

**VALENCES OF Ti and Cr in LUNAR CRYSTALLINE MELT BRECCIAS.** S. B. Simon<sup>1</sup> and S. R. Sutton<sup>2,3</sup>,  
<sup>1</sup>Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131 ([sbs8@unm.edu](mailto:sbs8@unm.edu)). <sup>2</sup>Dept. Geophysical Sci., 5734 S. Ellis Ave., <sup>3</sup>Center for Advanced Radiation Sources (CARS), The University of Chicago, Chicago, IL 60637, USA.

**Introduction:** We have investigated 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  $\text{Ti}^{3+}$  components and have divalent and trivalent Cr and V. We are now extending our study to large-scale impact melts to learn about their redox environments and for comparison with results for the internally melted samples. For this work an Apollo 15 crystalline melt breccia (CMB), 15445, and an Apollo 17 CMB, 76215, were analyzed by XANES (X-ray absorption near-edge structure spectroscopy). 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. Sample 15445 is thought to be Imbrium ejecta and 76215 is thought to have formed in the Serenitatis impact [3]. The present results are compared with our previous results for Apollo 16 CMBs 60315, 65015, and 68416 [4].

**Methods:** Polished thin sections 15445,256, 15445,293 and 76215,121 were studied. Areas to be analyzed by XANES 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  $\mu\text{m}$  X-ray beam. Valences were determined following the methods of [2]. Briefly, Ti K-edge XANES spectra of pure  $\text{Ti}^{4+}$ -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  $\text{Ti}^{4+}$  in octahedral coordination have low intensities and high energies. Any  $\text{Ti}^{3+}$  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  $\text{Cr}^{3+}$  or  $\text{Cr}^{2+}$  as in [5]. 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  $1\sigma$  errors for valence measurements are  $\pm 0.12$  (Ti) and  $\pm 0.05$  (Cr).

#### **Sample petrography and mineral chemistry:**

**15445.** This sample has magnesian plutonic and metamorphic lithic clasts in a matrix of mineral fragments and recrystallized glass [3]. We mainly analyzed matrix pyroxene and olivine grains, most of which, with  $\text{Fe}/(\text{Fe}+\text{Mg}) < 0.2$ , are less ferroan than their counterparts in the A-16 and A-17 samples considered here. Pyroxene  $\text{TiO}_2$  contents range from 0.2 to 1.3 wt%  $\text{TiO}_2$  and average 0.5 wt%. For  $\text{Cr}_2\text{O}_3$  the corresponding values are 0.4–1.7 and 0.6 wt%, respectively.

**76215.** This sample is vesicular. Pyroxene poikilitically encloses anhedral olivine and lath-shaped plagioclase. The sample has ~50 vol% plagioclase, 30% low-Ca pyx (2 wt%  $\text{CaO}$ ), and 10% high-Ca pyx and olivine [5,6], with minor ilmenite and metal. The low-Ca pyx we analyzed contains 0.7–1.3 wt%  $\text{TiO}_2$  and ~0.6 wt%  $\text{Cr}_2\text{O}_3$ . The high Ca-pyx contains 2.0–3.0 wt%  $\text{TiO}_2$  and 0.5–0.8 wt%  $\text{Cr}_2\text{O}_3$ .

**Results:** The ranges of pyroxene Ti valences are similar in all three suites, from ~3.6 to 4. Most Ti valences in pyroxene and olivine are within  $1\sigma$  of 4 (i.e., no  $\text{Ti}^{3+}$ ) but each sample also has some grains of each phase that are not within  $1\sigma$  of 4. In olivine, the suites have similar Ti valence ranges but Cr is generally reduced in the A-16 samples compared to 15445 and 76215. This is shown in Fig. 1, where the average valences of Ti and Cr are plotted. The average Cr valences are  $2.76 \pm 0.11$  (15445),  $2.69 \pm 0.12$  (76215),  $2.63 \pm 0.12$  (60315),  $2.61 \pm 0.08$  (65015), and  $2.54 \pm 0.07$  (68416). In the A-16 and A-17 samples, olivine also has reduced Cr compared to coexisting pyroxene, whereas in 15445 the olivine and pyroxene have nearly identical average valences (Fig. 1). The average valence of Ti in 76215 pyroxene is lower than the A-15 or A-16 pyroxene pyroxene averages. In neither pyroxene nor olivine are the Ti and Cr valences correlated with each other or (except for Cr valences in 15445 pyroxene) with FeO contents.

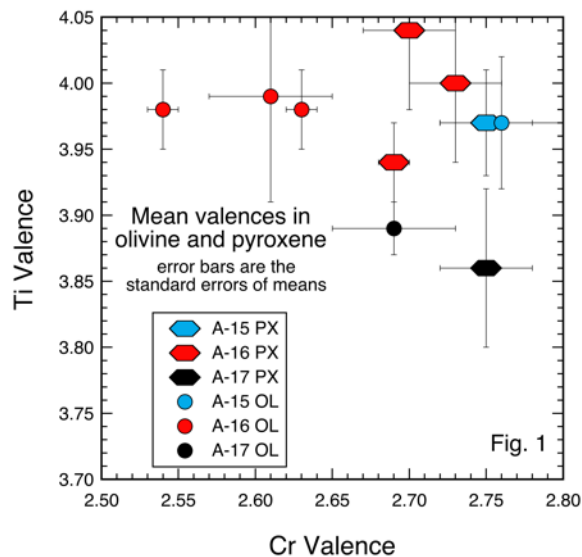
Proportions of the Ti cations that are in tetrahedral coordination are plotted against Ti valence in Fig. 2. Significant proportions of Ti,  $\geq \sim 20\%$ , occur in tetrahedral coordination. There is a correlation between these parameters in pyroxene (Fig. 2a) but not in olivine (Fig. 2b). Some correlation is to be expected, as  $\text{Ti}^{4+}$  can enter tetrahedral sites but  $\text{Ti}^{3+}$  does not.

#### **Discussion:**

**Comparison of Ti and Cr valences in CMBs and mare basalts.** The valence range of Ti in the CMB pyroxene, ~3.6–4, is similar to the ranges found for mare

basalt pyroxene [1, 2]. Cr in the CMB pyroxene (2.6–2.8) is slightly reduced compared to most pyroxene in A-17 high-Ti basalts, partially overlaps with A-14 aluminous basalts (2.7–2.85), and is within the wide range of Cr valences (2.3–2.8) in A-17 very low-Ti basalts [2]. In CMB olivine, however, Cr tends to be slightly oxidized compared to that in basalts. The valence range of Ti in the CMB olivine, ~3.7–4, is similar to the ranges found for mare basalt olivine [1, 2].

A difference between the CMB and basalt results is that in the CMBs, the valence of Cr in olivine in a sample tends to be slightly reduced compared to Cr in pyroxene in that sample, whereas in the basalts Cr is rather strongly reduced in olivine compared to pyroxene in the same sample [2]. This may be due to a change in redox conditions from relatively reducing to relatively oxidizing during basalt crystallization [2], possibly caused by extrusion-related  $H_2$  degassing, which can increase the  $fO_2$  of the residual melt [6]. Olivine crystallized earlier than pyroxene in the basalts analyzed; some grains crystallized at depth, well before eruption and any significant degassing. This could explain why Cr and V are reduced in early phases in A-17 basalts compared to later-crystallized phases [2]. The CMB melts, on the other hand, were not brought up from depth; their lack of this feature is consistent with this theory.



The proportions of Ti in tetrahedral coordination in pyroxene are affected not only by Ti valence but also by availability of Al. The correlation with valence seen in Fig. 2a is probably a reflection of the relatively low Al contents of pyroxene in the present samples. In contrast, in the relatively Al-rich pyroxene in the A-17 high-Ti basalt 74275, tetrahedral Ti proportions are not correlated with Ti valence [2]. With respect to olivine, in neither mare basalts nor CMBs are tetrahedral Ti proportions correlated with Ti valence.

**References:** [1] Simon S. B. and Sutton S. R. (2017) *M&PS* 52, 2051-2066. [2] Simon S. B. and Sutton S. R. (2018) *M&PS* 53, 2138-2154. [3] Meyer C. E. (2011) Lunar Sample Compendium. [4] Simon S. B. and Sutton S. R. (2018) *LPS XLIX*, Abst. #1232. [5] Goodrich C. A. et al. (2013) *GCA* 122, 280-305. [6] Sharp Z. D. et al. (2013) *EPSL*, 380, 88-97.

