

HIGH PRECISION OXYGEN ISOTOPIC MEASUREMENTS OF WATER EXTRACTED FROM SELECTED LUNAR SAMPLES. M. H. Nunn¹ and M. H. Thiemens¹, ¹Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, California, 92093-0356. E-mail: munn@ucsd.edu.

Introduction: Isotopic abundances vary greatly among planets and different classes of meteorites and constrain solar system formation models. Abundant elements that exist as more than two stable isotopes, such as silicon, magnesium, and oxygen, are particularly valuable in understanding how the solar system formed and evolved because the relative amounts of their isotopes reflect contributions of mass dependent and independent processes. Oxygen in meteorites and returned lunar samples appears in distinct phases with different production and equilibration mechanisms that occur on widely varying timescales. As such, analysis of oxygen isotopic ratios in multiple phases of a given sample is an ideal tracer of solar system evolution.

A wealth of measurements of oxygen isotopic abundances in different mineral phases of extraterrestrial samples have been made but the results do not imply consistent formation and equilibration histories. Oxygen isotopic analyses of water in these samples have been lacking due to the low concentration of water and the high degree of precision necessary to make these measurements useful. Recently, several groups have found much higher concentrations of water in lunar samples (up to 6050ppm) than previously thought [1-3]. The relative amounts of deuterium and hydrogen (D/H) in this water suggest comets are the dominant water source on the Moon, but correlation with a three-isotope system can be used to determine this conclusively [1].

Oxygen isotopic ratios in water from lunar surface samples may have been altered from their starting values by evaporation, interaction with solar wind, gardening due to micrometeorite bombardment, and volcanism, among other processes [i.e., 4-5]. Some of these processes occur predictably over long timescales so sample ages can be combined with isotopic studies to yield even more information.

We present here the first high precision measurements of $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ in water extracted from lunar material and discuss scenarios of water production, transport, and delivery that explain the observed ratios. The samples analyzed were returned on various Apollo missions and therefore come from different geographical locations on the lunar surface. This suite of breccias and basalts was selected based on the wide range in exposure ages, previous reports of high water content, and well-constrained D/H measurements in that water.

Methods: Water was extracted from selected 1-3g samples of lunar material by vacuum pyrolysis. A new, low volume, ultra low blank ($<0.1\mu\text{mol}$) system was built specifically for these measurements. To remove as much adsorbed terrestrial water as possible, each sample was pumped on a vacuum line at room temperature until outgassing had ceased. Samples were then heated step-wise to 50, 150, and 1000°C and held at each temperature for several hours. Heating at 50 and 150°C removed adsorbed terrestrial water not degassed by pumping alone and allowed for the extraction of pure lunar water in the 1000°C step. Samples were held at each temperature long enough to collect all evolved volatiles, considering limitations imposed by the rate of diffusion of species through the sample. The length of time at each temperature was chosen to maximize yield. Liberated volatiles were collected in a liquid nitrogen cold trap ($T \approx 77\text{K}$). While heating, degassing species had constant access to the cold trap, thus minimizing the potential for isotopic exchange with the sample tube. Water was quantitatively converted to molecular oxygen with bromine pentafluoride. This reaction is specific for water so oxygen collected for analysis was produced directly from water in the lunar sample. Oxygen isotopic ratios were measured on a double-collecting isotope ratio mass spectrometer.

This method has already been used in the high precision ($\delta^{17,18}\text{O} \leq 0.1\text{‰}$) analysis of micromolar quantities of water extracted from samples of ordinary and carbonaceous chondrites, and its accuracy was confirmed by analysis of terrestrial controls [5].

Results and Discussion: Water liberated during low temperature (50 and 150°C) heating of breccia and basalt samples was terrestrial in origin as evidenced by its $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ (i.e., $\delta^{17}\text{O} = 0.52 * \delta^{18}\text{O}$). High temperature heating (1000°C) of these samples released water with oxygen isotopic ratios deviating from terrestrial values, confirming their extraterrestrial origin.

A fraction of the volatiles released at 1000°C did not condense at liquid nitrogen temperature and is currently being analyzed. Although clearly not water, their characterization could elucidate the composition of other oxygen bearing reservoirs on the lunar surface. The Apollo 11 breccia from which these volatiles were generated has a cosmic ray exposure age of ~ 2.3 bil-

lion years [6]. Consequently, it may possess solar wind oxygen, and these results may be used to more precisely quantify the relative abundances of oxygen isotopes in solar wind.

Analysis of other lunar samples and assessment of the relative impact of lunar surface processes on oxygen isotopic composition is currently underway, and an in depth discussion of these results will be presented at the meeting.

References: [1] Greenwood, J. P. et al. (2011) *Nature Geoscience*, 4, 79-82. [2] Saal, A. E. et al. (2008) *Nature*, 454, 192-U38. [3] Hauri, E. H. et al. (2011) *Science*, 333, 213-215. [4] Farrell, W. M. et al. (2011) *A Wet vs. Dry Moon, LPI Contribution No. 1621*, 16. [5] Crider, D. et al. (2007) *AGU Spring Meeting*, Abstract # SM34A-07. [5] Nunn, M. H., Thiemens, M. H. (2011) *74th Annual Meteoritical Society Meeting*, Abstract #5438. [6] Thiemens, M. H. and Clayton, R. N. (1980) *EPSL*, 47, 34-42.