

## VALENCES OF CR IN UREILITE OLIVINE AND IMPLICATIONS FOR UREILITE PETROGENESIS.

C.A. Goodrich<sup>1</sup>, S.R. Sutton<sup>2,3</sup> and S. Wirick<sup>3</sup>. <sup>1</sup>Planetary Science Institute, 1700 E. Ft. Lowell, Tucson, AZ 85719 USA ([cgoodrich@psi.edu](mailto:cgoodrich@psi.edu)). <sup>2</sup>Dept. of Geophysical Sciences and <sup>3</sup>Center for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637 USA.

**Introduction:** Ureilites are coarse-grained (~mm) ultramafic achondrites whose petrogenesis is poorly understood [1-5]. Their olivine compositions (homogeneous in grain cores in each sample) span a large range, from Fo ~74 to 95, which cannot be explained by igneous fractionation [3,6-8]. A major question [2,9] is whether this large Fo range corresponds to variation in oxidation state, thus supporting redox models for ureilite petrogenesis.

One parameter that has been argued to support redox models is the occurrence of chromite in ureilites. Until recently, chromite had been reported only in a few of the most ferroan (Fo ~74-76) samples [10-17]. The absence of chromite in higher-Fo ureilites suggests formation at lower  $fO_2$ , out of the range of Cr<sup>3+</sup> stability. In addition, the Cr contents of ureilite olivine are high (usually reported as Cr<sub>2</sub>O<sub>3</sub>; Table 1), and it is commonly assumed that this is because Cr is in the 2+ valence state [2]. However, [18] reported chromite in a ureilite of Fo 85, which may undermine the inference that Fo is correlated with  $fO_2$  among ureilites.

Nevertheless, the valence state(s) of Cr in ureilite olivine have never been directly determined, and Cr<sup>3+</sup>/Cr<sup>2+</sup> may vary systematically with Fo or presence of chromite. We have begun to measure valences of Cr in ureilite olivines using x-ray absorption near edge structure analysis (XANES). We report first results, for 9 ureilites of various type [3] with Fo ~74 to 92 and including 3 of the 4 known chromite-bearing samples.

**Analytical Methods:** We used the Zeiss EVO 50 XVP scanning electron microscope at U. Mass. for SEI/BEI/EDS observations of all samples. Olivines were examined to locate areas unaffected by situ reduction or reaction with chromite.

Chromium K-edge XANES spectra were collected using the x-ray microprobe at Beamline X26A at the National Synchrotron Light Source (NSLS), Upton, NY. A channel-cut Si(111) monochromator was used to feed monochromatic x-rays to a dual K-B mirror system which focused the beam to ~7 microns. XANES spectra were measured in fluorescence mode using single and quad Vortex Silicon Drift Detectors (SDD) to collect Cr K<sub>α</sub> intensities in 5 eV steps from 5960 to 5980 eV, 0.2 eV steps from 5980 to 6015 eV and 2.5 eV steps from 6015 to 6100 eV. The valence determination method followed [19,20], using the normalized intensity of the derivative spectrum peak near 5994 eV produced by a 1s-4s electronic transition. This peak is strong in Cr<sup>2+</sup> spectra and essentially non-

existent in Cr<sup>3+</sup>. Intermediate valences were quantified by linear interpolation of spectra for end member standards with estimated precision of 0.05.

**Samples (Table 1):** All samples show typical reduction rims [2] on olivine. LEW 88774 and NWA 766 contain inferred primary chromite (3-6% and ~1%, respectively) as sub/anhedral grains up to ~1 mm [10-18]. These chromites are surrounded by mineralogically complex zones that are products of in situ reduction of chromite and/or reaction with Cr-rich shock-melt [10-18]. EET 96328 (,5) contains one chromite grain, as a nearly spherical ~50-μm inclusion in orthopyroxene (opx), with no reaction rim [18].

<b>Table 1</b> sample	type [3]	oliv Fo	oliv wt% Cr <sub>2</sub> O <sub>3</sub>	chr	Ref.
LEW 88774	augite	74.2	0.37	yes	10-13
LAP 03587	ol-pig	74.4	0.65	exsol.*	9,21
CMS 04048	ol-pig	76.2	0.75	exsol.*	9
NWA 766	ol-pig	76.7	0.42	yes	15-17
EET 96328	ol-opx	85.2	0.64	yes	9,22
ALHA77257	ol-pig	85.6	0.74		7,9
Y-74659	ol-opx	91.2	0.58		23
Y-791538	ol-opx	91.3	0.57		22,24
EET 87517	ol-opx	92.3	0.38		25

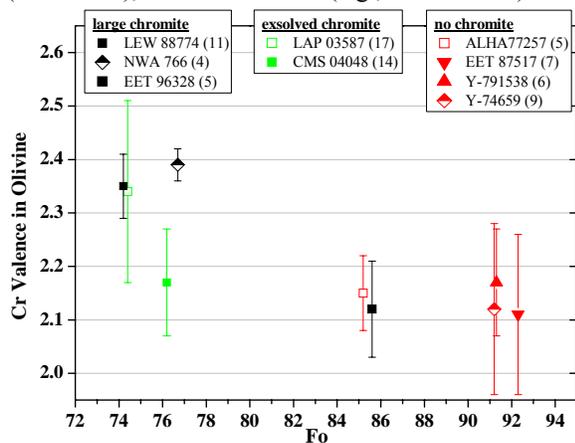
\*Chromite + pyroxene exsolutions discovered in this work.

**Results:** Figure 1 shows the mean Cr valence measured in olivine cores in each sample, as a function of Fo. The Fo 74-76 chromite-bearing samples LEW 88774 and NWA 766 show the highest mean valences (2.35 and 2.39, respectively). In contrast, the Fo 85 chromite-bearing EET 96328 shows significantly lower Cr valence (2.15), similar to that of the non-chromite-bearing ALHA77257 of similar Fo. SEM observations of the chromite grain in EET 96328 showed that it is has a narrow (≤ 2 μm) rim of Si,Al-rich glass and Ca-rich pyroxene, similar to the phases in the abundant melt inclusions in opx in this sample [26].

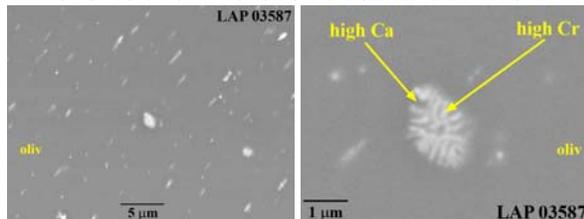
Of the 6 (nominally) non-chromite-bearing samples, 5 show mean Cr valence between 2.1 and 2.2, with rather large standard deviations (Fig. 1). The 6<sup>th</sup>, LAP 03587, shows higher mean Cr valence very similar to that of chromite-bearing sample LEW 88774 (of nearly identical Fo), but with the largest standard deviation (2.34±0.17). In re-examining some samples to look for sources of these large variations, we discovered that olivine in LAP 03587 and CMS 04048 contains tiny (mostly <1 μm) Cr- and Ca-rich inclusions, which tend to be elongated and aligned

with one another (Fig. 2). They appear to be symplectic (Fig. 2b) exsolutions similar to those in a variety of meteoritic, lunar, and terrestrial olivines [27-30], and have not previously been reported in ureilites. In LAP 03587, they are sufficiently abundant (~1 vol.%) that they must have been included in the ~7  $\mu\text{m}$ -size XANES analysis spots (Fig. 2a). In CMS 04048 they are sparser, and many of the XANES analyses probably avoided them. We also examined ureilites ALHA78019 (Fo 77) and LEW 85440 (Fo 92) and found none of these exsolutions.

Two traverses across olivine grains show contrasting patterns. In one (Y-74659), Cr valence drops in reduction rims (e.g., 2.27 to 2.02); in the other (Y-791538), it rises near rims (e.g., 2.07 to 2.15).



**Fig. 1.** Mean Cr valence in olivine cores in 9 ureilites, as a function of core Fo. Error bars are 1 standard deviation.



**Fig. 2.** Inclusions in olivine core in LAP 03587, inferred to be symplectic exsolutions of chromite + high-Ca pyroxene.

**Discussion:** The higher valence states of Cr in olivine in LEW 88774 and NWA 766 are consistent with the interpretation that they formed under more oxidizing conditions than most other ureilites, as suggested by their low Fo and primary chromite. The lower valence of Cr in olivine in EET 96328 suggests that the chromite grain in this sample [18] is not primary. It may be part of a melt inclusion, and/or a product of the late melt from which the opx grew [26].

Symplectic exsolutions of chromite + pyroxene in olivine most likely form by breakdown of 3+ ion-bearing olivine on cooling [28,30]. If this is the case, the mean Cr valence for LAP 03587 represents its bulk olivine (with the large variation due to sampling

random amounts of chromite). This high value is, again, consistent with formation in a more oxidizing environment than other ureilites, as suggested by low Fo. In CMS 04048, measured Cr valences (at least the mean) may be lower than that of the original bulk olivine if the XANES analyses largely missed the chromites. This sample requires further investigation.

All non-chromite-bearing ureilites show Cr valence between ~2.1 and 2.2 (confirming [2] that most of the Cr is 2+). Using  $\text{Cr}^{2+}/\text{Cr}^{3+}$  olivine/liquid partitioning data [31], this implies  $f\text{O}_2$  of ~IW-1 to -2, within the range estimated from olivine-metal-silica equilibria [32]. There is no apparent correlation of Cr valence with Fo. However, such a correlation is expected to be subtle [31], and could be obscured by the observed intra-meteorite variations. Our results suggest 3 secondary effects that might be responsible for these variations: 1) in situ reduction; 2) exsolution of chromite; 3) terrestrial weathering. Further work will be done to assess these.

**Summary:** Results for chromite- vs. non-chromite-bearing samples support redox control on ureilite Fo.  $f\text{O}_2$  determined for the non-chromite-bearing samples are consistent with low-pressure carbon redox control on the parent body [33]. Once we minimize secondary effects and analyze more samples, we can evaluate quantitatively whether these samples show the correlation of Cr valence with Fo that is predicted in such a model [33].

**References:** [1] Goodrich C.A. (1992) *Meteoritics* 27, 327. [2] Mittlefehldt D.W. et al. (1998) In *RIM* 36. [3] Goodrich C.A. et al. (2004) *Chemie de Erde* 64, 283. [4] Warren P.H. et al. (2006) *GCA* 70, 2104. [5] Goodrich C.A., Wilson L.W. (2011) *LPS* 42, #1246. [6] Mittlefehldt D.W. (1986) *GCA* 50, 107. [7] Goodrich C.A. et al. (1987) *GCA* 51, 2255. [8] Goodrich C.A., Delaney J.S. (2000) *GCA* 64, 2255. [9] Goodrich C.A. et al., *GCA*, submitted. [10] Prinz M. et al. (1994) *LPS* 25, 1107. [11] Warren P.H., Kallemeyn (1994) *LPS* 25, 1465. [12] Chikami J. et al. (1997) *MAPS* 32, 343. [13] Goodrich C.A. (2001) *MAPS* 36, A67. [14] Goodrich C.A., Harlow G.E. (2001) *MAPS* 36, A68. [15] Sikirdji M., Warren P.H. (2001) *MAPS* 36, #5395. [16] Warren P.H., Huber H. (2006) *LPS* 37, #2400. [17] Goodrich C.A. et al. (2007) *LPS* 38, #1434. [18] Jercinovic M.J., Goodrich C.A. (2011) *LPS* 42, #1152. [19] Sutton S.R. et al. (1993) *GCA* 57, 461. [20] Berry A.J., O'Neill H.St.C. (2004) *Am. Min.* 89, 790. [21] Warren P.H., Rubin A.E. (2010) *GCA* 75, 5109. [22] Goodrich C.A. et al. (2006) *MAPS* 41, 925. [23] Takeda H. (1987) *EPSL* 81, 358. [24] Takeda H. et al. (1989) *Meteoritics* 24, 73. [25] Singletary S., Grove T. (2003) *MAPS* 38, 95. [26] Goodrich C.A. (2001) *LPS* 32, #1300. [27] Bell P.M. et al. (1975) *Proc. LPSC* 6, 231. [28] Mosley D. (1984) *Am. Min.* 69, 139. [29] Goodrich C.A., Righter K. (2000) *MAPS* 35, 521. [30] Mikouchi T. et al. (2000) *MAPS* 35, 937. [31] Hanson B., Jones J.H. (1998) *Am. Min.* 83, 669. [32] Nitsan U. (1974) *JGR* 79 (5), 706. [33] Goodrich C.A. et al. (2007) *GCA* 71, 2876.