

**VALENCE OF Ti in LUNAR IGNEOUS ROCKS: THE FIRST DIRECT MEASUREMENTS.** S. B. Simon<sup>1</sup>, S. R. Sutton<sup>1,2</sup>, and L. Grossman<sup>1,3</sup>. <sup>1</sup>Dept. Geophysical Sci., 5734 S. Ellis Ave., The University of Chicago, Chicago, IL 60637; <sup>2</sup>Center for Advanced Radiation Sources (CARS), The University of Chicago; <sup>3</sup>Enrico Fermi Institute, The University of Chicago (sbs8@uchicago.edu).

**Introduction:** Ever since lunar samples were returned they have been known to have formed under reducing conditions, and the oxygen fugacity ( $fO_2$ ) under which they formed has been a subject of interest. There are many studies in the literature, with a general consensus of one log unit below the iron-wüstite buffer, or IW-1, as the best estimate of the  $fO_2$  of the lunar mantle [1]. The  $fO_2$  of the  $Ti_2O_3/TiO_2$  buffer lies several orders of magnitude below IW and most lunar pyroxene and olivine have high FeO contents, so lunar silicates have long been expected to have negligible  $Ti^{3+}/Ti^{4+}$  ratios. With the recent detection of  $Ti^{3+}$  in FeO-bearing chondrules [2], however, the assumption that FeO and  $Ti_2O_3$  cannot coexist is not safe. Despite decades of effort, some uncertainty remains regarding the  $fO_2$  of the lunar mantle and the presence of  $Ti^{3+}$  in lunar samples. For example, results for the  $fO_2$  of the Apollo 17 orange glass source region span most of the range of suggested lunar values, from IW-0.6 [3] to IW-2 [4]. Even for the higher value, experimental results suggest that ~10% of the Ti would be trivalent [5], and inferences of small  $Ti^{3+}$  components in lunar pyroxenes have been made on the basis of crystal chemistry [6,7]. From the work of [5], it appears likely that the lunar mantle contained significant amounts of  $Ti^{3+}$ , and although measurement of the valence of Ti in lunar rocks could decrease the uncertainty about the  $fO_2$  of their formation, such measurements have not been performed. The conclusion that the redox state of mare basalts was not significantly modified since they were generated [4] makes the valence of Ti in them a potentially valuable recorder of both the redox state of the lunar mantle and its spatial variability. We have used XANES (X-ray absorption near-edge structure) spectroscopy to measure the valence of Ti in a small but diverse suite of lunar igneous rocks.

**Samples and Methods:** The sample suite consists of two basalts and two plutonic rocks, selected to represent a range of sources, compositions and crystallization conditions. Samples are: 10020 (A-11 Ti-rich, low-K basalt); 15555 (A-15 low-Ti basalt); 15415 (A-15 anorthosite); and 76535 (A-17 troctolite). Areas of the polished thin sections to be analyzed were documented by SEM and analyzed by electron probe. Titanium K XANES spectra were collected using the GSECARS X-ray microprobe in fluorescence mode, with a 1  $\mu m$  X-ray beam. Valences were determined following the results of [8]. That study 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.

**Sample petrography and mineral chemistry:**

**10020.** This basalt has ~50 vol% clinopyroxene with 1-3 wt% each of  $TiO_2$  and  $Al_2O_3$ , 31% plagioclase laths ( $An_{82}$ ), 12% acicular ilmenite, and ~5% olivine phenocrysts ( $Fo_{70}$ ) [10].

**15555.** This basalt is vuggy and has less ilmenite, more olivine and coarser pyroxene than 10020, with 0.5-1 wt%  $TiO_2$  and 1-2 wt%  $Al_2O_3$  in the cpx [11]. Reported modes for this apparently heterogeneous sample are: cpx 40-65%; plag 25-35%; olivine 5-20%; opaques 2.7-5%; and mesostasis 0.2-5% [12].

**15415.** A pristine, unbrecciated anorthosite with ~98% coarse (~2-3 cm) plag ( $An_{96}$ ) and ~2% fine (~100  $\mu m$ ) augite ( $En_{39}Wo_{45}Fs_{16}$ ) and trace amounts of hypersthene ( $En_{57}Wo_3Fs_{40}$ ) and ilmenite [12].

**76535.** A troctolite composed of ~60 vol% plagioclase ( $An_{96}$ ), ~35% olivine ( $Fo_{87}$ ) and ~5% orthopyroxene ( $En_{84}Wo_1Fs_{11}$ ) with trace augite, metal and phosphate [10]. Both the opx and cpx have ~0.5 wt%  $TiO_2$  and ~1 wt%  $Al_2O_3$  [13].

**Results:** The valence of Ti in the pyroxene and olivine of each of these samples is given in Table 1. Values identified as “merge” are valences calculated from summation of spectra in an attempt to correct for orientation effects, whereas “mean” values are averages of results for individual spectra. In both basalts, all analyses are within  $2\sigma$  of 4.0, except for the analysis of pigeonite in 15555. Both analyses of troctolite 76535 are within  $1\sigma$  of 4.0. Some variability is seen in the analyses of 15415, which range from  $3.6\pm 0.1$  to  $4.3\pm 0.1$ . When all eight spectra are merged, however, the result is  $4.0\pm 0.1$ .

In addition, significant proportions of tetrahedrally coordinated (tet) Ti are observed, with higher values in

the highland samples than in the basalts. The pyroxene in the basalts tends to have 30-40% of its Ti in tetrahedral coordination, whereas that in 15415 averages 49% and the 76535 pyx analysis has 87% (Table 1).

Table 1. Valences of Ti in lunar olivine and pyroxene, measured by XANES.			
	Ti Val.	1 $\sigma$	Tet %
<b>10020</b>			
PX1	4.25	0.11	33
PX2	4.00	0.07	15
PX3	4.12	0.09	29
PX4	3.90	0.10	34
<b>PX Mean</b>	<b>4.07</b>	<b>0.15</b>	<b>28</b>
OL2	4.20	0.12	42
OL3	4.03	0.12	43
OL4	3.85	0.08	25
<b>OL Mean</b>	<b>4.04</b>	<b>0.14</b>	<b>34</b>
<b>15555</b>			
OL1 (low Fe)	3.91	0.13	86
OL2 (high Fe)	3.96	0.13	81
PIG	3.41	0.08	28
<b>76535</b>			
PX1	3.93	0.07	87
OL1	3.91	0.09	81
<b>15415</b>			
PX1	3.83	0.11	38
PX2	3.72	0.11	42
PX3	4.30	0.13	56
PX4	3.64	0.08	56
PX5	4.27	0.13	56
PX6	4.28	0.14	51
PX7	3.64	0.08	26
PX8	4.18	0.13	52
<b>15415 PX Merge</b>	<b>3.99</b>	<b>0.13</b>	<b>49</b>

**Discussion.** Most of the measurements of the valence of Ti in the basalts are within error of 4, favoring the previous estimates of the  $fO_2$  of the lunar mantle of  $\sim IW-1$  [1] rather than  $\sim IW-2$ . Based on experiments by [5] higher proportions of  $Ti^{3+}$  would be expected if the  $fO_2$  of crystallization were closer to  $IW-2$ . The presence of  $Ti^{3+}$  in lunar pyroxenes has, in the past, been inferred on the basis of the assumptions that all  $Ti^{4+}$  substitutes for divalent cations in octahedral sites, charge compensation is accomplished through a coupled substitution of two Al for two Si cations in tetrahedral sites, and that Ti/Al ratios in excess of 0.5 indicate the presence of a  $Ti^{3+}$  component [6,7]. The present results show that this conclusion is based on an oversimplified assumption and is not justified. Large proportions of Ti enter the tetrahedral site; these cations do not require a coupled substitution with Al for charge balance, and they can account for Ti cation abundances that are in excess of half the Al. For exam-

ple, the EMP analyses of 10020 pyx average 0.113 Ti and 0.203 Al cations per six oxygens. This gives 0.011 Ti cations in excess of half the Al, and the analyses average 0.032 tetrahedral Ti cations. For this sample,  $Ti^{3+}$  was not detected by XANES, and its presence need not be inferred to account for the Al/Ti ratios, though a small component cannot be ruled out.

The  $Ti^{4+}$  cation has a larger ionic radius than the  $Si^{4+}$  cation, and it has been shown experimentally [14] that the substitution of  $Ti^{4+}$  for  $Si^{4+}$  is favored by high temperatures and low pressures. It is also geochemically favored in environments with limited availability of Al for coupled substitutions. The availability of Al appears to be the dominant factor, as illustrated by comparison with Al-,Ti-rich pyroxene that is known as "fassaite" [15], found in meteoritic refractory inclusions. Although fassaite formed at high temperatures (1230°C [16]) and low pressures ( $\sim 10^{-3}$  bar), conditions that favor tet Ti substitution, all of its Ti is in octahedral coordination [15,17]. This is apparently due to the high  $Al_2O_3$  contents of the gas or liquid from which it formed; fassaite typically contains  $\sim 20$  wt%  $Al_2O_3$ . Lunar pyroxene has much higher proportions of tet Ti than fassaite and much lower Al and Ti contents. Also, compared to mare pyx, the lunar plutonic pyx has somewhat higher tet Ti proportions despite having formed at higher pressure, and it is Al-poor.

The pyx tet sites have lower symmetry than the octahedral sites, making orientation effects important in the XANES analyses. We can overcome this obstacle by (a) collecting spectra of a grain at different orientations and merging the spectra; and (b) analyzing multiple grains in a sample and merging the spectra, canceling the effects if the grains are randomly oriented. We applied the latter technique to 15415, and with individual Ti valence measurements ranging from 3.6 to 4.3, the merged spectrum gives a value of 4.0. In future work we will investigate the orientation effects further.

**References:** [1] Wadhwa M. (2008) *RiMG* 68, 493-510. [2] Simon S. et al. (2008) *LPS XXXIX*, abst. #1271. [3] Sato M. (1976) *PLSC 7<sup>th</sup>*, 1323-1344. [4] Karner J. et al. (2006) *Am. Min.* 91, 270-277. [5] Krawczynski M. et al. (2009) *LPS XL*, abst. #2164. [6] Weill D. et al. (1971) *PLSC 2<sup>nd</sup>*, 413-430. [7] Papike J. et al. (1998) *RiM* 36, 7-1 – 7-11. [8] Farges F. et al. (1997) *Phys. Rev. B*, 56, 1809-1819. [9] Simon S. et al. (2007) *LPS XXXVIII*, abst. #1892. [10] Beatty D. and Albee A. (1978) *PLPSC 9<sup>th</sup>*, 359-463. [11] Papike J. et al. (1976) *RGSP 14*, 475-540. [12] Meyer C. (2011) *Lunar Sample Compendium*. [13] Dymek R. et al. (1975) *PLSC 6<sup>th</sup>*, 301-341. [14] Sepp B. and Kunzmann T. (2001) *Am. Min.* 86, 265-270. [15] Dowty E. and Clark J. (1973). *Am. Min.* 58, 230-242. [16] Stolper E. (1982) *GCA* 46, 2159-2180. [17] Haring M. et al. (2012) *LPS XLIII*, abst. #2601.