A UNIFYING THEORY FOR H-BEARING VOLATILES ON THE MOON. Z.D. Sharp[1], F.M. McCubbin[1,2] and C. K. Shearer[1,2], [1]Dept. Earth & Planet. Sci., Univ. New Mexico, Albuquerque, NM 87131, zsharp@unm.edu, [2]Inst. of Meteorics, Univ. New Mexico, Albuquerque, NM 87131, fmccubbi@unm.edu, cshearer@unm.edu.

Introduction: The discovery of hydrogen-bearing phases in select Apollo samples opened up the possibility that the Moon was not as anhydrous as previously assumed [1]. Measurable hydrogen has now been found in volcanic glass beads, apatite grains, and melt inclusions in olivine grains ing glass beads [2-4]. The abundance and source of hydrogen remains in doubt, with 'water contents' approaching those of the Earth's depleted upper mantle having been proposed as an upper limit. The proposed H (ice?) detected at the lunar poles e.g., [5] has been suggested to be sourced from mantle degassing [2].

The idea of a water-rich lunar mantle appears to contradict 1) high Cl-isotope values of lunar materials, which indicate anhydrous degassing [6], 2) modeling of the mineralogy of KREEP basalts and iron metal-bearing mare basalts [7], which place an upper limit of ~10 ppm H_2O for the lunar interior, 3) D/H ratios of lunar apatites with δD as high as 1000‰, which were interpreted as a cometary water source [8], and 4) the immeasurably low H content of the vast majority of lunar samples.

Elkins-Tanton and Grove [7] modeled changes in the water content of lunar basalts with increasing degrees of crystallization of a lunar magma ocean and concluded that mantle water contents must have been low. They suggested that water sourced from impacts may explain high hydrogen contents in apatite. They also show that at the very low $f(O_2)$ values of the Moon, H_2 is a dominant species in the O-H system. We show here that the low lunar $f(O_2)$ and predominance of H_2 gas at shallow levels explains *all* of the apparent contradictions outlined above and provides for a new interpretation for volatile behavior in the Moon.

H speciation in the Moon: The oxygen fugacity ($f(O_2)$) of the lunar mantle may be as much as ~5 orders of magnitude lower than that of Earth [9]. On Earth, H_2O is the dominant phase in the H-O system for the upper mantle, whereas on the Moon, H_2 will predominate. The different speciation has important implications.

1) The diffusion rate of H_2 in basalt is >100 times higher than for water [10]. A shallow-level magma can degas H_2 far more rapidly than H_2O, explaining the immeasurably low H content in most lunar basalts. In an unbuffered system, loss of H_2 would increase the H_2O/H_2 ratio, but as long as Fe metal is present, the $f(O_2)$ and H_2O/H_2 ratio will be buffered, allowing for continued loss of H_2.

2) Only samples that were rapidly quenched (glass beads) or preserved as melt inclusions could retain any measurable H. In fact, it is likely that H_2 gas is the volatile species responsible for fire-fountain eruptions of pyroclastic deposits represented by the Apollo 17 high-Ti orange glass. During ascent, H_2 solubility likely decreases dramatically, providing a source for H_2 and explaining the preservation of H in the glass beads.

3) H_2 degassing and loss to space would significantly increase the D/H ratio of the melt. Assuming a Earth-like initial D/H ratio, a δD value in excess of 600‰ is achieved by kinetic considerations alone if only 95% of H_2 is lost from a magma. Such levels of deuterium enrichment are nearly impossible to achieve if H_2O were the degassing species.

4) Fe metal is stable at high $f(H_2)$ values, eliminating the thermodynamic/mineralogical constraint on lunar water contents. Although OH⁻ is an important species in the silicate melt at high pressure even at high $f(H_2)$, during ascent, the degassing will be more ideal, which will insure low H_2O contents in the degassed phase..

5) H_2 will degas far more rapidly than HCl or metal chlorides. The high Cl isotope ratios of the Moon require an anhydrous magma during Cl degassing, but do not preclude an H-rich melt prior to Cl loss.

6) The moderately high OH⁻ contents of apatites reflect the OH⁻ content of the melt. If saturated in both H_2 and OH⁻, then this ratio will be fixed by solubility and $f(O_2)$ buffers.

In contrast to the Moon, the $f(O_2)$ of Earth's upper mantle is far higher, near QFM [11], and this high value has existed since the early Hadean [12]. At low $f(O_2)$ values, H_2 is an important volcanic volatile species. If significant H-degassing and volatile loss explains the higher $f(O_2)$ of the Earth, it must have occurred very early in Earth's history [12-13], at a time when temperatures and volatile transfer rates to the surface were high [14]. The different $f(O_2)$ between the Earth and Moon may simply reflect the higher proportion of H in the early Earth relative to the Moon (Fig. 1). H loss would drive the $f(O_2)$ to higher values, which would have the effect of reducing the fraction of H_2 present in a degassing lava. By the time $f(O_2)$ values of QFM were reached, the fraction of H_2 would be negligible, effectively arresting any further loss of H_2 to space and fixing $f(O_2)$. Reincorporation of surface-degassed material back into the Earth's mantle would raise the overall upper mantle $f(O_2)$. In contrast, if the

Moon had a much smaller initial fraction of H, and/or a higher fraction of Fe metal, then its $f(O_2)$ would not be displaced to significantly higher values. The strikingly different $f(O_2)$ values of Earth and Moon may be a consequence of differing amounts of initial H, with Mars representing an intermediate value. The high δD values of both bodies compared to the solar ratio [15] support this idea.

The H (ice?) present at the surface of the Moon today cannot be derived from the interior given the low $f(O_2)$ of the Moon. Water is not stable under such conditions, and evolved H_2 gas would be lost to space. We suggest that 'ice' observed at the lunar poles is a late feature, delivered to the Moon after it had cooled.

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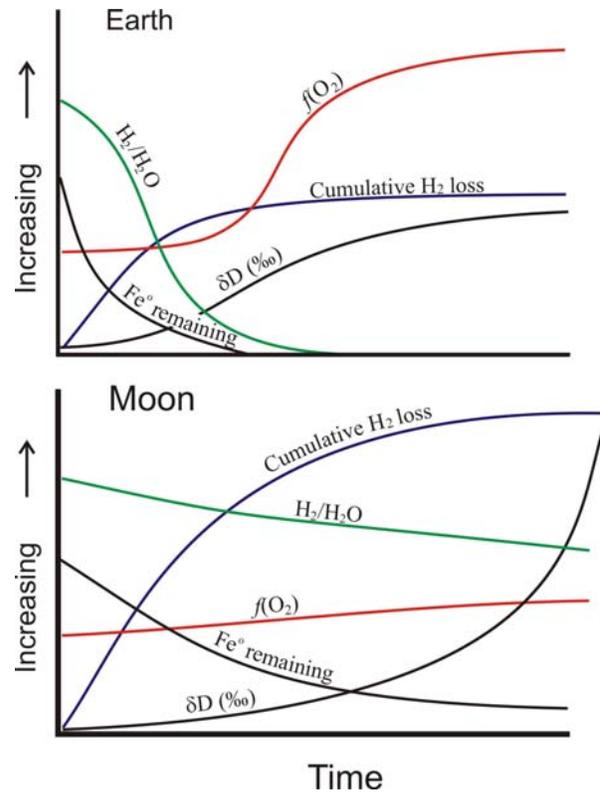

Fig. 1. Stylized illustration of geochemical changes in the upper mantle of Earth and Moon during early H_2 loss to space. H_2 loss on Earth results in Fe^o oxidation. The H_2/H_2O ratio drops, the rate of H_2 loss to space decreases, and $f(O_2)$ rises as the Fe^o-FeO buffer is exhausted. δD, after an initial rise, becomes constant. On the Moon, Fe^o is not exhausted because the initial Fe^o/H ratio is higher than on Earth. $f(O_2)$ remains nearly constant, δD increases exponentially, and nearly all H is lost from the body.