OXYGEN ISOTOPIC ANALYSES OF WATER EXTRACTED FROM SELECTED LUNAR SAMPLES.
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Introduction. The oxygen isotopic composition of the bulk rock comprising many of the samples collected on the lunar surface by NASA's Apollo missions have been determined, but comparable measurements of the relatively rare water phase in these samples have proven much more difficult to obtain. If carried out successfully, these results, in conjuction with measurements of the isotopic composition of celestial bodies that could have delivered water to the Earth and Moon, could help elucidate the major source(s) of water to the Earth-Moon system. The development of a highly precise experimental technique to extract and analyze water bound in rock and soil samples has enabled us to measure the oxygen isotopic composition of lunar water in samples where water was deemed absent [1, 2]. The specimens chosen for analysis were collected on the Apollo 11, 12, 14, and 17 missions so they represent most of the range of geographic locations on the lunar surface that have been sampled by the Apollo program. These samples were selected to maximize the range in surface exposure age (21 m.y. to 2.75 b.y.).

Method. Water is extracted from lunar samples by heating stepwise to 50, 150, and 1000°C while collecting liberated volatiles in a liquid nitrogen cold trap. The fluorination reagent bromine pentafluoride (BrF_5) is used to quantitatively convert water to molecular oxygen, the oxygen isotopic ratios ($^{18}O/^{16}O$ and $^{17}O/^{16}O$) of which are then determined on a dual inlet isotope ratio mass spectrometer (IRMS) (see [3] for detailed methods).

Results. The samples initially studied, in order of increasing exposure age, are 10049 (21 m.y.), 14305 (27.6 m.y.), 12039 (76 m.y.), 79035 (660 m.y.), and 10060 (2.75 b.y.). Samples 10049 and 12039 are basalts, while 10060, 14305, and 79035 are breccias. In general, samples exposed on the lunar surface longer contained more water (Figure 1).

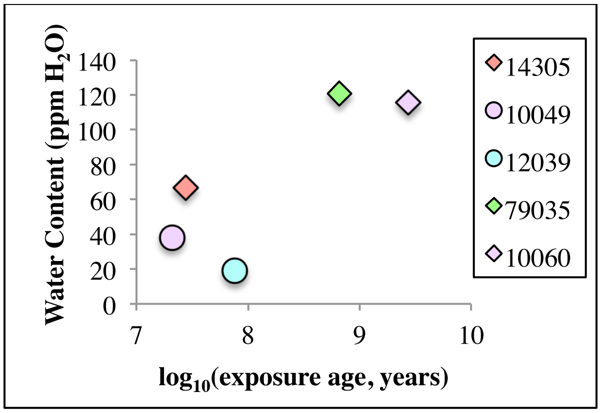

Figure 1. Relationship of water content and surface exposure age of lunar samples 10049, 14305, 12039, 79035, and 10060. Diamonds and circles represent breccias and basalts, respectively.

The oxygen isotopic composition of water extracted from the selected lunar samples in each heat step is distinct and indicates at least three isotopically distinct oxygen bearing reservoirs are sampled during the three heat steps (Figure 2).

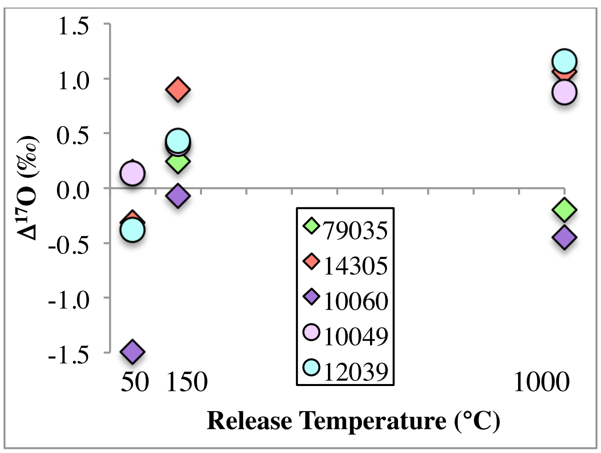

Figure 2. Oxygen isotopic composition of water extracted from lunar samples. The $\Delta^{17}O$ value is a measure of the deviation from perfectly mass dependent fractionation in the formation and equilibration of the specific fraction of water being analyzed ($\Delta^{17}O = \delta^{17}O - 0.52*\delta^{18}O$). Data points marking water extracted at 50°C from 79035 and at 150°C from 10049 are beneath the markers for 10049 and 12039, respectively.

Discussion. Samples 10049 and 12039 are basalts, while 14305, 79035, and 10060 are breccias. As shown in Figure 1, the clustering of samples 10049, 14305, and 12039 in a low exposure age/low water content group and that of samples 79035 and 10060 in a high exposure age/high water content group suggests exposure age is more deterministic of water content than petrology.

The low temperature heat steps (50°C and, to a lesser extent, 150°C) remove physisorbed molecular water, which is largely terrestrial, atmospheric water that must be removed to collect a clean sample of extraterrestrial water. The highest temperature heat step at 1000°C liberates tightly bound, structural water and water trapped in glasses that is the least readily exchanged with surrounding oxygen reservoirs and consequently the most likely to reflect a primordial water composition. The $\Delta^{17}O$ of water in 10049, 14305, and 12039 increases with increasing heating temperature (Figure 2). In contrast to this trend, the $\Delta^{17}O$ of water in 79035 and 10060, which have the longest surface exposure age of the samples studied, increases between 50 and 150°C and then decreases to below 0‰ in the 1000°C heat step. In addition to water, high temperature (1000°C) heating of 79035 released 84ppm nitrogen, which was collected separately and analyzed. This N_2 possesses a $\delta^{15}N$ value of -155.058 ± 0.381‰, which is remarkably similar to N_2 previously extracted from 79035 by stepwise heating at 1000°C, which had a $\delta^{15}N$ value of ~ -180‰ [4]. This N_2 was shown to have its origin in the solar wind [4]. Incoming solar wind oxygen would be stored similarly to nitrogen. These facts, combined with the unique pattern of isotopic compositions of water extracted from the most exposed samples (10060 and 79035), suggest water liberated by heating at 1000°C could have a solar wind origin.

Results of stepwise heating studies of additional lunar samples will also be presented and discussed.

References. [1] Epstein, S. & Taylor, H. P. Jr. (1973) *Proc. 4th Lunar Sci. Conf.*, *2*, 1559-1575. [2] Epstein, S. & Taylor, H. P. Jr. (1974) *Proc. 5th Lunar Sci. Conf.*, *2*, 1839-1854. [3] Agee, C. B. et al. (2013) *Science*, *339*, 780-785. [4] Clayton R. N. and Thiemens M. H. (1980) *Proc. Conf. Ancient Sun,* 463-473.