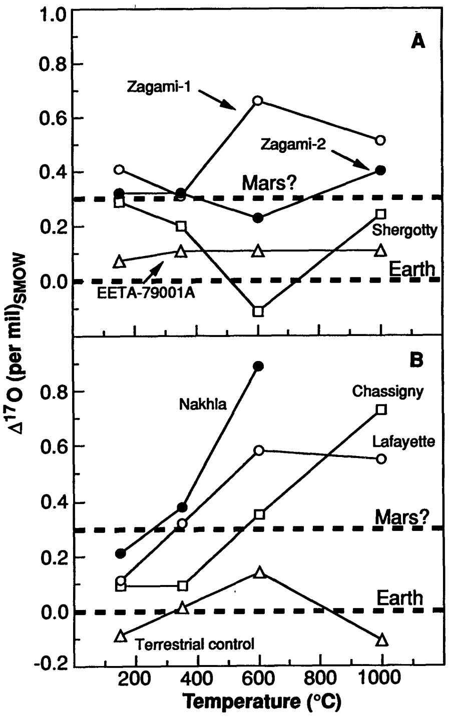

Fig. 3. $\Delta^{17}O$ of SNC waters and a control sample as a function of pyrolysis temperature. The dotted lines show the ^{17}O excesses on Earth (0.0 per mil) and on the SNC parent body (0.3 per mil, Mars?). (**A**) Shergottites. (**B**) Nakhlites, Chassigny, and a terrestrial control. Waters entirely of terrestrial origin fall within ±0.1 per mil of the Earth line, whereas waters entirely of martian origin fall within ±0.1 per mil of the Mars line. Samples that are mixtures of the two fall between these limits. Some SNC waters, especially those from Chassigny, Lafayette, and Nakhla, have ^{17}O excesses markedly higher than those indicated by their respective whole-rock values, showing that these waters have not reached oxygen isotopic equilibrium with their host rock.

oxygen isotopic composition, as do meteorites of different classes. Mars, in contrast to Earth, lacks plate tectonics, the mechanism by which isotopic homogenization occurs on Earth. For example, Muehlenbachs and Clayton (*26*) found that terrestrial oceans are buffered to a relatively constant oxygen isotopic composition by exchange between seawater and basalt at midocean ridges where the plates are being generated. Thus the whole ocean is cycled through the oceanic crust in a few million years; as a result, any isotopic anomalies that might have been present between the hydrosphere and lithosphere on Earth were quickly erased.

Alternatively, the hydrosphere on Mars could initially have been in equilibrium with the lithosphere but changed its composition over time as a result of the influx of isotopically distinct material such as comets. A change in the isotopic composition of the atmosphere (and hydrosphere) may also have resulted from photochemical processes leading to loss of oxygen from the planet. Some such processes are known to have anomalous oxygen isotopic behavior (*27*) and may lead to non–mass-dependent isotope fractionation in the ozone chemistry of Earth's atmosphere (*28*). Again the two reservoirs could have remained separate because an efficient mixing mechanism such as plate tectonics was lacking.

A discussion of such processes, in the context of a comprehensive model for interpretation of hydrogen, carbon, and oxygen isotope abundances in the martian surface reservoir, has been presented by Jakosky (*29*). The present work provides some of the necessary input data for further development of such models.

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$Ti_8C_{12}^+$–Metallo-Carbohedrenes: A New Class of Molecular Clusters?

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During the course of studying the dehydrogenation reactions of hydrocarbons by titanium atoms, ions, and clusters, an exceptionally stable and abundant cluster which contains 8 titaniums and 12 carbons was discovered. "Titration" reactions with ND_3 reveal the uptake of eight molecules, pointing to the fact that the titanium atoms are at exposed positions of similar coordination. A dodecahedral structure of T_h point group symmetry is proposed to account for the unusual stability of this molecular cluster. The $Ti_8C_{12}^+$ dodecahedron has 12 pentagonal rings and each of the rings is formed by two titanium and three carbon atoms, where each titanium is bound to three carbons. Based on the model, it is expected that neutral Ti_8C_{12} would be a stable metallo-carbododecahedral molecule and may comprise one member of a new class of molecules, namely metallo-carbohedrenes.

HEREIN WE REPORT EVIDENCE OF a class of cage-like molecular clusters, namely metallo-carbohedrenes. During the course of detailed studies made in our laboratory to investigate dehydrogenation reactions of hydrocarbons induced by metal ions, atoms, and clusters (*1*), we discovered the formation of an unusually abundant and stable cationic species with a molecular weight of 528 atomic mass units (amu), which we have now established as containing 8 titanium atoms and 12 carbons. The evidence for our findings and a suggested structure (see Fig. 1) are the subject of this report.

The reported observation of the molecule C_{60} (*2*) has prompted extensive activity in fullerenes and related carbon-cluster research (*3, 4*). A group at AT&T Bell Laboratory reported the successful doping of alkali metal atoms into C_{60} crystals to produce a new superconductive material (*5*). Smalley and co-workers obtained evidence for the incorporation of lanthanium in the interior of C_{60} (*6*), a structure that has been born out by more extensive studies. Also, other researchers have reported the ability to incorporate He^+ within the fullerene ball (*7*). In addition to the above doping, Smalley's group (*8*) has found that a few carbon atoms in C_{60} can be replaced by nonmetal boron elements in the C_{60} cage without substantially destabilizing the entire fullerene. However, to the best of our knowledge, cage-like molecules that we term metallo-carbohedrenes, in which a number of metal atoms incorporate with carbons to form a symmetrical network, have not been reported heretofore.

The experimental method employed in the present work is based on our newly developed MS/MS system which we have described elsewhere (*1*). The new molecular cluster that we report here was generated through reactions of titanium with any of the following vapors: CH_4, C_2H_2, C_2H_4, C_3H_6, or C_6H_6. The details of the experiments will be given elsewhere (*9*).

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