

**THE ISOTOPIC COMPOSITION OF MOLECULAR WATER FORMED BY HYDROGEN REDUCTION OF IRON OXIDES: A PROXY FOR ENDOGENOUS WATER FORMED FROM SOLAR WIND IMPLANTATION.** A. M. Gargano<sup>1,2,3</sup>, Z. Sharp<sup>3,4</sup>, and J.I. Simon<sup>2</sup>. <sup>1</sup>Lunar and Planetary Institute, Houston TX 77058 (agargano@lpi.usra.edu), <sup>2</sup>NASA Johnson Space Center, Houston TX 77058, <sup>3</sup>Center for Stable Isotopes, University of New Mexico, Albuquerque, 87131, <sup>4</sup>Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, 87131.

**Introduction:** Many workers have successfully utilized a variety of lunar materials to infer the sources and processing history of volatiles on the Moon. In situ techniques via NanoSIMS have enabled a plethora of hydrogen isotope measurements of isolated grains in regolith and apatite within igneous rocks, revealing an extraordinarily large range of  $\delta D$  values from  $\sim -900$  to  $+1000\%$  [1]. The lowest of these  $\delta D$  values are related to the incorporation of solar wind hydrogen, which is pure  $^1\text{H}$ . Exposure to solar wind results in structural damage to crystalline phases, forming ubiquitous tens-to-hundreds of nanometer thick amorphous rims on mature regolith grains [2]. Solar wind implantation of  $\text{H}^+$  is also thought to result in the formation of nanophase  $\text{Fe}^0$  (npFe), a quantitative metric of surface exposure time (e.g.,  $\text{Is}/\text{FeO}$ ) [3]. The formation of npFe can be generally described via the reaction:  $\text{Fe}^{2+}\text{O} + \text{H}_2 = \text{Fe}^0 + \text{H}_2\text{O}$ , resulting in the formation of endogenous molecular water reservoirs.

**Endogenous molecular lunar water:** Throughout the surface exposure of lunar regolith (average residence time is  $\sim 10$  Ma), solar wind bombardment produces endogenous molecular water in the regolith formed via reduction of  $\text{Fe}^{2+}$  and the formation of npFe. The amount of endogenous water formed from the regolith reservoir can be estimated from the npFe abundance, yielding  $\text{H}_2\text{O}$  abundances in the range of  $\sim 600$   $\mu\text{g/g}$  in mature regolith.  $\text{H}_2\text{O}$  shielded from photo-destruction may condense in permanently shadowed regions and ultimately become concentrated at the lunar poles over geologic time. These  $\text{H}_2\text{O}$  reservoirs are critical for future lunar resource management activities, and the isotopic composition of such water informs where it was derived from (e.g., endogenous vs. exogenous). In this work, we measure the hydrogen and oxygen isotope composition of water derived from high temperature hydrogen reduction of Fe-oxides, such as ilmenite [4]. This process is relevant to high-T nebular processes, early Earth and may be extended to isotopic fractionation occurring from solar wind bombardment of lunar regolith.

**Experimental design:** We performed hydrogen reduction of Fe-oxides (hematite and ilmenite) by a simple flow-through furnace - trap system. Pure hydrogen gas was cryogenically purified through a liquid nitro-

gen trap and continuously passed through samples held in silica-glass tubes at temperatures ranging from  $400$ - $1000^\circ\text{C}$  for 2-6 hours. Initial materials were ‘pre-baked’ by heating to  $150^\circ\text{C}$  with flowing hydrogen for 20 minutes prior to reaction. Molecular water produced from the reduction reaction was cryogenically trapped, vacuum distilled, and separated into aliquots for hydrogen and triple oxygen isotope analyses. The product water was measured for hydrogen isotope compositions by Zn reduction [5] on a Delta V IRMS and the oxygen isotope compositions were measured by  $\text{CO}_2$ - $\text{H}_2\text{O}$  equilibration at  $25^\circ\text{C}$  for 24 hours by TILDAS laser spectrometer. The initial triple oxygen isotope compositions of the minerals were measured by laser fluorination on a MAT 253 IRMS. All measurements were performed at the University of New Mexico, Center for Stable Isotopes.

**Results:** Hematite was synthesized by reacting  $\text{Fe}^0$  powder in air within a horizontal tube furnace at  $600^\circ\text{C}$  for 48 hours. The triple oxygen isotope composition of the product  $\text{Fe}_2\text{O}_3$  has a higher  $\Delta^{17}\text{O}$  and lower  $\delta^{18}\text{O}$  value than the oxidizing air source (Fig. 1). A natural gem-quality ilmenite was used in the experiments.

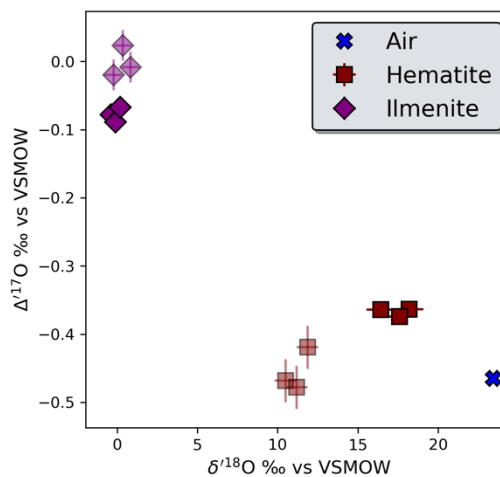


Figure 1:  $\delta^{18}\text{O}$  vs  $\delta^{17}\text{O}$  values of waters, minerals, and air. Water compositions are plotted as faded symbols and initial minerals as solid symbols. Data are averages of three analyses with error bars representing standard deviation between repeat analyses.

Hematite and ilmenite reduction lead to different hydrogen and oxygen isotope fractionations. The

$10^3 \ln(\alpha_{\text{H}_2\text{O}-\text{H}_2})$  of product waters are a function of reaction temperature (Fig. 2). Waters derived from ilmenite reduction fall along and slightly above the theoretical  $\text{H}_2\text{O}-\text{H}_2$  fractionation [6], whereas the  $\delta\text{D}$  values of waters derived from hematite reduction exhibit lower  $\alpha$  values.

In contrast to hydrogen, the oxygen isotope compositions of product waters are not effected by temperature. The  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values of water derived from hematite reduction are lower than the initial composition, whereas waters derived from ilmenite reduction have the same  $\delta^{18}\text{O}$  values with slightly higher  $\Delta^{17}\text{O}$  values (Fig. 2).

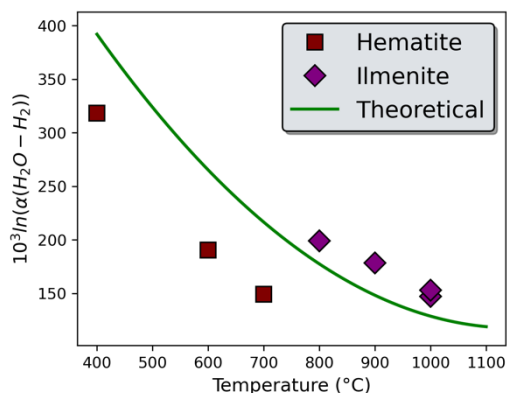


Figure 2: Temperature vs.  $10^3 \ln(\alpha_{\text{H}_2\text{O}-\text{H}_2})$  values of experimental products and theoretical data [6]. Individual data are averages of 4 analyses.

**Discussion:** The reduction of Fe-oxides is well studied in the metallurgical literature [7]. In the case of ilmenite, direct reduction of  $\text{Fe}^{2+}$  to  $\text{Fe}^0$  occurs via the reaction:  $\text{FeTiO}_3 + \text{H}_2 = \text{Fe}^0 + \text{TiO}_2 + \text{H}_2\text{O}$ . In contrast, hematite reduction occurs *via* several intermediate steps to  $\text{Fe}_3\text{O}_4$  and  $\text{FeO}$  to  $\text{Fe}^0$ . This difference in reaction scheme likely contributes to the differences in the  $\alpha_{\text{H}_2\text{O}-\text{H}_2}$  values of hematite and ilmenite.

Gravimetric results indicate near-total conversion of hematite to iron metal, and partial conversion of ilmenite to  $\text{TiO}_2 + \text{Fe}^0$ , with some intermediate phase such as pseudobrookite (Fig. 3). Despite the retention of some oxygen, no difference in the H and O isotope compositions of waters produced from ilmenite extractions occurring over 3 and 6 hours at 1000 °C are observed, suggesting that minimal influence of partial extractions are imprinted on the isotopic compositions of our measured waters.

**Conclusion and ongoing works:** The  $\alpha_{\text{H}_2\text{O}-\text{H}_2}$  values of ilmenite and hematite were determined as a function of temperature by heating in a stream of  $\text{H}_2$ . If applied as a proxy for the composition of molecular water produced via solar wind hydrogen implantation

at 0°C, the  $\delta\text{D}$  value of water would be  $\sim -400\%$ , similar to many measurements made on lunar samples.

We are currently in the process of performing additional experiments with mineralogical determinations to quantify the mineralogical phase relationships, as well as the reduction degree to be presented at the meeting.

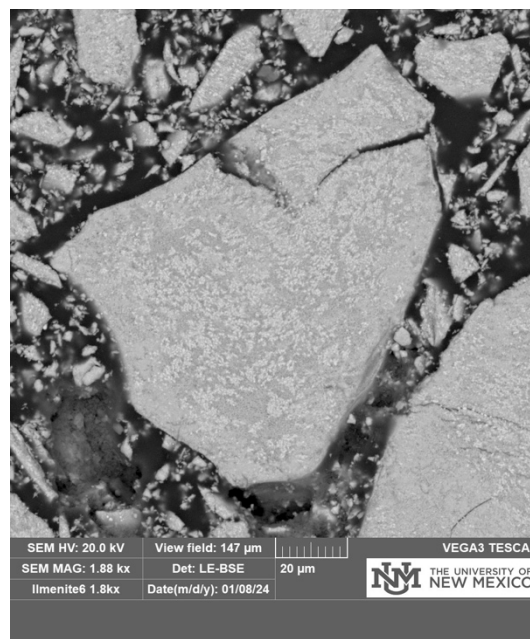


Figure 3: BSE image of reduced ilmenite charge held at 1000 °C for 6 hours.

**References:** [1] McCubbin, F. et al. (2023). *Reviews in Mineralogy and Geochemistry*, 89.1, 729-786. [2] Keller, L. P. & McKay, D. S. (1997). *GCA*, 61(11), 2331-2341. [3] Morris, R. (1980) *LPSC*, 11, 1697-1712. [4] Christofferson, R. et al. (1996) *MAPS*, 31.6, 835-848. [5] Friedman, I. (1953) *GCA*, 4.1, 89-103. [6] Richet, P. et al. (1977) *Annual Review of Earth and Planetary Sciences*, 5.1, 65-110. [7] Spreitzer, D. & Johannes S. (2019) *Steel Research International*, 90.1.