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MARTIAN CARBON DIOXIDE: CLUES FROM ISOTOPES IN SNC METEORITES;

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INTRODUCTION. Attempts to unravel the origin and evolution of the atmosphere and hydrosphere on Mars from isotopic data have been hampered by the impreciseness of the measurements made by the Viking Lander and by Earth-based telescopes. The SNC meteorites which are possibly pieces of the Martian surface offer a unique opportunity to obtain more precise estimates of the planet's volatile inventory and isotopic composition. Recently, we reported results on oxygen isotopes of water extracted by pyrolysis from samples of Shergotty, Zagami, Nakhla, Chassigny, Lafayette and EETA-79001 [1]. Now we describe complementary results on the stable isotopic composition of carbon dioxide extracted simultaneously from those same samples. We will also report on ^{14}C abundances obtained by accelerator mass spectrometry (AMS) for some of these CO_2 samples.

METHODS. After overnight evacuation at room temperature, powdered samples of Chassigny (2.0 g), EETA-79001 (lith A: 3.1 g; lith B: 3.2 g), Lafayette (3.0 g), Nakhla (2.1 g), Shergotty (3.1 g) and Zagami (2.9 g, 3.4 g) were heated under high vacuum and the volatiles evolved condensed into a cold-trap at -209°C. Non-condensable gases were discarded. Each sample was heated step-wise to 150°C, 350°C, 600°C and 1000°C, and held at those temperatures for 1 hr. Carbon dioxide was cryogenically separated from water by warming the cold-trap up to -79°C. The CO_2 was purified by exposing it to silver phosphate and by repeated passes through a cold-trap at -130°C. Finally it was isotopically analyzed on a triple-collecting ratio mass spectrometer.

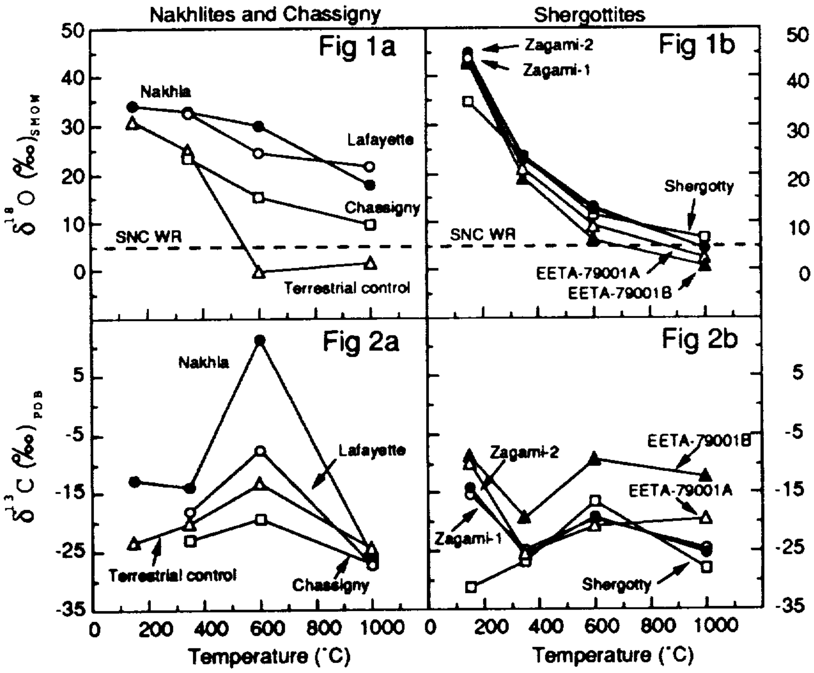
RESULTS. Total carbon dioxide yields (wt%) were: Chas., 0.082; EETA-79001A, 0.036; EETA-79001B, 0.046; Laf., 0.211; Nak., 0.125; Sher. 0.088; Zag., 0.064, 0.049. The shergottites (EETA-79001A, B, Shergotty, Zagami) were generally lower in total carbon contents than the nakhlites (Lafayette, Nakhla) and Chassigny. In contrast to water, carbon dioxide yields for individual samples increased at higher extraction temperatures. The quantity of gas collected per temperature step ranged from 0.2 to 50 μmol CO_2 - well above blank levels (0.007 to 0.021).

Isotopic results for CO_2 analyses, as a function of pyrolysis temperature, are summarized in Figs. 1 and 2. Fig. 1 shows the variation in $\delta^{18}O$ values of the SNC. The oxygen isotopic composition varies from 1 to 45‰, and there is a wide variation within individual meteorites. $\delta^{18}O$ values generally decrease with increasing temperature.

Fig. 2 shows the variation in $\delta^{13}C$ values of the SNC. Carbon isotopic ratios range from -31‰ to +11.4‰. Although there is considerable variation in $\delta^{13}C$ values at each temperature cut, the largest variation is clearly in the 350-600°C step. In Chassigny, Shergotty and the nakhlites the $\delta^{13}C$ values peak in 350-600°C step. This peak is most pronounced in Nakhla and appears to be a charateristic feature of this meteorite since it has been observed in a similar temperature range by most workers [3, 4, 5, 6]. Except for 350-600°C step in Nakhla all the $\delta^{13}C$ values are negative. With the exception of EETA-79001 the highest temperature cuts have $\delta^{13}C$ values of -25±1‰. Comparison of our yield or isotopic results with those of other workers are not straight forward since they either used smaller samples or combustion techniques. The only studies that allow direct comparison are those of Watson et al. who studied Nakhla [3, 4]. Our data for Nakhla are in reasonable agreement with theirs.

DISCUSSION. It is clear from Fig. 1 that the $\delta^{18}O$ of CO_2 decreases with temperature because it approaches oxygen isotopic equilibrium with the bulk rock (+4 to 5‰). Similar results were obtained for a terrestrial control sample. The shergottites have suffered greater exchange than Chassigny and the nakhlites possibly reflecting the lower volatile content of the shergottites. Karlsson et al [1], reported that $\delta^{18}O$ values of some SNC water decrease with temperature and attributed this behavior to kinetic isotope effects. However, in light of the $\delta^{18}O$ data for the CO_2 it is evident that the $\delta^{18}O$ of the water is affected by isotopic exchange with the carbon dioxide that evolves simultaneously. Thus, we find that for each SNC meteorite the $\Delta^{18}O(CO_2\text{-}H_2O)$ systematically decreases as a function of temperature. The observed $\Delta^{18}O$ values are generally higher than theoretical equilibrium values for the same temperature range. The most plausible explanation is that the two gases equilibrated to a lower temperature once they evolved out of the hot region of the sample tube before they were quenched in the cold-trap. Since the molar CO_2/H_2O ratio per cut (0.002 to 10.6) increases with increasing temperature the water is most affected at higher tempertures. Because of the oxygen isotope exchange among CO_2, H_2O and residual silicates during extraction, information on values of the Martian atmospheric gases is lost. However, $\Delta^{17}O$ values may be retained as discussed in Karlsson et al. [1].

The simplest interpretation of the carbon isotope data (Fig. 2) is that they represent contributions of carbon from four distinct sources: the terrestrial atmosphere, the terrestrial biosphere, the Martian atmosphere and the Martian mantle. Carbon extracted in the two lowest temperature steps (24-350°C) is thus mostly likely to a mixture of adsorbed terrestrial CO_2(-7‰) and terrestrial organic matter (-26‰), whereas the highest temperature step (600-1000°C) is most likely to be dissolved Martian magmatic carbon which according to Wright et al. [5] has a $\delta^{13}C$ between -20 and -30‰. Our data show a tight cluster around -25±1‰ suggesting a more uniform $\delta^{13}C$ for the Martian mantle. The 350-600°C step may represent a mixture of a Martian atmospheric carbon and terrestrial sources. Carbonates decrepitate in this temperature range under vacuum. The high Nakhla $\delta^{13}C$ value, +11.4 ‰, is most likely associated with the breakdown of carbonate which is known to be abundant in the meteorite [6]. Wright et al. [5] reported slightly lower $\delta^{13}C$ values of +6 to +9‰ for Nakhla carbonate. ^{14}C data obtained by AMS on Nakhla carbonate suggest a preterrestrial origin. If the 11.4‰ value for Nakhla is due to carbonate, then it is possible to estimate a $\delta^{13}C$ value for the Martian atmosphere. Assuming that the carbonate was calcite and formed in equilibrium at 0°C with Martian CO_2 then the $\delta^{13}C$ value of Martian CO_2 would have to be at about 0‰. This result suggests that the atmosphere may be more enriched in ^{13}C than the Martian mantle. As in the case of the oxygen isotope results for SNC waters reported by Karlsson et al. [1], this difference in carbon isotopes may be due to lack of interaction between the atmosphere and lithosphere on Mars because of the absence of plate tectonics on the planet and might imply either an extraplanetary origin for the atmospheric CO_2 or heavy-isotope enrichment of the atmosphere due to preferential exscape of ^{12}C compounds to space [7].



CONCLUSIONS. During pyrolysis of SNC meteorites, CO_2 may experience considerable oxygen isotopic exchange with the host rock, particularly at high temperatures. As CO_2 and H_2O evolve out of the samples they also exchange oxygen isotopes. Great care must therefore be taken in interpreting oxygen isotope values for these gases when using pyrolysis. Shergottites are intrinsically lower in H_2O and CO_2 than Chassigny and the Nakhlites and hence the oxygen isotopic composition of these gases in shergottites are more likely to be altered by isotopic exchange with the host rock. This may explain why the ^{17}O anomalies reported by Karlsson et al [1] are absent or less pronounced in the shergottites.

The carbon isotopic data are probably unaffected by the pyrolysis process and may thus give undisturbed $\delta^{13}C$ values for the various carbon reserviors within the samples. Our data suggest that the Martian atmosphere is enriched in ^{13}C relative to the Martian mantle. This isotopic difference may be entirely of inorganic origin and not due to biological processes such as photosynthesis.

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