

HYDROGEN, CARBON AND OXYGEN ISOTOPIC COMPOSITION OF VOLATILES IN NAKHLA;
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Introduction. The nakhlites contain "iddingsite", a poorly defined hydrous alteration product of olivine [1], that has been speculated to be preterrestrial in origin. Since these meteorites have been proposed to have originated on Mars [2], which has an atmospheric D/H ratio 5.15 times SMOW [3] (corresponding to a δD of +4150 per mil; all δD values reported herein are relative to SMOW), measurement of the D/H ratios of the nakhlites could help to determine if the alteration processes that affected these meteorites were indeed preterrestrial. Moreover, if we accept a martian origin for these meteorites and their alteration, measurement of the stable isotope ratios of their alteration phases and comparison to the corresponding atmospheric ratios could provide insights into the nature and origin of fluids interacting with martian igneous rocks.

Previous hydrogen isotope measurements on nakhlites and shergottites have yielded highly variable results. A published δD value for Nakhla is -37 per mil with a yield of 2.2 μ moles of H_2 per gram of sample [4], which differs significantly from the reported value of +456 per mil measured on 81.6 μ moles of H_2 extracted from 2.8 g of the Lafayette nakhlite [4]. Published values for Shergotty range from -47 [4] to +878 per mil [5] with yields of 1-7 μ moles of H_2 per gram of sample [4,5,6]. In all these previous reports, data were obtained after "precombustion" of the sample at temperatures of 350-450°C [4,5,6], which was intended to eliminate terrestrial contamination by organic matter and/or adsorbed water. However, terrestrial iddingsite is typically comprised of a mixture of phases including goethite, smectites, and sometimes carbonates, and it begins to break down at temperatures as low as ~250°C [1]. Thus valuable information on the alteration phases may be lost in the precombustion step employed by previous workers. Our work therefore focuses on isotopic data for gases extracted from Nakhla by stepwise heating at the low temperatures at which iddingsite is expected to break down.

Experimental procedure. Fragments of Nakhla (~1 g from USNM 5891 and ~2 g from a Harvard University specimen) were coarsely crushed in air. The Harvard sample had fusion crust that was removed prior to crushing. The crushed samples were heated under vacuum in Pt crucibles using either an induction coil or resistance furnace. The use of the induction coil allowed higher temperatures (to above the liquidus) to be achieved, but precise measurement of the temperature at any step is difficult. The results obtained using resistance heating have thus far been limited to 600°C, but the temperature at each step is precisely known. H_2O and CO_2 released from the sample were frozen into a liquid nitrogen trap. Gas that did not freeze was then exposed to a copper oxide furnace at 500°C to oxidize it to condensable components. The small amount of non-condensable gas that remained after this procedure was pumped away. The CO_2 and H_2O released by heating were then cryogenically separated. H_2O was reduced to H_2 in a uranium furnace at 700°C and yields were measured manometrically. Data are reported without corrections for blanks or memory effects, but based on previous characterization of the extraction line used in this study, we estimate that these corrections will increase the δD of our samples by only a small amount. Isotope ratios were measured mass spectrometrically.

Results. Hydrogen (from released H_2O), carbon and oxygen (from released CO_2) results from a resistance heating extraction are shown in Figure 1. Gases were collected at 110, 200, 300, 400 and 600°C. Problems prevented analysis of the D/H ratio of the gas collected at 300°C, and CO_2 samples collected at the two lowest temperature steps amounted to less than 1 μ mole and were not analyzed isotopically.

The integrated yield of hydrogen for the sample shown in Figure 1 is 77 μ moles H_2 per gram of sample, equivalent to 0.138 weight % H_2O . Excluding the 110°C temperature step, the yield was 53 μ moles per gram of sample with a δD of +63 per mil. δD values increase from -83 per mil in the 110°C step to +173 per mil in the 600°C step. The hydrogen content is greatest in the 110°C step and decreases with increasing temperature. Although there are slight variations between samples, those heated by induction give comparable results. Based on the results obtained in the induction-heated samples, yields and δD continue to decrease above 600°C.

Carbon and oxygen results on the released CO_2 are similar to those that have been previously reported for Nakhla and some other SNCs [7,8,9]. The total CO_2 yield was 26 μ moles per gram of sample. Using the isotopic analyses from the 300, 400 and 600°C temperature collections, the bulk $\delta^{13}C_{PDB}$ is +0.6 per mil and the bulk $\delta^{18}O_{SMOW}$ is +31 per mil. The heaviest components ($\delta^{13}C_{PDB}$ of +22 per mil and $\delta^{18}O_{SMOW}$ of +34 per mil) were collected at temperatures between 300 and 400°C.

Discussion. The 300-400 and 400-600°C steps in the resistance heating procedure yielded hydrogen with δD values of +138 and +173 per mil, both of which are heavier than any known terrestrial samples. Similarly heavy results were obtained in the intermediate temperature steps of the induction heating extractions (although there is

some range in the results from sample to sample), but we do not find results nearly as heavy as the +878 per mil value reported by [5] for Lafayette. The release of water in this low temperature range is consistent with the breakdown of the phases that constitute the iddingsite between ~250 and 650°C. Although we must directly confirm that the gases released in this temperature range are indeed released on breakdown of alteration products in the meteorite and not from some other source within the sample, our tentative identification of these anomalously heavy, low-temperature components with the iddingsite would indicate that the alteration of this meteorite was preterrestrial. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in these temperature steps are also unusually heavy for comparable terrestrial rocks. These data can also be understood in terms of the breakdown of iddingsite and suggest that the alteration of this meteorite involved both hydration and carbonation. We note that the release of CO_2 does not necessarily imply the presence of discrete carbonate minerals in the iddingsite, since terrestrial Fe-hydroxides are known to contain carbonate ions that are volatilized at low temperature [10].

The higher yield and lower δD and $\delta^{13}\text{C}$ in the lowest temperature fractions are suggestive of a component of terrestrial contamination in the low temperature steps of the extractions. Although there is likely some terrestrial contamination in the fraction extracted at low temperatures, the fact that such high δD and $\delta^{13}\text{C}$ values are observed indicates that the low temperature gas should not be discarded in a preheating step as has been done by previous workers. We emphasize, however, that the δD and $\delta^{13}\text{C}$ values reported here for the lowest temperature steps, and perhaps for all of the extractions, represent lower limits on the actual values. We also cannot rule out partial exchange of the iddingsite with terrestrial atmospheric water after the meteorite fell.

Although not as high as the present martian atmosphere, the high δD values are consistent with a martian origin for these meteorites. If, as is often the case for terrestrial occurrences, the iddingsite is a product of deuteric alteration, these δD values may reflect the composition of hydrothermal fluids with contributions both from atmospheric (i.e., meteoric) and magmatic sources. If the nakhlites are from Mars, expectation of high δD values was reasonable due to the known deuterium enrichment in the martian atmosphere. The carbon and oxygen results are more difficult to assess in these terms. The isotopic composition of carbon (in CO_2) in the martian atmosphere is 0-80 per mil enriched relative to the terrestrial mantle [11,12]. Our results are consistent with these data, although this is not significant given the large errors in the measurements of the martian atmosphere. The highest $\delta^{13}\text{C}$ value we measured from Nakhla is inconsistent with terrestrial carbonate formation, which would be expected to produce $\delta^{13}\text{C}$ values near 0 per mil [8,9]. Measurement of oxygen isotopes in atmospheric CO_2 by Viking gave a $\delta^{18}\text{O}$ value of 0 ± 30 -50 per mil [11]. Again, CO_2 from Nakhla gives similar values. Our $\delta^{18}\text{O}$ values are within the range of terrestrial carbonates but the correlations with the carbon and hydrogen results leads us to conclude that these values are also preterrestrial.

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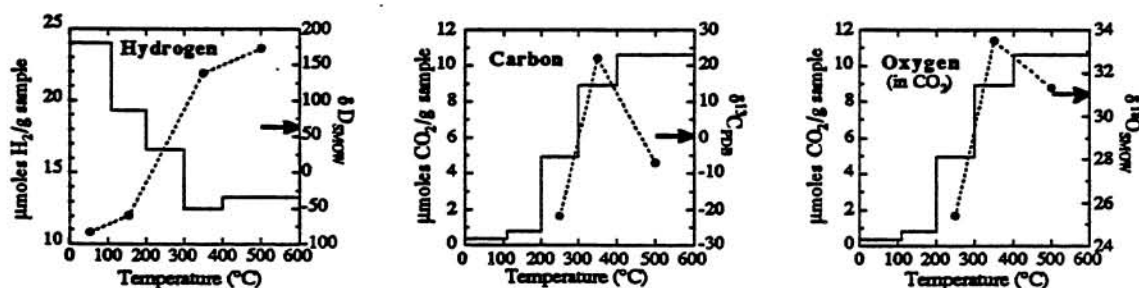


Fig. 1. Yield and isotopic measurements for a stepwise heating extraction of a 1.17 gram aliquot of Nakhla (USNM 5891). Solid lines show the yield and filled circles with dashed lines show isotopic composition for each temperature step. Isotopic composition data are displayed at the middle temperature of each temperature step. Arrows indicate bulk isotopic composition.