WÜSTITE IN THE ALMAHATA SITTA POLYMICT UREILITE: IMPLICATIONS FOR OXYGEN DURING ASTEROIDAL DIFFERENTIATION.

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Introduction: Oxygen is a potentially important non-metal in metallic systems but it has long been neglected in all but the Earth´s core [1-3]. In the Fe-O system, a miscibility gap between Fe-rich and FeO-rich liquids occurs at the low pressures and temperatures pertinent to asteroidal core formation processes. As an additional consequence, standard solid-liquid experiments cannot be done in the binary Fe-O system unlike the binary Fe-S, Fe-C, and Fe-P systems. Thus experimental data on the effect of oxygen on the partition behavior of siderophile trace elements (e.g., W, PGEs, etc.) are lacking. Preliminary experimental work to determining the effect of oxygen has been conducted in the Fe-S-O system [4], but natural samples mirroring this system are lacking in meteorite science so far.

Here we report evidence for oxygen in metallic melt systems preserved in the form of wüstite (FeO) within the Almahata Sitta sample MS-166 [5]. This unique sample bears high potential to further investigate the effect and behavior of oxygen in metallic systems *in-situ* in a natural sample and allows insights into trace element behavior. Moreover, the assemblage might be an important piece in the puzzling petrogenesis of the ureilites and in core formation on asteroids and planets in general. The specific stability field (low-fO_2 and high-T) of wüstite and its preference to react with silicates under all but the most silica-undersaturated environments (e.g., metallic melt systems) account for its rarity in crustal rocks [6]. Wüstite has been described in some extraterrestrial samples, but in many instances it is the product of partial oxidation of metal in e.g., meteorite fusion crusts, the host rock or magnetic spherules [7-9].

Experimental and Analytical Methods: The sample was studied by optical and electron optical microscopy and major element compositions were determined by EPMA (JEOL JXA 8900 superprobe) using natural and synthetic standards of well known compositions. Trace element abundances were determined by LA-ICP-MS at the NHMFL following established procedures [10]. A selected portion of the intergrowth between the large metal grains (Fig. 4d in [5]) was separated by FIB technique and subsequently studied with a Philips CM20 FEG TEM (at 200 kV) for mineral identification and characterization on a submicron scale with a Thermo-Noran EDX and Gatan PEELS attached. EELS was performed to determine the Fe^{2+}/Fe^{3+} ratio in wüstite.

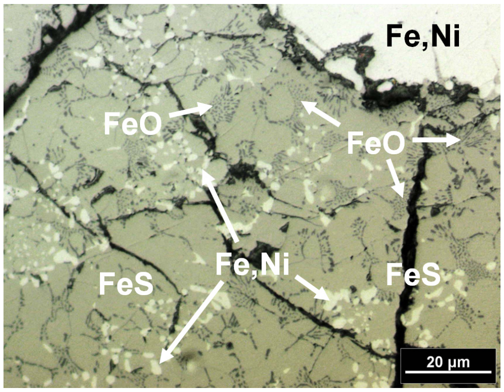

Fig. 1. Reflected light image of a representative portion of the quenched sulfide-metal-oxide intergrowth in MS-166. FeO points to wüstite grains. FeS=troilite; Fe,Ni=metal.

Results: Wüstite was found in Almahata Sitta sample MS-166 [5, their Figs. 4c,d]. The sample is characterized by large metal grains (cores: 7-9 wt% Ni) with Ni-richer portions (up to ~23 wt% Ni) surrounded by Ni-rich metal nuggets (up to ~33 wt% Ni) embedded in an intergrowth of troilite, wüstite, and minor tiny Ni-rich metal grains. The boundary areas of the metal grains exhibit irregular cracks that penetrate several micrometers into the host metal. Minor ureilitic material (Fa_{3-14}, $Fs_{2-13}Wo_{0.5-1.5}$) was found attached to the assemblage. Wüstite occurs as rounded to elongated crystals intergrown with interstitial troilite and minor metal (Fig. 4d in [5]). The estimated average oxygen content of the assemblage is ~12 wt% (range ~8-18 wt%). One portion of MS-166 (Fig. 1) shows troilite as slightly rounded grains with an interstitial filling of tiny wüstite and small metal grains. The oxygen content is lower in this portion (av. ~3 wt%, range 1.5-4.5 wt%). This wüstite-bearing texture resembles (quenched) experimental liquids in an O-bearing metallic liquid [4].

SAED patterns obtained by TEM from the rounded Fe-oxide crystals clearly identify them as nonstoichiometric, i.e. Fe-deficient, wüstite ($Fe_{1-x}O$). Diffraction patterns of zone axis [100] show the fundamental NaCl-type reflections (e.g., 020, 002) surrounded by superstructure reflections (Fig. 2). Symmetry forbidden reflections with mixed odd/even indices (e.g., 011) occur as well, but show no or only weak superstructure reflections indicating Fe site defect clusters and a Fe/O ratio slightly less than unity. These magnetite-like defect clusters are characterized by vacant octahedral Fe sites and interstitial, tetrahedrally coordinated Fe atoms [11]. EELS spectra of wüstite grains reveal a relatively high Fe^{3+} content of ~16-18%. Based on SAED patterns obtained on the [100] and [110] zone axes we find the superstructure in MS-166 wüstite to be P' close to the P" case that forms by slow cooling or subeutectoid aging of more Fe-deficient compositions [12], indicating that the MS-166 wüstite had sufficient time to evolve towards the P" structure. Internally, the wüstite crystals are practically free of dislocations, subgrain boundaries, and planar defects. Each globule-shaped grain is a single crystal and there appear to be no obvious orientation relationships between neighboring grains. Further minerals identified include chromite within wüstite and an amorphous Fe-phosphate (Fig. 2).

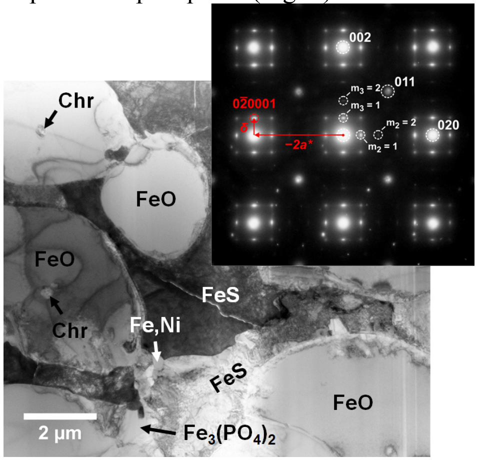

Fig. 2. TEM-Bright Field image with contiguous crystal domains of troilite (FeS) and wüstite (FeO) with inserted zone axis [100] SAED pattern of wüstite. Fe,Ni=Ni-rich metal, Chr=chromite, $Fe_3(PO_4)_2$=amorphous Fe-phosphate.

The presence of wüstite indicates low oxygen fugacity, i.e. reducing conditions. Siderophile trace element measurements on both metal grains and the bulk intergrowth of troilite, wüstite, and tiny Ni-rich metal grains reveal that the metal grains are strongly enriched in compatible siderophile elements and interelement correlations indicate that the metal grains formed via fractional crystallization [13]. Based on modeling, the low-Ni metal grains (cores) crystallized from a melt with ~15-25 wt% S using a CI-relative starting composition [13]. These abundances are in the same range as estimated for the S-rich metallic liquid involved in ureilite petrogenesis [14,15]. The O-bearing assemblages give results for siderophile trace element partition behavior that are in general accordance with experimental results in an O-bearing metallic melt system, in particular, the lower partitioning behavior of W (Fig. 3; [4]).

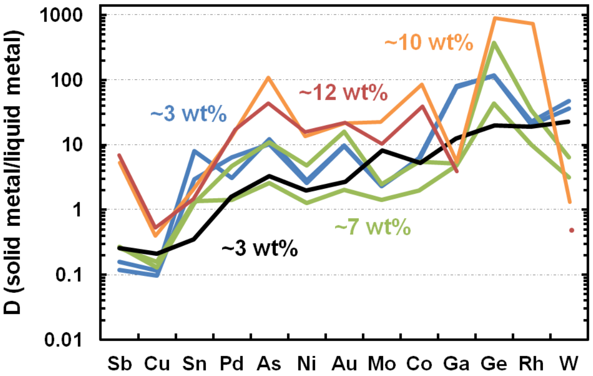

Fig. 3. Comparison of partition coefficients from Fe-S-O experiments [4] (black, red, and orange) and data obtained from MS-166 (green and blue). Wt%-values indicate oxygen content. The S-content in the experiments is ~20 wt% and ~21 (green) and ~30 wt% (blue) in the analyses of MS-166.

Discussion: The results of this study indicate that the sulfide-metal-oxide assemblage is in some physical contact with the ureilitic material in Almahata Sitta. Furthermore, we suggest that the assemblage might represent a first sample of the missing S-rich metallic liquid involved in ureilite petrogenesis together with MS-158 [5]. If this proves to be the case, this melt was (at least in parts) rich in oxygen and formed under reducing conditions to account for the preservation of wüstite. On a larger scale, the examined sample MS-166 is the first evidence for the role of Fe-S-O metallic melts during asteroidal differentiation processes.

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