

**VALENCES OF Ti, V and Cr in APOLLO 17 BASALT PYROXENE: COMPARISON OF HIGH-Ti and VERY LOW-Ti BASALTS.** 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:** Elements that occur in more than one valence state are potential  $fO_2$  indicators, and determination of their valences in a sample can constrain the  $fO_2$  at which it formed and record features of its petrogenetic history. With respect to lunar samples, three such elements are Ti ( $Ti^{3+}$ ,  $Ti^{4+}$ ), Cr ( $Cr^{2+}$ ,  $Cr^{3+}$ ) and V ( $V^{2+}$ ,  $V^{3+}$ ). The valences of these elements (specifically, their average valence in an analytical volume) can be readily measured nondestructively by XANES (X-ray Absorption Near-Edge Structure) spectroscopy. The  $Ti^{4+}$  cation can occur tetrahedrally- and octahedrally-coordinated sites in olivine and pyroxene, and in addition to valence, the pre-edge structure of the absorption spectrum is also sensitive to the coordination environment of the cation. We have analyzed high-Ti and very low-Ti (VLT) basalts from the Apollo 17 site to compare the relationships in them and to look for implications as to similarities and differences in their sources.

**Samples:** Polished thin sections of two high-Ti (70017 and 74275) and three VLT (70006,371; 70007,289; 70007,296) samples were studied. Both high-Ti samples were studied by [1] and many others. Sample 70017 is medium-grained and vesicular; 74275 has coarse olivine megacrysts [2] and dunite inclusions [2,3,4,5] in a finer groundmass of olivine, pyroxene, and plagioclase. All three petrographically distinct types of olivine were analyzed by XANES previously [7,9]. The VLTs are lithic fragments from the A-17 deep drill core and described by [6]. All three are dominated by pyroxene and plagioclase, with minor olivine and chromite. In addition to the XANES data reported for the high-Ti basalts by [7], new data for the VLTs are reported here.

**Methods:** Areas of the sections to be analyzed were documented by scanning electron microscope and analyzed by either energy-dispersive spectroscopy or wavelength-dispersive analysis (electron probe). XANES spectra were collected using the GSECARS X-ray microprobe in fluorescence mode, with a 1  $\mu m$  X-ray beam. Valences of Ti were determined following the results of [8], as described in detail elsewhere [9]. The valence of V was determined from the absolute intensity of the pre-edge peak ensemble compared to glass standards as in [10]. The valence of Cr was determined using Fe-free glass standards with  $Cr^{3+}$  or  $Cr^{2+}$  as in [11]. For each analytical spot, spectra were collected at two to four different orientations and then merged to minimize orientation effects. Valences, representing averages for

the analytical volumes, are reported as values from 3 to 4 for Ti and from 2 to 3 for V and Cr.

**Results:** Valence and coordination results are summarized in Figs. 1 and 2. Valences are plotted against the FeO component ferrosilite (Fs) in Fig. 1 and against the percentages of  $Ti^{4+}$  in tetrahedral coordination in Fig. 2. In Fig. 1 there is very little overlap between the high-Ti basalts and the VLTs, mainly due to the higher FeO contents of pyroxene in the latter. There is much overlap in ranges of Ti valences, with most of the pyroxene in both suites having  $Ti^{3+}$  components of 0 to 30%. Valences of Cr, however, extend to much lower (more reduced) values in the VLTs than in high-Ti basalt pyroxene. Another difference between VLTs and high-Ti basalts is that in pyroxene in the VLTs, Ti and Cr valences and proportions of Ti in tetrahedral sites increase with increasing FeO contents, a trend not observed in the high-Ti basalts. In 74275, <20% of the Cr is divalent. In 70017 average Cr valences range from 2.7-2.85 and they are anticorrelated with tet Ti percentage. In contrast, in the VLTs, both Ti and Cr tend to be more oxidized with increasing tet Ti proportions (Fig. 2). In the high-Ti basalts, there is no correlation between Ti valences and either FeO content or tet Ti percentage.

Valences of V have a wider range in the VLTs (~2.55-2.95) than in the high-Ti samples (~2.65-2.85). In both suites there is no correlation between V valence and FeO content.

Chromite is the principal oxide phase in the VLTs studied here [6], so it was also analyzed. The XANES analyses show that the valence of Cr in VLT chromite is within  $1\sigma$  error (0.05) of 3.0; the proportion of  $Cr^{2+}$  in the chromite is <5%.

**Discussion:** Figures 1 and 2 clearly show contrasting systematics for the high-Ti basalts compared to the VLTs. The simplest explanation for the trends of increasing oxidation state of both Ti and Cr with increasing FeO content in pyroxene (Fig. 1) is that oxidation occurred during crystallization of pyroxene in the VLTs. In addition, chromite is an early-crystallizing phase in VLTs [12] and it is  $Cr^{3+}$ -rich, so chromite fractionation may have caused early depletion in  $Cr^{3+}$  relative to  $Cr^{2+}$  and contributed to the Cr valence trend seen in those samples.

It is worth noting, however, that early phases in all basalts studied thus far have reduced Ti and/or Cr valences compared to later crystallization products. In early pyroxene in A-14 aluminous basalts, Ti is reduced

relative to later-formed pyroxene [9]. An olivine phenocryst in A-15 basalt 15555 has higher  $Cr^{2+}/Cr^{3+}$  in its core than in its rim [9]. Olivine is an early phase in many basalts, and, in addition to the trends shown in Fig. 1, in both VLTs and in high-Ti basalts, the valence of Cr in olivine is reduced compared to that in pyroxene. The first-order interpretation is that the early, deeper crystallization environments were more reducing than the later, shallower ones. This could be the result of  $H_2$  degassing of basaltic melts with decrease in confining pressure, increasing the  $fO_2$  of the residual melt [13]. In contrast, initial results for A-16 crystalline melt breccias [14], which did not undergo extrusion from depth, show similar intrasample Ti and Cr valences in olivine and pyroxene.

The cause of the contrasting valence-coordination relationships (Fig. 2) is less intuitive. While a positive

correlation between Ti valence and tetrahedral proportions is not surprising, it is not clear why there should be such a relationship between Cr valence and tet Ti in the VLTs and an anticorrelation in the high-Ti basalts.

**References:** [1] Hodges and Kushiro (1974) *PLSC 5th*, 505-520. [2] Walker D. et al. (1976) *EPSL*, 30, 27-36. [3] Meyer C. and Wilshire H. (1974) *LS V*, 503-505. [4] Delano J. and Lindsley D. (1982) *LPS XIII*, 160-161. [5] Shearer C. et al. (2015) *M&PS* 50, 1449-1467. [6] Wentworth S. et al. (1979) *PLPSC 10<sup>th</sup>*, 207-223. [7] Simon S. and Sutton S. (2017) *LPS XLVIII*, Abstract #1030. [8] Farges F. et al. (1997) *Phys. Rev. B*, 56, 1809. [9] Simon S. and Sutton S. (2017) *M&PS* 52, 2051-2066. [10] Sutton S. et al. (2005) *GCA* 69, 2333-2448. [11] Goodrich C. et al. (2013) *GCA* 122, 280-305. [12] Vaniman D. and Papike J. (1977) *PLSC 8<sup>th</sup>*, 1443-1471. [13] Sharp Z. et al. (2013) *EPSL*, 380, 88. [14] Simon S. and Sutton S. (2018) This volume. Abstract #1232.

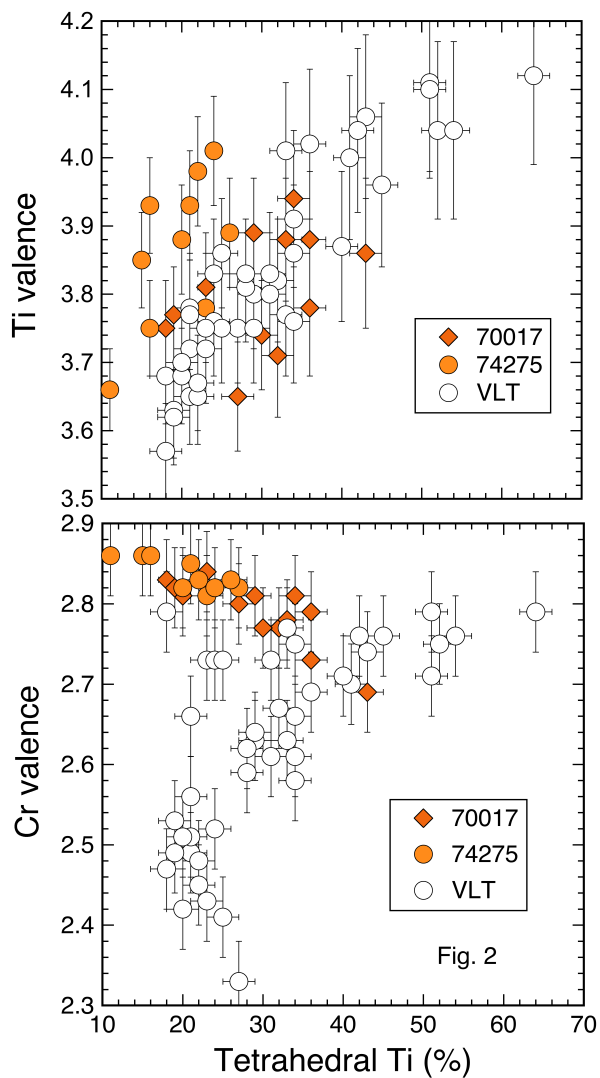
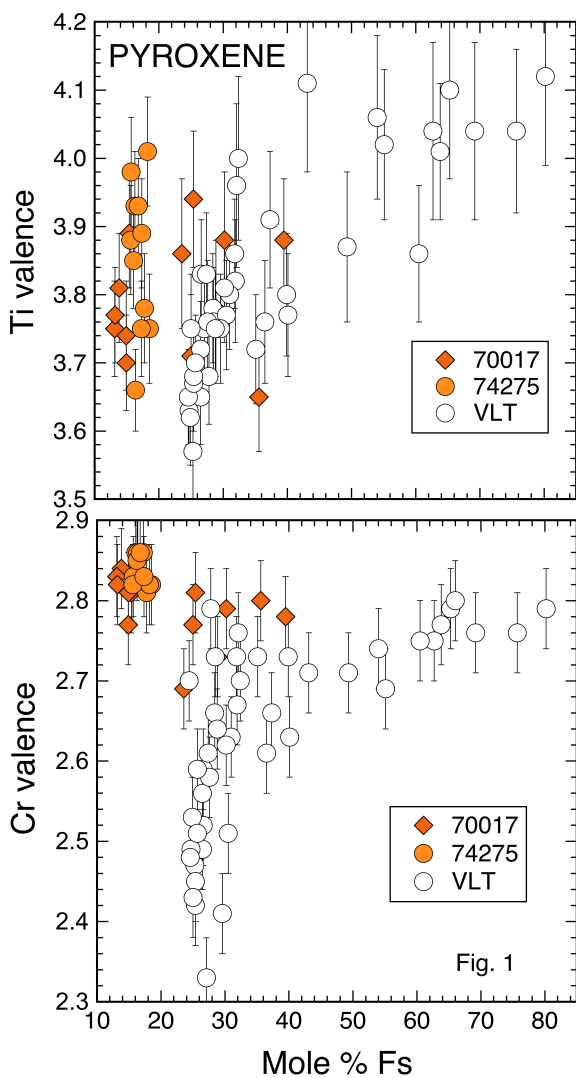


Fig. 1

Fig. 2