VALENCES OF Ti and Cr in APOLLO 16 IMPACT MELT ROCKS. S. B. Simon[1] and S. R. Sutton[2,3], [1]Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131(sbs8@unm.edu). [2]Dept. Geophysical Sci., 5734 S. Ellis Ave.; [3]Center for Advanced Radiation Sources (CARS), The University of Chicago, Chicago, IL 60637, USA.

Introduction: We have been investigating the valences of Ti, Cr and V in lunar basalts [1,2] in order to learn about redox conditions in their source regions, and in the lunar interior in general. That work has revealed that those samples have small Ti^{3+} components and have divalent and trivalent Cr and V. Here we extend that work to large-scale impact melts to learn about their redox environments and for comparison with results for the internally melted samples. For this work three Apollo 16 crystalline melt breccias (CMBs), 60315, 65015, and 68416 were analyzed by XANES (X-ray absorption near-edge structure spectroscopy). This is the first such study of this sample type. In addition to average valences of the multi-valent cations, the coordination environments of Ti (octahedral vs. tetrahedral) are also determined by this non-destructive method.

Methods: One or two polished thin sections of each sample 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. Valences were determined following the results of [3], 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^{4+} 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 of Ti are reported as values between 3 and 4, representing averages for the analytical volumes, with precisions based on spectral fitting uncertainties. The valence of Cr was determined using Fe-free glass standards with Cr^{3+} or Cr^{2+} as in [4]. For each analysis spot, for both Ti and Cr, spectra were collected at three or four different orientations and merged to minimize orientation effects. Average 1σ errors for valence measurements are ±0.12 (Ti) and ±0.05 (Cr).

Sample petrography and mineral chemistry:

60315. This sample is a poikilitic rock consisting of approximately 50 vol% plagioclase, 35% orthopyroxene, 7% olivine, 5% augite, and 3% opaques [5,6]. Pyroxene and olivine poikilitically enclose plagioclase.

Plagioclase is anhedral to subhedral, typically 50-100 μm across. Pyroxene typically contains 2.5 wt% CaO, 1% TiO_2, 0.6 wt% Cr_2O_3, and 10-12 % FeO. Olivine is Fo_{71-77} with ~0.1 wt% of TiO_2 and Cr_2O_3.

65015. In this sample pyroxene poikilitically encloses anhedral to subhedral plagioclase and olivine. The sample has ~60 vol% plagioclase, 29% low-Ca pyx (2 wt% CaO), and 6% high-Ca pyx [7,8], with 18 wt% CaO. The low-Ca pyx contains 0.5-1 wt% TiO_2 and ~0.5 wt% Cr_2O_3. The high Ca-pyx contains 1.4-2.5 wt% TiO_2 and 0.5-0.7 wt% Cr_2O_3.

68416. This sample is different from the other two. Described as "basalt-textured" [9], with ~80 vol% plagioclase, and ~15% pyroxene and minor olivine both interstitial to abundant plagioclase laths. Pyroxene has a wider range of FeO contents, 9-20 wt%, than the other samples considered here, and its TiO_2 and Cr_2O_3 contents range from 0.3-1.4 and 0.2-1.0, respectively.

Results: Valence results are summarized in Fig. 1a (pyroxene) and Fig. 1b (olivine). No trivalent Ti was detected in 65015 pyroxene; 60315 has the most reduced pyroxene, with four grains having average valences between 3.6 and 3.7; valences in 68416 range from 3.75 to 4. In all three samples, most Cr valences in pyroxene are between 2.6 and 2.8. In olivine, 60315 has the widest ranges of both Ti (3.68-4) and Cr (2.4-2.8) valences. Most olivine has Ti valences of 3.9±0.1 or higher, so most analyses are within 1σ of 4. The analytical uncertainty on the Cr valences is ±0.05, so no analyses are within error of 3 (Fig. 1b). In neither pyx nor olivine are the Ti and Cr valences correlated.

Proportions of the Ti cations that are in tetrahedral coordination are plotted against ferrosilite (Fs) content in Fig. 2 (pyroxene) and against fayalite (Fa) in Fig. 3 (olivine). Here the 68416 data are quite different from the results for the other samples. Its pyroxene has a wider range of Fs contents, and olivine in 68416 contain more FeO, than 60315 and 65015. Most of the pyroxene in the latter samples has higher proportions of tet Ti than that in 68416. In contrast, olivine in 68416 has higher tet Ti proportions and FeO than the other samples. Thus, there is little overlap between the 68416 data and that for the other samples in Fig. 3. Pyroxene in the CMBs has higher tet Ti proportions than most mare basalt pyroxene [10].

Discussion: The valence ranges of Ti in the CMB pyroxene and olivine are similar to the ranges in those phases in mare basalts [2,10]; Cr in the CMB pyroxene is slightly reduced compared to most pyroxene in A-17

high-Ti basalts and A-14 aluminous basalts, and within the range of Cr valences in very low-Ti basalts [10]. In CMB olivine, however, Cr tends to be slightly oxidized compared to that in basalts.

The CMBs have similar valence ranges to each other, but 68416 and 60315 differ in texture and bulk composition, and are thought to derive from different melt sheets [6,11]. The different tet Ti systematics may be due to different crystallization sequences. In 60315, olivine was early (before plag) and has lower tet Ti proportions (Fig. 3) and higher Al_2O_3 contents [6] than ol in 68416, in which olivine crystallized after plagioclase [12]. Pyroxene in 60315 also has higher Al_2O_3 contents than that in 68416 [6], but also has higher tet Ti proportions than 68416 pyx (Fig. 2); the reason for this relationship is not clear.

A difference between the CMB and basalt results is that in the CMBs, the Cr valence ranges of pyroxene and olivine are similar whereas in the basalts Cr is reduced in olivine compared to pyroxene in the same sample
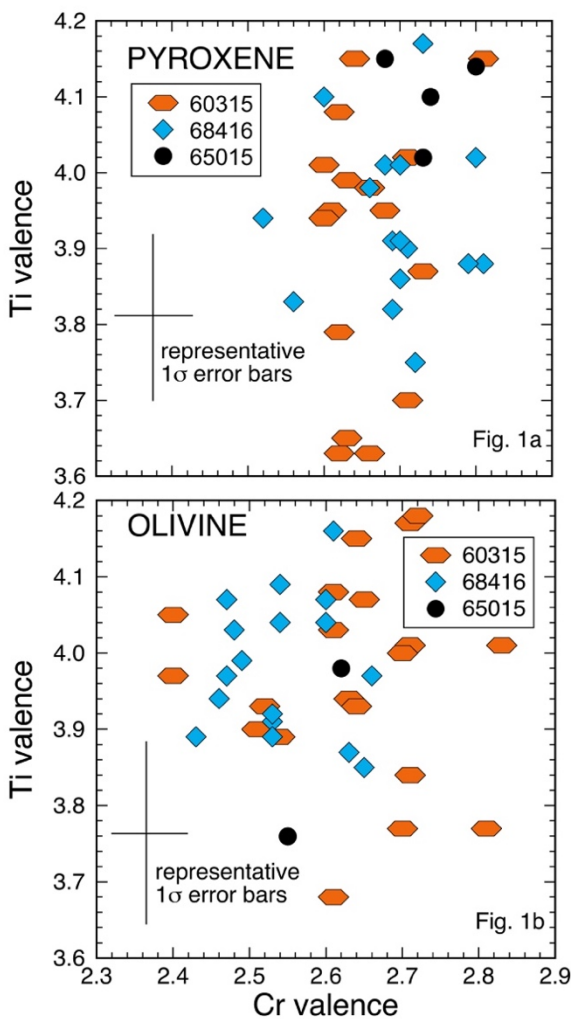
[2,10]. This may be due to a change in redox conditions from relatively reducing to relatively oxidizing during basalt crystallization [10], possibly caused by H_2 degassing, which can increase the fO_2 of the residual melt [13]. The CMB melts were not brought up from depth, so their lack of this feature is consistent with this theory.

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Fig. 1a

Fig. 1b

Fig. 2

Fig. 3