

**PETROGRAPHY AND SIDEROPHILE GEOCHEMISTRY OF METAL AND SULPHIDE IN UREILITES.** R. D. Ash<sup>1</sup> C.A. Goodrich<sup>2</sup>, J.A. Van Orman<sup>3</sup> and W. F. McDonough<sup>1</sup>, <sup>1</sup>Department of Geology, University of Maryland, College Park, MD20742, USA (rdash@geol.umd.edu), <sup>2</sup>Planetary Science Institute 1700 E. Ft. Lowell Dr., Tucson AZ 85719, USA, <sup>3</sup>Department of Geological Sciences, Case Western Reserve University, Cleveland OH44120, USA.

**Introduction:** Ureilite formation remains an intractable planetary science problem, despite years of analyses and an ever increasing number of samples to analyse. There is agreement that these olivine-rich achondrites formed by igneous processing that included redox reactions akin to smelting. But these olivine-pyroxene metal-graphite rocks cannot have been derived from a wholly melted parent body as evinced by non-equilibrated bulk oxygen isotopes.

Amongst the many curiosities of ureilite petrogenesis are the large range of observed iron content and its failure to correspond with silicate Mg#. Following our previous work on the distribution of siderophiles in the metallic phases of ureilites [1-3], we have determined siderophile abundances in metallic and sulphide phases in a suite of Antarctic ureilites, with a variety of mineralogical and petrogenetic characteristics. Our goals were to expand the range of ureilite types for which there is detailed mineralogical and chemical information, and to further our understanding of their formation.

**Samples and Analytical:** This suite of Antarctic ureilites have been petrologically characterised and their metals and sulphides analysed by LA-ICP-MS. Spot sizes for the LA analyses were largely determined by the grain size of the minerals of interest, ranging from 12µm to 80µm. Standards were Hoba and Coahuila for metals and a UMD standard, JB sulphide for the sulphides.

**Petrology:** We have studied metal, sulphides, and related phases in olivine+low-Ca pyroxene (lpyx) ureilites LAP 03587 (Fo 75), ALHA78019 (Fo 76), ALHA78262 (Fo 78), CMS 04048 (Fo 78), LAP 02382 (Fo 79), GRA 95205 (Fo 79), ALHA81101 (Fo 81), EET 96042 (Fo 82) PCA 82506 (Fo 85), EET 83225 (Fo 87) and LEW 85440 (Fo 92), as well as augite-bearing ureilite EET 96328 (Fo 88). ALHA81101 is very highly shocked [4]: its olivine is completely mosaiced and most of its pigeonite has been shock melted and recrystallized. In contrast, ALHA78019, PCA 82506, ALHA78262, LAP 03587, GRA 95205 and CMS 04048 are of exceptionally low shock state, and contain abundant euhedral graphite. LAP 02382 has an equigranular texture, conspicuously lacking any fabric, which is unusual for a ureilite.

As in previous samples [1], two types of primary metal are observed: 1) Grain boundary metal is by far the most abundant type, although in most samples at least some of it has been oxidized due to terrestrial weathering (in LEW 85440, EET 96328 and EET 83225 almost no grain boundary metal is unaltered). 2) Cohenite-phosphide-metal-sulphide spherules occur as inclusions in silicates (predominantly lpyx), and are rare. PCA 82506 and EET 96328 have unusually high concentrations of these spherules. In the samples we studied previously, sulphides were extremely rare and no analyses were obtained [1]. In contrast, sulphides were common in many of the samples studied here, and 3 of them (EET 96042, LAP 02382 and CMS 04048) have exceptionally high sulphide contents.

**Grain Boundary Metal:** Grain boundary metal in all samples is kamacite (Ni=0.1-7.3 wt.%), with low S (below detection limit of EMPA) and P (<0.6 wt.%) contents, although in most samples we also observed rare, fine-grained intergrowths of schreibersite (Fe<sub>3</sub>P) and metal. To first order, Ni and Co in grain boundary metal are well correlated among most samples (including data of [1]) with Ni/Co ~0.62×CI. However, several samples show significant scatter relative to this value. In contrast, Cr and Si contents are not correlated with Ni, and vary widely. Although many of the samples have Si contents that are near or below detection limit, others show distinctly higher values, ranging up to ~3.5-5.5 wt.% in EET 96042. There is no apparent correlation of Si content of the grain boundary metal with petrographic or silicate compositional characteristics, including degree of secondary reduction [5]. Most samples have low Cr (<0.2 wt.%) contents, but a few show distinctly higher values ranging up to 0.6 wt.%. Again, there is no apparent correlation with petrographic or compositional characteristics, including degree of secondary reduction, Cr<sub>2</sub>O<sub>3</sub> content of olivine, or presence/absence of Cr-rich sulphides.

**Spherules:** The cohenite-metal-phosphide-sulphide spherules observed here are similar to those studied previously [1,8], with the exception that chromite (which is extremely rare in ureilites overall) was found in one spherule in LAP 02382.

**Sulphides:** We distinguish 3 types of sulphide in the samples studied: 1) low-Cr (0.3-0.7 wt.%) troilite,

sometimes containing blebs of (apparently) unmixed metal; 2) intermediate-Cr (~2.1-3.6 wt.%), troilite, observed only in LAP 02382; 3) sulphides consisting of a lamellar intergrowth of a very high-Cr phase and a lower-Cr phase (Fig. 1). It was not possible to resolve the two phases in most analyses, which showed Cr contents from ~5-20 wt.%. However, one coarse lamella of the high-Cr phase produced an analysis consistent with nearly pure daubreelite (ideally  $\text{FeCr}_2\text{S}_4$ ): 19.9% Fe, 0.1% Ni, 1.5% Mn, 0.4% V, 0.1% Ti, 32.1% Cr, 42.5% S. These intergrowths probably formed by exsolution of daubreelite from high-Cr troilite at  $T \leq 650^\circ\text{C}$  [6]. They have not been described previously in ureilites but may explain reports of widely varying Cr in ureilite sulphides [7].

#### Siderophile trace elements:

**Grain Boundary Metal** As we showed previously [2] the most important reservoir for siderophile trace elements is the grain boundary metal. Most show enrichments in the more refractory siderophiles to between 10-100x chondritic, with varying degrees of fractionation, while the volatile elements are less enriched by a factor of about 10.

The PGE abundances in the metal of ALHA81101 are low, typically between 1 and 10x chondritic (unlike metals in most other ureilites which are typically 10-100x chondritic). It is also, like the whole rock, essentially unfractionated from chondritic. As with the major and minor siderophiles PGE abundances are low, typically *ca.*2x chondritic and with a flat pattern. A similar phenomenon is observed for the shocked ureilite Hughes 009 [2]. The low concentration of HSE's may be related to shock but the mechanism of depletion and the fate of the HSE remains obscure.

**Spherules:** As we observed previously [2] the spherule siderophile abundances are indistinguishable from those of the grain boundary metal.

**Sulphides:** The PGE and other HSE concentrations in most sulphides are below detection (detection limits are variable but largely dependent upon spot size, hence smaller grains have higher detection limits) but some sulphides in EET96042 yield useful data for some siderophiles. Where data have been obtained they show a consistency between chemically and petrographically diverse sulphides and these concentrations are elevated compared to compositions predicted for a coexisting sulphide-metal combination at 1050C – a temperature used to reproduce the observed metal HSE abundances using the models of [3]. The consistent values between differing grains would preclude the HSEs being sampled from co-existing metal.

The few data obtained for LAP02382 sulphides show Os concentrations that are consistent with the predictions of the Van Orman model [3]; a few other elements measured also agree with predictions. However one grain has a pattern that is similar to that predicted for sulphide but at two orders of magnitude higher than expected for the PGEs. Again this is not due to included metal phases as the pattern is not that of the metal. The reason for this remains obscure.

The metal in the three ureilites that contain abundant sulphides (EET 9601, CMS 04048, LAP 02382) show no systematic difference in their siderophile behaviour when compared with those without sulphide – the only exception being that all three show a greater Pd depletion than samples devoid of sulphide. Pd is the PGE with the greatest affinity for sulphide, but the upper limits on the measured Pd abundance in the sulphide would require a huge quantity of sulphide to produce the observed effect.

In all measured sulphides the Cu is clearly chalcophilic.

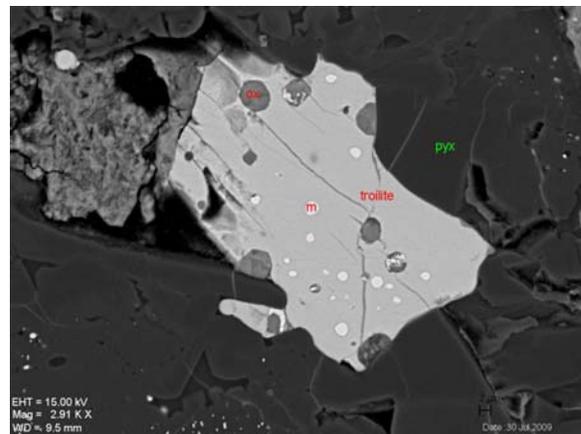


Fig. 1. High-Cr sulphide with exsolved daubreelite (ideally  $\text{FeCr}_2\text{S}_4$ ) in EET 96042.

**References:** [1] Goodrich C.A. et al. (2009) LPS 40, #1132. [2] Ash R.D. et al. (2009) LPS 40, #1422. [3] Van Orman J.A. et al. (2009) LPS 40, #1986. [4] Berkley J.L. (1986), *Meteoritics* 21, 169. [5] Wittke J.H. (2007) *MAPS* 42, #5246. [6] El Goresy A. and Kullerud (1969) *Carnegie Inst. Washington Yearbook*, 67,197. [7] Berkley J.L. et al. (1980) *GCA* 44, 1579. [8] Goodrich C.A. and Berkley J.L. (1986) *GCA* 50, 681.