PETROGRAPHY AND GEOCHEMISTRY OF METALS IN ALMAHATA SITTA UREILITES.

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Introduction: Ureilites are ultramafic achondrites, predominantly composed of olivine and pyroxenes with accessory carbon, metal and sulfide. The majority of ureilites are believed to represent the mantle of the ureilite parent body (UPB) [1]. Although ureilites have lost much of their original metal [2], the metal that remains retains a record of the formative processes. Almahata Sitta is predominantly composed of unbrecciated ureilites with a wide range of silicate compositions [3,4]. As a fall it presents a rare opportunity to examine fresh ureilite metal in-situ, and analyzing their highly siderophile element (HSE) ratios gives clues to their formation. Bulk siderophile element analyses of Almahata Sitta fall within the range observed in other ureilites [5]. We have examined the metals in seven ureilitic samples of Almahata Sitta (AS) and one associated chondrite fragment (AS#25).

Methods: *Electron-beam techniques:* Imaging (using a LEO 1455VP SEM with Oxford Instruments INCA software) and major element composition analyses (using a WDS Cameca SX100 EMPA) were conducted at the NHM. EBSD analysis was conducted at the University of Glasgow using an EDAX-TSL system attached to a Quanta 200F field-emission SEM that was operated in low vacuum mode.

LA-ICP-MS: Analyses to obtain trace element compositions were performed at NASA JSC using a New Wave UP-193 SS laser ablation system attached to a Thermo Element2-XR ICP-MS. Laser power was 1-2 GW/cm^2, with a repetition rate of 10 Hz. Spot sizes of 20 to 100 µm were used, depending on metal grain size. Some grains were too small to analyze. The Filomena and Hoba iron meteorites, NIST 610 glass, and NBS 1168 and NBS 1178 steels were used as standards. Ni values from EPMA were used for internal calibration for all samples except AS#15, #25 and #33 where Fe+Co+Ni were summed to 100 wt%. The following isotopes were analyzed: ^{29}Si, ^{31}P, ^{34}S, ^{53}Cr, ^{54}Fe, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{61}Ni, ^{62}Ni, ^{63}Cu, ^{65}Cu, ^{66}Zn, ^{69}Ga, ^{72}Ge, ^{74}Ge, ^{75}As, ^{95}Mo, ^{101}Ru, ^{103}Rh, ^{105}Pd, ^{106}Pd, ^{121}Sb, ^{182}W, ^{185}Re, ^{192}Os, ^{193}Ir, ^{194}Pt, ^{195}Pt and ^{197}Au.

Petrography and chemistry: Metals in AS occur as interstitial grain-boundary vein metal, inclusions in silicates, associated with carbon, or in reduction rims, as seen in other unbrecciated ureilites [6]. Reduction rim metal in silicates is not discussed further here as it is a secondary product [6,7]. Some AS samples contain significantly more metal than seen in "typical" ureilites. Grain boundary metal, whilst most common, is very fine-grained and as such causes significant problems for spot HSE analysis. Sulfide (as troilite) is present in all samples. High-Si metals [8] (e.g. suessite) have not been found in AS. Metal compositions are reported in weight % unless otherwise stated.

AS#7: is an anomalous fragment, described as porous [4] with a high percentage of metal. Included metals occur in both olivine and low-Ca pyroxene (LCP), although interstitial metal grains and those associated with porous areas are much larger. Compositional variation (Ni~1.7-3.8%, Co~0.2-0.3%, Si~<dt-1.9%, P~0.2-1.3%) is smaller than found for other metal-rich samples, but a wide range in Ir/Pd~1.1-8.5 is observed.

AS#15: is an augite-bearing ureilite with LCP (Wo~5/En~84) and olivine (Fo~92) [4]. Most metal occurs as interstitial veins, with one yielding Ir/Pd~1.4.

AS#22: shows a typical ureilitic texture with olivine (Fo~80.3), and two distinct LCPs (Wo~4.7/En~79.0 and Wo~9.5/En~73.9). Non-reduction metal occurs only along grain boundaries with varying compositions (Ni~2.8-5.9%, Co~0.2-0.4%, Si~0.02-2.2%, P~0.1-0.3%). Ir/Pd varies from 2.2 to 3.2.

AS#25: is an H5 chondrite collected within the AS fall area, although the relationship with AS ureilites is unclear [4]. Metal is unweathered. Ir/Pd~0.8-1.1.

AS#27: consists of olivine (Fo~85.2) and LCP (Wo~5.1/En~81.5). Some metal has unusually high Ni contents (up to 11.3%) compared to other ureilites (<6% [6]), with grains included in LCP being highest. High-Ni metals have previously been reported in polymict ureilite breccias [8] but those may have an exogenic origin. The range of metal compositions (Ni~5.0-11.3%, Co~0.3-0.5%, Si~0.02-0.3%, P~0.2-1.34%) is widest in the LCP-included metals. Those at grain boundaries and associated with carbon have a smaller range in Ni (5.3-5.8%). HSE ratios are closest to chondritic in this sample, with Ir/Pd~0.9-1.7.

AS#33: is made up of multiple small (~1mm) fragments, only some of which have silicate attached. Most of the mass consists of large metal blebs (some >200 µm in diameter) with kamacite cores and taenite rims, in sulfide. Fine-scaled metal dendrites are present in some areas of the sulfide. This sample is similar to metal-rich areas in AS sample MS-166 reported in [3].

in [3]. AS#33 is the most enriched sample in refractory HSEs with a maximum Ir/Pd=45.9; but also shows the largest variation, with a minimum Ir/Pd=2.3.

AS#36: is completely disaggregated and as a consequence has very little interstitial metal attached. The sample is composed of olivine (Fo~90.4), and two distinct LCP (Wo~5.0/En~86.6 and Wo~9.2/En~82.3). One metal inclusion in an olivine was found (Ni~4.4%, Co~0.3%, Si~0.04%, P~0.2%). The rest of the metal occurs as veins in olivines, often starting at the edges of the grains (Ni~2.9%, Co~0.2%, Si~0.6%, P~0.3%). A vein yielded an Ir/Pd ratio of 10.7.

AS#44: is an olivine-dominated (Fo~79.0) ureilite with some pigeonite (Wo~11.2/En~71.5), which displays an unusual texture reminiscent of those reported in impact smelted ureilites [9]. Three types of interstitial metal occur in this sample: "typical" ureilite vein metal, interstitial metal with no detectable internal compositional variation, and metal grains with highly variable internal compositions and unusual internal textures. Kamacite dendrites in sulfide have also been found. Small phosphides are observed in association with the "typical" grain boundary metal, and the compositionally variable grains contain up to 7% P (but with no increase in Ni, i.e. not phosphide inclusions). The presence of compositionally variable metal in this sample contradicts [10]. Internally homogenous metals vary in composition between different grains (Ni~1.7-5.6%, Co~0.2-0.5%, Si~0.07-1.6%, P~0.07-1.6%). Ir/Pd varies between grains (3.7-17.5).

Micro-textures: EBSD mapping of metals (including a dendrite) in AS#7, #22 and #44 reveals they are made up of multiple subgrains (~3 µm to ~120 µm long), which do not appear well texturally equilibrated (inferred from a lack of features such as 120° triple junctions) despite the grains being chemically uniform. Some of these subgrains show internal deformation. Most subgrains show maximum misorientations ~10°. Typically there is ~50° mismatch between subgrains.

Discussion and conclusions: Siderophile element compositions of ureilites are attributed to two metallic end-members (one refractory-rich, the other refractory-poor and chondrite-like) [2 and references therein]. Multiple processes may affect metal HSE relative abundances, including the removal of a low-temperature Fe-S melt (the effect of which is dependant on S content) and the controversial smelting process [2,11,12]. As non-reduction metals are the primary carrier of HSE in ureilites [11], it is informative to compare our results with bulk ureilite data and modeling of the these two processes [2,12].

AS#7, #36 and #44 all closely resemble the majority of previously analyzed ureilites and HSE ratios correspond with the model from [2] for removal of high percentages of metallic melt (60-80%). This is surprising in the case of the more metal-rich AS#7 and #44 and may imply a a subsequent redistribution of metallic material as suggested by [12]. AS#33 yields highly variable and grain-dependent results. AS#15, 22 and #27 differ significantly from other ureilites [2], with all suggesting removal of lower percentages of metallic melt. The combination of unusually high Ni contents and almost chondritic HSE ratios indicate that metal in AS#27 is unlike any previously found in ureilites. In agreement with previous work [2,11,13], we find no correlation between siderophile element characteristics and silicate Mg# in AS. Almahata Sitta metals show some unique features, both texturally and chemically, when compared with previously studied unbrecciated (a.k.a. monomict) ureilite samples [6,11,13].

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Figure 1: Siderophile element abundances for representative grains from each AS sample, normalized to Co and CI chondrite. Elements are arranged in decreasing order of volatility.