VALENCES OF Ti, V and Cr in APOLLO 17 HIGH-Ti BASALTS.  S. B. Simon\textsuperscript{1} and S. R. Sutton\textsuperscript{1,2}, \textsuperscript{1}Dept. Geophysical Sci., 5734 S. Ellis Ave.; \textsuperscript{2}Center for Advanced Radiation Sources (CARS), The University of Chicago, Chicago, IL 60637, USA (sbs8@uchicago.edu).

Introduction: 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$_2$O$_3$/TiO$_2$ buffer lies several orders of magnitude below the iron-wüstite (IW) buffer; and (b) Fe$^{2+}$ 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\footnote{S. R. Sutton personal communication.} origin. XANES spectra were nondestructively by XANES (X-ray Absorption Near-Edge Structure) spectroscopy. Our initial work [6,7,8] 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]. Sung et al. [4] reported absorption bands in the visible to near-infrared region of spectra A-17 pyroxene that were attributed to Ti$^{3+}$. They estimated Ti$^{3+}$ proportions to be 30-40% from electron probe analyses but assumed that Ti did not enter tetrahedral sites. XANES work on A-17 glasses and basalt compositions led Krawczynski et al. [9] to conclude that $\sim$10% of the Ti in their source region could be trivalent, and Karner et al. [10] inferred an $fO_2$ of IW-2 for A-17 orange glass from its V valence. To see if the pyroxene and olivine in A-17 basalts do indeed contain Ti$^{3+}$ and/or reduced V and Cr, we analyzed two samples, 70017 and 74275.

Samples and Methods: One polished thin section of each sample was studied. Areas of the sections to be analyzed were documented by SEM and analyzed by energy-dispersive spectroscopy. XANES spectra were collected using the GSECARS X-ray microprobe in fluorescence mode, with a 1 µm X-ray beam. Valences were determined following the results of [11], who demonstrated that Ti K-edge XANES spectra of pure Ti$^{4+}$-bearing minerals fall into 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. 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 precisions based on spectral fitting uncertainties. The valence of V was determined from the absolute intensity of the pre-edge peak ensemble compared to glass standards as in [12]. The valence of Cr was determined using Fe-free glass standards with Cr$^{3+}$ or Cr$^{2+}$ as in [13]. For each analytical spot, spectra were collected at two to four different orientations and then merged to minimize orientation effects.

Sample petrography and mineral chemistry: 70017. The texture and mineral chemistry of this medium-grained vesicular basalt were reported by [14,15]. Its mode is 50% pyroxene, 26% plagioclase, 22% ilmenite, and minor amounts of olivine, troilite, metal, silica and mesostasis. Olivine and ilmenite crystallized before pyroxene and plagioclase. Early pyroxene is relatively Ti-, Al-rich augite; contents of these minor elements decreased as crystallization continued toward pigeonite composition [14].

74275. Also studied by [15], this sample is finer-grained than 70017. It has olivine phenocrysts, smaller pyroxene phenocrysts, and acicular ilmenolite with ilmenite rims in a groundmass of augite and plagioclase. Olivine is more abundant in this sample than in 70017 (~15 vs. ~1 vol%) and more magnesian (Fo$_{76.85}$ vs. Fo$_{59.72}$). Pyroxene in this sample is richer in TiO$_2$ (3.6-6.1 wt%) than that in 70017 (1.6-3.6 wt%) [16].

Results: Preliminary XANES data for vanadium indicate mixtures of V$^{2+}$ and V$^{3+}$ for olivine and pyroxene. Average pyroxene valences are 2.75±0.07 in 70017 and 2.87±0.05 in 74275. Average V valences in olivine are lower, 2.60±0.16 in 70017 and 2.53±0.05 in 74275. More extensive results are available for Ti and Cr (50 pyroxene and 18 olivine analyses).

Valence of Ti and Cr in pyroxene. Results are summarized in Fig. 1. In 70017, Ti valence ranges from 3.65±0.08 to 3.94±0.10 and averages 3.79±0.08. For 74275, the range and average are 3.66±0.06 to 4.01±0.08 and 3.86±0.11, respectively, quite similar to 70017. The valences of Ti and Cr do not vary systematically with ferrosilite (Fs) (Fig. 1). The valence of Cr (Fig. 1b) has a wider range in 70017, 2.69±0.05 to 2.84±0.05, than in 74275, 2.81±0.05 to 2.86±0.05.

Valence of Ti and Cr in olivine. Results are summarized in Fig. 2. Just three analyses were obtained for 70017, all for olivine less magnesian than that analyzed in 74275, and containing no Ti$^{4+}$. Both Ti and Cr are more reduced in 74275 olivine than in 70017 olivine. In both samples Cr is more reduced in the olivine than in the coexisting pyroxene. As the plots show, in
pyroxene the Cr valence is $\geq 2.7$, and in olivine it is $\leq 2.7$. In 70017, Ti is more reduced in pyroxene (avg. 3.8) than in olivine (avg. 4.0), and in 74275 the Ti valences in olivine and pyroxene average 3.9.

Proportions of Ti in tetrahedral coordination in pyroxene. As in previous work [6,7,8] significant proportions are observed. Pyroxene in 74275 generally has lower proportions of tet Ti (11-27%) than that in 70017 (18-43%), likely due to its higher Al$_2$O$_3$ contents (5.0-9.6 wt% in 74275 vs. 1.3-4.9 wt% in 70017) [8].

Discussion: These two rocks have very similar bulk compositions but different crystallization sequences [15], accounting for the differences in pyroxene composition. Unlike that in 70017, pyroxene in 74275 crystallized before Fe-Ti oxides and plagioclase and thus has higher Al and Ti contents and lower tet Ti proportions. Although the latter feature has been associated with lower Ti$^{4+}$ proportions, the range of valence of Ti in pyroxene is about the same in both samples (Fig. 1a), and it shows no correlation with Fs component, tet Ti proportions, or atomic Ti/Al ratio. It is worth noting that almost all pyroxene valence results are not within error of 4.0. Pyroxene in both A-17 samples tends to have larger Ti$^{4+}$ components than was found for pyroxene in A-14 aluminous basalts [7], but smaller ones than the 30-40% inferred by [4].

The large difference in average Cr valence between the pyroxene (2.83±0.02) and olivine (2.38±0.11) in 74275 is of interest. It was suggested [17] that the coarse, magnesian olivine “megacrysts” in this rock are exotic fragments; Delano and Lindsley [18] agreed with [17] that the 74275 bulk composition is not that of the parental melt but concluded that, unlike a dunite clast also found in 74275 [17], the coarse olivine grains could be related to the host rock. Our data are consistent with these suggestions that the olivine and pxy in 74275 did not crystallize from the same melt.