OXYGEN FUGACITY OF MARE BASALTS AND THE LUNAR MANTLE.APPLICATION OF A NEW MICROSCALE OXYBAROMETER BASED ON THE VALENCE STATE OF VANADIUM. C.K. Shearer[1], J. Karner[1], J.J. Papike[1], and S.R. Sutton[2,3] . [1]Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131 cshearer@unm.edu. [2] Department of Geophysical Sciences and [3] Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637.

Introduction: The ability to estimate oxygen fugacities for mare basalts and to extend these observations to the lunar mantle is limited using bulk analysis techniques based on buffering assemblages or the valence state of iron. These limitations are due to reequilibration of mineral assemblages at subsolidus conditions, deviations of mineral compositions from thermodynamic ideality, size requirements, and the limits of the iron valence at very low fO_2. Still, these approaches have been helpful and indicate that mare basalts crystallized at fO_2 between the iron-wüstite buffer (IW) and the ilmenite breakdown reaction (ilmenite = rutile + iron) [i.e. 1-3]. It has also been inferred from these estimates that the lunar mantle is also highly reduced lying at conditions below IW. Generally, these data cannot be used to determine if the mare basalts become increasingly reduced during transport from their mantle source and eruption at the lunar surface and if there are differences in fO_2 among mare basalts or mantle sources. One promising approach to determining the fO_2 of mare basalts is using the mean valence of vanadium (2+, 3+, 4+, 5+) determined on spots of a few micrometers in diameter using synchrotron x-ray absorption fine structure (XAFS) spectroscopy [4-8]. The average valence state of V in basaltic glasses is a function of fO_2, temperature, V coordination, and melt composition. Here, we report the initial results of this approach applied to lunar pyroclastic glasses.

Analytical Approach: In this initial study we selected pyroclastic glasses from the Apollo 15 and 17 collection for analysis. This included the A15 green glasses (green A-E), A15 yellow glass, A17 orange glass, and A17 VLT glass. These glasses represent examples of near-primary high-Ti (orange), intermediate-Ti (yellow), and very low-Ti (VLT, Green) mare basaltic magmas. Individual pyroclastic glasses were analyzed for major and minor elements (including S) using a JEOL 8200 EMP. Liquidus temperatures for the glass compositions used in this study were either calculated or taken from experimental results in the literature [9,10]. The concentration of V and S in the glasses had been previously determined by a Cameca ims 4f ion microprobe. The vanadium K XAFSS spectra was measured using the undulator-based microprobe at Sector 13 (GeoSoilEnviroCARS) at the Advanced Photon Source, Argonne National Laboratory. X-ray microprobe techniques are described in detail elsewhere [4-8]. The vanadium K edge spectra vary

systematically with valence state. In particular, a pronounced pre-edge feature is observed near 5470 eV whose energy and intensity increases with valence state. The relationships among peak intensities, average vanadium valence, temperature, and composition were established from several sets of reference glasses. MicroEXAFS measurements made on one of the A15 Green glasses were of sufficient quality to provide first-shell coordination information [4,5].

Results: The concentration of V in the lunar glasses are as follows: A17 VLT glass = 120-140 ppm, A15 Green glass (groups A-E) = 150-170 ppm, A15 Yellow glass = 110-140 ppm, and A17 Orange glass = 100-280 ppm. The S content exhibits significant variability in the pyroclastic glasses and reflect the extent of volatile loss during eruption. The concentration of S in these lunar glasses are as follows: A17 VLT = 200-350 ppm, A15 Green = 60-210 ppm, A15 Yellow = 300-700 ppm, and the A17 Orange = 100-300 ppm.

Vanadium valence for the lunar volcanic glasses ranges from 2.7 to 2.9 (Figure 1). There is a difference among the glasses with the A17 orange glass having the lowest V valence (2.7) and the A17 VLT glass having the highest (2.9). The A15 green and yellow glass exhibit some overlap (2.8-2.9). As expected, these values are substantially lower than measurements made on terrestrial basaltic glasses (3.7-4.2) [6-8]. The A15 green glass spectrum was fit well by V3+ in octahedral coordination with 6 V-O bonds at a distance of 1.97 Å.

Differences in vanadium valence in these basaltic glasses reflect temperature, fO_2, and melt composition. Using these relationships, the lunar glass beads give a range of estimated fO_2 from IW-1.9 to IW-3.8 (temperature corrected to 1400℃ [9,10]). The calculated fO_2 are the highest for the A17 VLT glasses and the lowest for the A17 Orange glass. Overall, these calculated fO_2 values for the lunar glass are about 0.9 to 2.8 log units below previous estimates [1,2,3].

Discussion:

V valence in lunar glasses. The difference in the V valence state between the Moon and the Earth has a significant effect on element partitioning in basaltic systems. Compared to the Earth, V should be less incompatible (D <0.08 versus >0.4) in lunar olivine because olivine prefers V^{3+} to V^{4+}. This behavior is reflected in the overlap of V in basaltic magmas derived from compositionally diverse lunar magma ocean cumulate sources.

The V valence in these pyroclastic glasses appears to be related to composition. The V in the high-Ti glasses tend to have the lowest valence. Does this reflect the melt composition, the nature of the mantle source for these basalts or the eruptive mechanism? More than a function of Ti, the V valence in these glasses may be a measure of the extent of volatiles lost in eruption and the extent of reduction associated with this volatile loss. These pyroclastic glasses were a product of volatile-driven fire-fountaining. Volatile-loss is indicated by not only the mode of eruption, but by volatile-coatings on glass bead surfaces and lower volatile contents of the glasses relative to crystalline mare basalts of similar composition. For example, the S content of the lunar glasses (60-700 ppm) is less than the mare basalts (400-2600 ppm). In that the solubility of S in mare basalts increases with Ti content (VLT basalts ~ 500 ppm S, high-Ti basalts ~ 2000 ppm S), the V valence is partially a function of the difference between potential S in the melt and remaining S (= the amount of S loss). Thus a reaction such as $V_2O_3 + S = 2VO + SO$ could be partially responsible for V reduction. Another potential reaction that could be responsible for the reduction of V (and other multivalent species in the basaltic melt) involves the oxidation of C [1,3]: $V_2O_3 + C = 2VO + CO$. S could be partitioned into the volatile phase produced by this reaction.

fO_2 of the lunar pyroclastic glasses. Here and in companion abstracts [7,8] we have demonstrated that the fO_2 can be determined on small volumes of samples using XAFS spectroscopy. In the case of lunar magmatism, the real power of this approach is the ability to make these determinations non-destructively on individual pyroclastic glass beads. The estimated fO_2 for most of these glasses lie between the IW buffer and the ilmenite breakdown reaction (Ilm=Ru + I). This is consistent with previous determinations. The fO_2 recorded in these glasses reflect magmas that were produced under reduced mantle conditions (below IW) and further reduced to varying degrees by the variable oxidation of volatile species C and S. Differences within and among individual glass groups reflects differences in volatile loss. The extremely low fO_2 calculated for the orange glass is at conditions at or below the breakdown of ilmenite to metal and rutile. Based on mineral assemblages in devitrified orange glass which contain ilmenite, this appears to be unlikely. However, devitrification does occur at temperature below the liquidus and probably at higher fO_2. In addition, based on the S content of the orange glass it did experience more S loss (therefore more reduction) than the other pyroclastic glasses. Sutton et al [6,7] demonstrated that Ti content can affect V K pre-edge intensity resulting in lower V valence. To further investigate the lower V

and fO_2 implied by the orange glass, we will develop standards with TiO_2 contents similar to the A17 orange glass.

References: [1] Sato (1976) *PLSC VII*, 1323-1344. [2] BVSP (1981) 375-376. [3] Fogel R.A. et al. (1995) *GCA* 59, 201. [4] Sutton et. al. (1993) *GCA* 57, 461-468. [5] Sutton et al. (2002) RIMG 49, 429-483. [6] Sutton et al. (2004) GCA in review. [7] Sutton et al (2004) *LPS XXXV* (this cd-rom), [8] Karner et al. (2004) *LPS XXXV* (this cd-rom) [9] Longhi (1993) *GCA* 56, 2235-2252. [10] Papike et al. (1999) *Planetary Materials*.

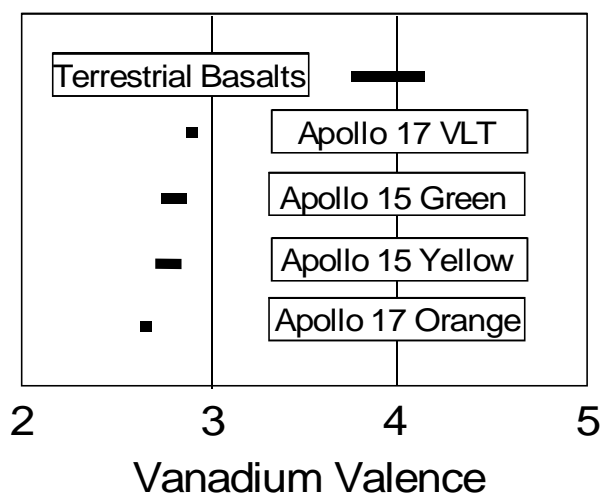Figure 1. Mean V valence for terrestrial glasses [6,7] and lunar pyroclastic glasses.

Figure 2. Estimates of f_{O_2} and temperature for the very low-titanium basalts represented by the A15 Green and A17 VLT glasses. Ilm=ilmenite, Ru=rutile, Usp=ulvospinel.