

THE ABUNDANCE AND STABLE ISOTOPIC COMPOSITION OF VOLATILES RELEASED FROM WEATHERING PRODUCTS DURING STEPPED HEATING OF NAKHLA AND LAFAYETTE; L.L. Watson, S. Epstein and E.M. Stolper, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125.

Overview: As part of our continuing study of hydrogen in SNC phases we report hydrogen isotopic data from water released by stepped heating of Nakhla and Lafayette. Although the water content of Lafayette is greater than three times higher than Nakhla, release patterns and δD values are very similar for both meteorites. Above 200°C both samples release water with δD values greater than terrestrial water, confirming that the alteration of these meteorites was preterrestrial. Due to the presence of a terrestrial component (observable at low temperatures) the highest measured δD values of $\sim +800$ may be a lower limit to the true δD of the original weathering products.

Introduction: We report the latest results of our continuing study of the hydrogen isotope ratios of various SNC phases and their implications for the history of water on the SNC parent planet, which we assume to be Mars [1,2]. Since the D/H of water in the current martian atmosphere is highly distinctive at ~ 5 times greater than SMOW [3] (corresponding to a δD value of $\sim +4000$, all δD values are reported in units of per mil relative to SMOW), the hydrogen isotopic composition of the water contained in SNC hydrous phases might be a useful tracer of water that once resided in the martian atmosphere or that has isotopically exchanged with it.

Specifically, we report the yield and hydrogen isotope ratios of water released by of stepped heating of aliquots of Nakhla and Lafayette, two of the three nakhlites. In addition, preliminary results of the study of CO₂ also released during heating are reported. The nakhlites contain "iddingsite" [4,5,6], a poorly defined hydrous alteration product of olivine [7]. By studying the volatiles released from these alteration materials we hope to constrain the isotopic composition of the fluids involved in weathering processes in the martian crust.

Previous hydrogen isotopic measurements on various SNCs have yielded highly variable results. A published δD value for Nakhla is -37 with a yield of 2.2 μmoles of H₂ per gram of sample [8], which differs significantly from the reported value of $+456$ measured on 81.6 μmoles of H₂ extracted from 2.8 g of the Lafayette nakhlite [9]. Our previous studies [10,11] produced preliminary data for Nakhla which also show it to contain water significantly enriched in D (δD values up to $\sim +500$). Published values for Shergotty range from -47 [8] to $+878$ [9] with yields of 1–7 μmoles of H₂ per gram of sample [8,9,12]. In most of these previous reports, data were obtained after "precombustion" of the sample at temperatures of 350–450°C [8,9,12], 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 $\sim 250^\circ\text{C}$ [7]. Thus valuable information on the alteration phases may be lost in the precombustion step employed by previous workers. Our study therefore focuses on gases extracted from the nakhlites by stepwise heating including the low temperatures at which iddingsite is expected to begin to break down. In addition, our work represents the first study of the hydrogen in more than one nakhlite by the same procedure.

Experimental procedure: Two ~ 1.3 g aliquots of Nakhla (from USNM 5891) and two ~ 0.6 g aliquots of Lafayette (from the Field Museum of Natural History sample ME 2116) were heated stepwise on a vacuum extraction system specially designed and built for these small samples. For each pair of meteorite aliquots, one was heated in the presence of hot (850°C) copper oxide (referred to as the "combusted" samples), and one was heated under vacuum with no oxygen (referred to as the "pyrolysis" sample). Each meteorite aliquot was coarsely crushed in air immediately before loading on the extraction line. Samples were heated in a quartz boat to temperatures of 120, 200, 300, 400, 600, and 1050°C. During each 2–2.5 hour heating step, gases were frozen in a liquid nitrogen trap. In the pyrolysis experiments, the yield of non-condensable gases was measured. The CO₂ and H₂O released by heating were then cryogenically separated. H₂O was reduced to H₂ in a uranium furnace at 750°C and yields were measured manometrically. Data are reported without corrections for blanks or memory effects, but based on characterization of the extraction line used in this study, we estimate that these corrections will change the δD of our samples by only a small amount (blanks have been measured to be < 0.5 μmoles H₂ at each temperature step; at the highest temperature steps where yields are lowest, the reported δD values could increase by a maximum of $\sim 50\%$ – the corrections for lower temperature steps would be significantly less). Isotope ratios were measured mass spectrometrically.

Results: Hydrogen yields and isotopic compositions at each temperature step of the four extractions are shown in Figure 1. The amount of water released from both Nakhla samples between 600 and 1050°C was too small for isotopic measurement. The 300–400°C Lafayette combustion sample was lost and thus not analyzed isotopically.

For both Nakhla and Lafayette the integrated total hydrogen yields are very similar for the combustion and pyrolysis and are essentially identical to those of Karlsson [13] with Nakhla containing 60.9 to 63.5 μmoles per gram of sample (corresponding to 0.110 to 0.114 weight % water) and Lafayette containing 209.2 to 215.4 μmoles per gram (0.377 to 0.388 weight % water). The largest amount of water is released at during the 120°C step, and in general, the hydrogen yields decrease with increasing temperature, with the exception of a leveling out or slight peak in the 200–300°C step. In all cases the δD values increase with increasing temperature. The highest δD values for Nakhla are $+688$ and $+706$ collected in the 400–600°C step of the combustion and pyrolysis samples, respectively.

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Even heavier is the water collected in the 600–1050°C steps of the two Lafayette aliquots, with δD values of +872 and +772 for the combustion and pyrolysis samples, respectively.

Discussion: All samples collected above 200°C have δD values heavier than any known terrestrial hydrogen samples. These data prove unequivocally that the alteration material in the nakhlites could not have formed on Earth. Our new data thus confirm previous conclusions based first on H-isotopic measurements [9,11,12] and later on oxygen isotopic measurements [13] and mineralogical studies [5,6] that the alteration is preterrestrial. The most striking feature of the results is the similarity in release patterns and isotopic compositions of Nakhla and Lafayette, despite a greater than three-fold difference in their total water contents. These results suggest that Lafayette was simply weathered to a higher degree in an environment similar to that in which Nakhla was altered. Although not as high as the present martian atmosphere, the high δD values are consistent with a martian origin for these meteorites.

The water release pattern for the samples is similar to that observed in our previous work [10,11] and in the work of Karlsson [13]. The higher yield and lower δD in the lowest temperature fractions suggest the presence of a component in the low temperature steps of the extractions that has exchanged with terrestrial water. However, the high δD relative to typical terrestrial materials in all but the lowest temperature steps and the progressive increase in δD with temperature indicates that there is still some extraterrestrial component in all but the lowest temperature step (and perhaps even in this one). This observation argues against the practice of discarding water extracted in these low temperature steps. Although the presence of a terrestrial component in the low temperature steps may indicate that even the highest δD values should be taken as lower limits to those actually present in the alteration products at the time of their formation, the observation that both Nakhla and Lafayette, samples with different terrestrial histories and total water contents, contain water of similar isotopic composition, may imply that a δD value of \sim +800–900 is close to the true value. This lower limit falls within the range of δD values measured by ion microprobe for amphiboles and biotite (\sim +500 – +2000) contained in magmatic inclusions in Chassigny and the shergottites [14]. These values have also been postulated to result from interaction of these samples with fluids in the martian crust [14].

In addition to hydrogen, CO₂ was collected at each temperature step. In general our CO₂ results are similar to those previously measured for the nakhlites [15]. We do not report the results in detail at this time due to the presence of additional gas species that follow CO₂ in our extraction procedure. We believe the gas to be largely SO₂, and this is consistent with the presence of S in the alteration material [5,6]. Further investigation of these results is needed to assess adequately the effect of the other gases on yields and isotopic measurements of the CO₂.

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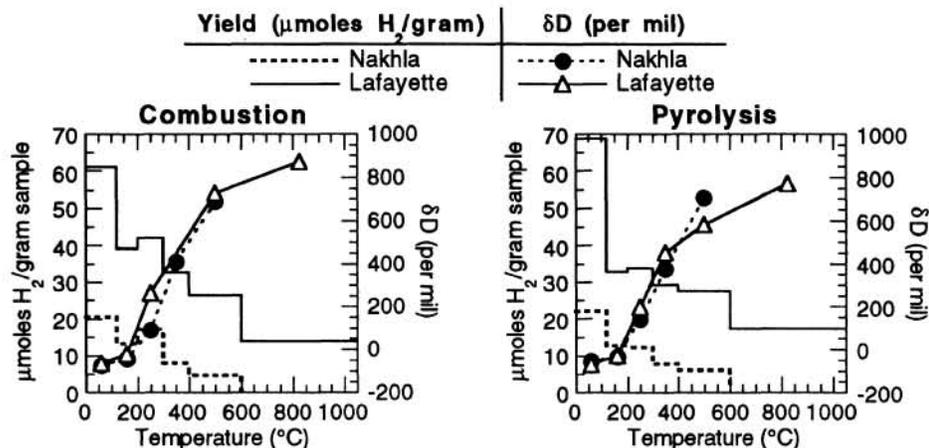


Fig. 1. Yield and hydrogen isotopic measurements for stepwise combustion and pyrolysis of four nakhlite aliquots. Yields (axis to the left) are shown as steps and δD values (axis to the right) as the connected points at the middle temperature of each heating step. Data for Nakhla are displayed with dashed lines and Lafayette with solid lines. Nakhla did not release enough gas for isotopic analysis above 600°C. The δD value of the 300–400°C Lafayette combustion sample was not measured.