## DISTINCT VOLATILE RESERVOIRS IN THE MOON: EVIDENCE FOR LATE ADDITION OF VOLATILES AND WATER.

G. Jeffrey Taylor[1] and Katharine L. Robinson, [1]Hawai'i Inst. of Geophys. and Planetology, Univ. of Hawai'i, 1680 East-West Rd., Honolulu, HI 96822; gjtaylor@higp.hawaii.edu.

Introduction: Recent measurements of the H_2O concentrations in lunar pyroclastic glasses [1,2], mare basalts [3,4], and evolved, KREEP-related lunar rocks [5,6] have shown that H_2O is present in the lunar interior. The concentration in the bulk Moon is highly uncertain, because of variation among analyzed material and the difficulty in determining the precise amounts in magmas, and assumptions in modeling the amount in the mantle source regions. Lunar magmas appear to range in H_2O from MORB-like, about 1000 ppm [1,2], to a few tens of ppm in mare basalt magmas [3,4], to about 10 ppm in evolved, KREEPy magmas [5,6]. Sharp et al. [7] suggest that most magmas contain less than few ppm. Here we examine the potential cause of this heterogeneous distribution of H_2O inside the Moon, with emphasis on the relation between H_2O and highly volatile elements.

Highly Volatile Elements: Elements substantially more volatile than potassium, particularly those that condense below ~750 K, are potentially diagnostic of volatile loss during lunar formation, depletion in the early Earth and Moon-forming impactor, or late addition. The chalcophile elements are particularly useful as they would not have segregated into a small metallic lunar core and the low S in the Moon allows them to behave as lithophile elements. Their partition coefficients are not well established in all cases, but it is clear from Fig. 1 that they exhibit a range of geochemical behavior in igneous systems, ranging from compatible to incompatible, depending on mineralogy. The important point is that during partial melting or fractional crystallization (including in the magma ocean), the highly volatile elements ought to be strongly fractionated from each other.

Fig. 1. Partition coefficients of highly volatile elements; data from the GERM database (http://earthref.org/KDD/).
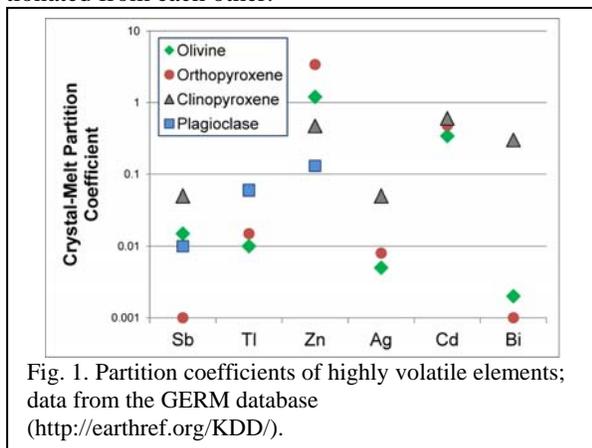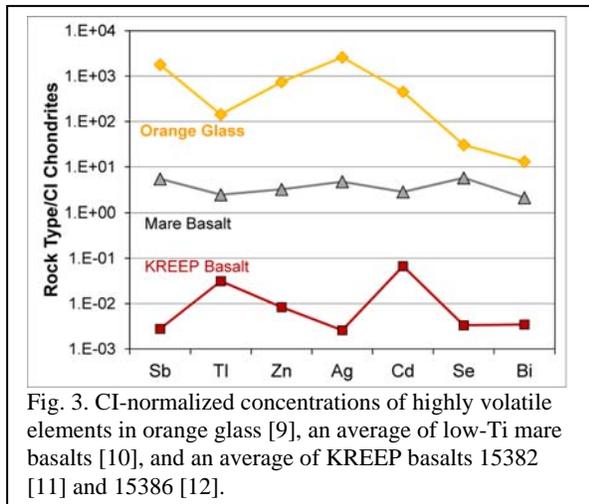
Although established tradition is to use nebular condensation temperatures to indicate volatility, other measures are possible. In the case of lunar volcanic samples, it is practical to use the emanation coefficient [8], defined as $E = (C_o - C)/C_o$, where C_o is the concentration of a volatile element in a magma before eruption and C_f is the concentration in the magma after it cools. E is determined from detailed studies of terrestrial volcanic deposits. Emanation coefficients for the highly volatile elements under consideration are shown in Fig. 2.

Fig. 2. Emanation coefficients for highly volatile elements.
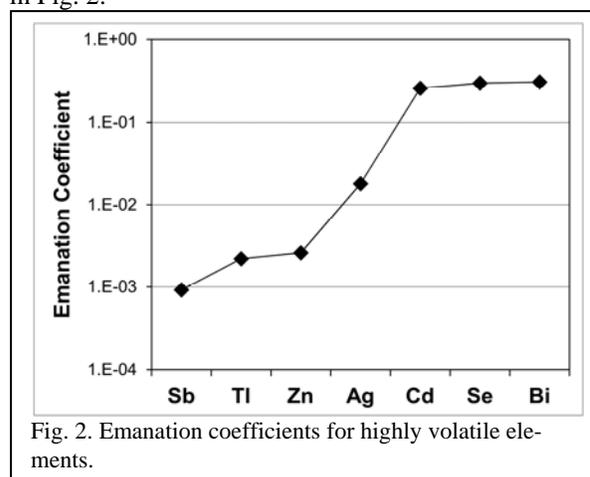
Volatile Elements in Lunar Igneous Rocks: It has been known for decades that lunar pyroclastic glasses are rich in volatiles [e.g. 9], substantially enriched over CI chondrites (Fig. 3, where the elements are listed in order of increasing emanation coefficient, hence volatility). Now we know their pre-erupted magmas contained considerable H_2O. Mare basalts are depleted in highly volatile elements compared to orange glass, but enriched compared to CI chondrites (Fig. 3). KREEP basalts and their differentiates such as quartz monzodiorites and felsites are depleted compared to the other rocks and to CI chondrites (Fig. 3).
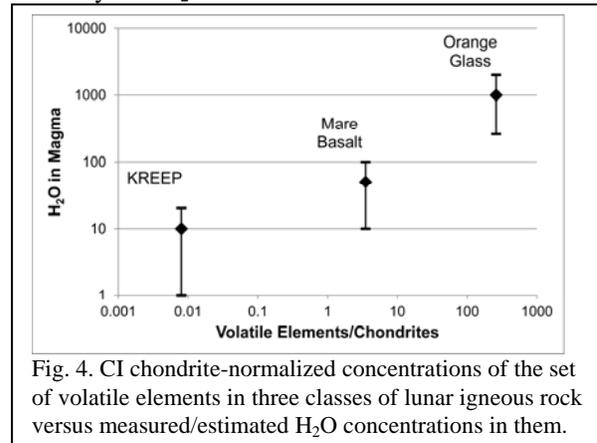
The strikingly uniformly depleted pattern shown by mare basalts suggests a contribution from chondritic materials, without subsequent fractionation. If the chondritic component was present in the magma ocean when the mare basalt source regions were forming, the elements would have fractionated from each other because of their different levels of compatibility in major minerals (Fig. 1). This raises the question of whether a chondritic component was added to the lunar mantle after the mare basalt source regions accumulated.

Fig. 3. CI-normalized concentrations of highly volatile elements in orange glass [9], an average of low-Ti mare basalts [10], and an average of KREEP basalts 15382 [11] and 15386 [12].

The possibility of a late addition to the Moon is supported by the concentrations of highly volatile elements in KREEP basalts and orange glasses, though the case is far from straightforward. KREEP basalts vary over an order of magnitude in their abundances of volatile elements, but the variation is not correlated with partition coefficient. Considering that volatile elements were measured in only two samples (15382 and 15386), some of the scatter is likely due to poor sampling. If so, KREEP basalts may also have roughly chondritic levels of volatile elements. It is particularly striking that KREEP basalts are not systematically enriched in volatile incompatible trace elements. The data in Fig. 1 suggests that KREEP basalts ought to have higher concentrations of Ag compared to Cd, opposite to what is observed. This suggests that these elements were not present in the magma ocean, whose crystallization led to strong enrichments in incompatible elements such as the REE. The concentration of volatile elements in orange glass trends down from Cd to Se to Bi, the elements with the highest emanation coefficients. This might reflect loss upon eruption.

Although the mean compositions of the three groups of rocks scatter (Fig. 3), it is clear that they have distinctly different concentrations of volatile elements. Analysis of glasses and apatite in lunar samples indicates that these groups vary in H_2O concentrations, with KREEP basalts and differentiates having the lowest amount of H_2O and pyroclastic glasses having the highest. Fig. 4 shows this trend, where the geometric mean of volatile element concentration for each group is plotted against an estimate of the H_2O content in the magmas. The mean H_2O content of each group is shown by the filled symbol, and the range of plausible concentrations is indicated by the error bars. Except for orange glass, where analyses of melt inclusions in olivine have pinned down the H_2O concentration in the pre-eruption magma [2], magma H_2O con-

tents are highly uncertain. However, it is clear that KREEP-related magmas (basalts, felsites) have substantially less H_2O than do mare basalts.

Fig. 4. CI chondrite-normalized concentrations of the set of volatile elements in three classes of lunar igneous rock versus measured/estimated H_2O concentrations in them.

If the volatiles were added to the Moon by impacting planetesimals [e.g., 13], the objects did not have H_2O contents like those of CI chondrites (10 wt%). If the H_2O was enriched to the same extent as the high volatile elements, then a few tenths of a wt% would be enough. As [13] point out, the projectiles might also have delivered most of the lunar inventory of highly siderophile elements, which, like highly volatile elements in mare basalts, are also present in chondritic relative abundances [14]. To prevent concentration of incompatible volatile elements (and H_2O) in KREEP, this late addition would have happened after the magma ocean had almost completely solidified. However, a solidified magma ocean would have formed a thick ferroan anorthosite crust that would form a barrier to deep impact emplacement of siderophiles and volatiles [15]. Perhaps the volatile and siderophile elements and their accompanying H_2O were added by one or a few large impacts, perhaps confined to what would become the Procellarum KREEP Terrane.

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