VALENCE OF Ti, V and Cr in the REDUCED APOLLO 14 BASALTS 14053 and 14072. S. B. Simon[1] and S. R. Sutton[1,2], [1]Dept. Geophysical Sci., 5734 S. Ellis Ave.; [2]Center Adv. Radiation Sources (CARS), The University of Chicago, Chicago, IL 60637, USA (sbs8@uchicago.edu).

Introduction: The oxidation states of the transition metals in lunar samples have been subjects of some interest and controversy ever since the samples became available for study. The presence of trivalent Ti in lunar pyroxene has been inferred from electron probe [1, 2] and spectroscopic [3, 4] analyses, even though (a) the fO_2 of the Ti_2O_3/TiO_2 buffer lies several orders of magnitude below the iron-wüstite (IW) buffer; and (b) Fe^{3+} was reported [5], although [3] disputed the claim. The valences of Ti, V and Cr in the olivine and pyroxene of lunar igneous rocks, important indicators of the fO_2 of their source regions, can be readily measured nondestructively by XANES (X-ray absorption near-edge structure) spectroscopy. Our preliminary work [6] showed little Ti^{3+} but much higher than expected proportions of Ti in tetrahedral coordination; both observations call into question inferences of Ti^{3+} based on Ti/Al ratios >0.5 [1, 2].

In contrast, meteoritic Ti-, Al-rich pyroxene ("fassaite" [7]) has higher Ti contents but no Ti in tetrahedral sites [7], presumably due to the high availability of Al. Because high Al activity favors octahedral Ti, and trivalent Ti only enters octahedral sites in pyroxene, we extend our search for lunar Ti^{3+}-bearing pyroxene to two Al-rich basalts from the Apollo 14 site. Valences of Cr and V are also being investigated because they are redox indicators applicable to higher oxygen fugacities than Ti^{3+}/Ti^{4+}.

Samples and Methods: One polished thin section of 14053 and one of 14072 were studied. Areas of the sections to be analyzed were documented by SEM and analyzed by electron probe. XANES spectra were collected using the GSECARS X-ray microprobe in fluorescence mode, with a 1 μm X-ray beam. Titanium valences were determined following the results of [8], who demonstrated that Ti K-edge XANES spectra of pure Ti^{4+}-bearing minerals fall into two, distinct valence-coordination clusters on a plot of pre-edge peak intensity *vs.* energy. Those with all Ti in tetrahedral coordination have high intensities and low energies, whereas those with all Ti in octahedral coordination have low intensities and high energies. Any Ti^{3+} present in olivine and pyroxene is expected to be in octahedral coordination, yielding a third data cluster, pre-edge peaks with relatively low intensity and low energy [9]. Titanium valences in unknowns were determined by applying the lever rule to mixing lines for XANES results for standards representing these three endmember occurrences. Valences are reported as values between 3 and 4, representing averages for the analytical volumes, with uncertainties based on X-ray counting statistics. The valence of V was determined from the absolute intensity of the pre-edge peak ensemble compared to glass standards as in [9]. The valence of Cr was based on the intensity of the 1s-4s peak and standardized using spectra from Fe-free glasses dominated by Cr^{3+} or Cr^{2+} as in [10]. Valences of V and Cr are expressed as values between 2 and 3. For each analytical spot, spectra were collected at several different orientations and then merged (Ti) or the results averaged (Cr) to minimize orientation effects.

Sample petrography and mineral chemistry: Samples 14053 and 14072 have been considered paired [11], but [12] reported trace element differences that argue against this.

14053. An ophitic basalt with pyroxene grains up to 5 mm across enclosing plagioclase laths [13]. This sample was described as "the most reduced rock from the moon" [11] based on petrographic evidence for subsolidus reduction of Cr-ulvöspinel to chromite+ilmenite+Fe metal, and fayalite to metal + SiO_2. The pyroxene analyzed for this study has a wide range of compositions, representing early, Mg-rich ($En_{61}Wo_{12}Fs_{27}$) to late, Fe-rich ($En_4Wo_{19}Fs_{77}$) materials. Three coarse olivine grains, Fo_{64-68}, were analyzed.

14072. Also has pyroxene and plagioclase in an ophitic texture, plus rare olivine phenocrysts [13]. This sample has also been described as "intensely reduced" [14]. A narrower range of pyroxene ($En_{64}Wo_9Fs_{27}$-$En_{25}Wo_{25}Fs_{50}$) and a wider range of olivine (Fo_{35-61}) compositions than in 14053 were analyzed.

Results: Preliminary XANES data for vanadium indicate mixtures of V^{2+} and V^{3+} for olivine and pyroxene. Pyroxene valences in the two rocks are similar, with V^{3+} dominant. For olivine, the V valence in 14053 is more reduced than that in 14072. More extensive results are available for Ti and Cr.

Valence of Ti and Cr in pyroxene. Results are summarized in Fig. 1. In 14053, Ti valence ranges from 3.73 ± 0.08 to 4.19 ± 0.13 (1σ) and averages 4.00 ± 0.18. For 14072, the range and average are 3.42 ± 0.07 to 4.17 ± 0.13 and 3.89 ± 0.23, respectively. The valences of both Ti and Cr tend to increase with ferrosilite (Fs) content, especially in 14053, where, in early pyroxene (~30 mole % Fs), ~20% of the Ti is trivalent and ~25% of the Cr is divalent. For 14072, most analyses indicate little or no Ti^{3+}, but the two

most reduced values, 3.42±0.07 and 3.66±0.07, occur in two of the most Fs-poor analysis spots.

Valence of Ti and Cr in olivine. Results are summarized in Fig. 2. Just three analyses were obtained for 14053, all less fayalitic than the olivines analyzed in 14072, and containing no Ti^{3+}. Two of the analyses of olivine in 14072, with valences of 3.77 and 3.81±0.13, have ~20% trivalent Ti and the other five analyses are within error of 4.0. The measurements of Cr valence in 14053 olivine range from 2.48±0.06 to 2.69±0.04, reduced compared to the pyroxene in that sample and compared to both olivine and pyroxene in 14072.

Proportions of Ti in tetrahedral coordination. As in our preliminary study [6] but unlike other previous studies we find significant proportions of the Ti in pyroxene to be in tetrahedral coordination. In 14053 the range is 30-66% and in 14072 it is 20-60%. This component must be considered when interpreting Ti/Al ratios in lunar pyroxene. In 7 of 10 olivine analyses, all of the Ti^{4+} is in tet sites, and two others have ~80%.

Discussion: The pyroxene results indicate that both rocks began crystallizing under conditions where small proportions of the Ti, ~10-20%, and ~75% of the Cr were trivalent. The increase in Ti valence in 14053 seen with continued crystallization could reflect drawdown of highly compatible Ti^{3+} relative to Ti^{4+} in a closed system where redox re-equilibration did not occur. The Cr valence trend (Fig. 1b) reflects the increasingly oxidized conditions. It has been suggested [11] that 14053 underwent subsolidus reduction due to impact heating to 800-900°C that mobilized solar wind-implanted H. Studies of the valence of Ti in equilibrated chondrites [15] indicate that the valence of Ti in pyroxene and olivine is not readily reset by parent-body metamorphism, even to grade 6 (Tmax ~950°C), so it is not surprising that the Ti in 14053 was not strongly reduced by the impact event. On the other hand, Cr exsolves from olivine at the very onset of chondrite metamorphism [15], possibly forming new phases and changing valence states. It is thus possible that the valences of Cr and V in olivine in 14053, reduced compared to those in 14072, were affected by the event that gave rise to the reduced assemblages observed in 14053 [11].

References: [1] Weill D. et al. (1971) *PLSC 2nd*, 413-430. [2] Papike J. et al. (1998) *RiM 36*, 7-1 – 7-11. [3] Burns R. et al. (1973) *PLSC 4th*, 983-994. [4] Sung C-M. et al. (1974) *PLSC 5th*, 717-726. [5] Cohen A. (1973) *LS IV*, 151–153. [6] Simon S. et al. (2014) *LPS XLV*, Abstract #1063. [7] Dowty E. and Clark J. (1973) *Am. Min. 58*, 230-242. [8] Farges F. et al. (1997) *Phys. Rev. B*, 56, 1809-1819. [9] Sutton S. (2005) *GCA 69*, 2333-2348. [10] Bell A. et al. (2014) *Am. Min. 99*, 1404-1412. [11] Taylor L. A. et al. (2004) *Am. Min. 89*, 1617-1624. [12] Neal C. and Kramer G. (2006) *Am. Min. 91*, 1521-1535. [13] Meyer C. (2011) *Lunar Sample Compendium*. [14] Haggerty S. (1977) *PLSC 8th*, 1809-1829. [15] Simon S. et al. (2015) *LPS XLVI*. Abstract #2141.

Fig. 1a

Fig. 1b

Fig. 2a

Fig. 2b