The Fate of Metals in the Solar Nebula: From Condensation to Oxidation, Sulfidation, and Nitridation.

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Introduction: Metallic minerals are important constituents of chondritic meteorites and keep records about solar nebula processes. Os-Ru-Mo-Ir bearing refractory metal nuggets (RMNs) are excellent candidates for the first solids condensed from the solar gas and some appear unaltered since their formation [1]. Their chemical composition agrees remarkably well with predicted condensation sequences, constraining formation temperature between 1400 and 1600 K at 10^{-4} bar total pressure. [2] predicted condensation of refractory metal alloys into three different crystal structures, as hcp alloys of Ru and Os, bcc alloys of Mo and W, and as fcc alloys with Ir, Fe, Ni. Later mixing produced the observed opaque assemblages (OA) in CAIs. [3] favored condensation into a single refractory metal alloy. These predictions were based on the observation of micrometer sized OA, which contain oxidized, sulfidized, and exsolved phases. In these assemblages Mo occurs as molybdenite, W as scheelite, Os and Ru as hcp alloy and Pt and Ir in Fe,Ni alloy, sometimes associated with Fe,Ni sulfides (Fig. 1a). Understanding the mode of formation of these assemblages, and therefore the conditions of CAI processing, clearly requires knowledge about the initial state of refractory metal condensates. Furthermore, knowledge of the speciation and processing of Mo, Ru, Os, and W appears interesting in terms of understanding of the origin and preservation of nucleosynthetic anomalies observed in isotopes of these elements [4,5,6].

Lower temperature metal condensates, rich in Fe and Ni, are abundant, but usually not preserved in their pristine states due to oxidation and sulfidation, melting, evaporation, or parent body metamorphism and alteration. Sulfidation of metals through reaction with H_2S in the solar nebula is though to have created sulfide minerals such as troilite (in ordinary chondrites) and pyrrhotite/pentlandite (e.g., in CM carbonaceous chondrites). Especially in CM chondrites, sulfides have long been regarded as results of aqueous alteration at low temperatures. However, recent studies revealed that many of them must have formed in the solar nebula [7].

A peculiar case of sulfide mineralogy in meteorites are phosphorus- and chromium-bearing Fe,Ni sulfides in CM2 chondrites. They are characteristic accessory phases, but enigmatic in their mineralogy and origin. Extensive textural and microanalytical data has been provided by [8] and a TEM study by [9] has shown that the material is nanocrystalline, but was unsuccessful to identify its crystal structure. [10] experimentally showed that P-enriched sulfides as well as Fe monosulfides and pentlandite can form from P-bearing metals during reaction with H_2/H_2S gas at temperatures around 600 K. Remarkably, the relict metal in CM chondrites is typically enriched in Cr and P, close to a composition that could be expected for a nebula condensate [11]. Connections between these phases appear intriguing to explore.

The tools we use for our studies are the analytical transmission electron microscope (TEM) and the focused ion beam (FIB) technique for pinpointed thin film preparation.

Refractory metal nuggets (RMN): We studied the crystallography of a population of submicrometer-sized particles chemically extracted from the Murchison CM2 chondrite, where they initially most likely resided enclosed within CAI mineral grains. These RMNs initially described by [1] escaped oxidation and sulfidation and have presumably retained their original structure and composition. We found that all particles studied are monophase, often euhedral, single crystals (Fig. 1b). The electron diffraction patterns of all grains can be unequivocally indexed in terms of an hcp metal structure (space group $P6_3/mmc$). This also includes grains, which are compositionally dominated by metals that are non-hcp structured at ambient conditions, such as Mo and Ir (amounting up to ~67 at%). The diffraction patterns show no evidence for exsolution, compositional modulation (e.g., spinodal decomposition leading to diffuse satellite reflections) or superstructure formation. Results of EDX spectroscopy in scanning TEM mode at high spatial resolution (< 10 nm) indicate the absence of compositional zoning across individual grains, except for small Fe (and likely Ni) deficits at the outermost margins of some grains (less than 20 nm from the surface).

The condensation model of [1] indicates that upon cooling of a solar gas the metal condensates become increasingly Fe-rich. The fact that we only find hcp structured RMNs suggests that the condensation of cubic Fe,Ni alloys, accounting for the bulk metal content of chondrites, did not succeed in a continuous manner, but required nucleation of a new metal phase. The initially homogeneous formation of refractory metal grains strongly supports that heterogeneous OAs

observed in CAIs are secondary products formed in-situ, as detailed by [12]. The processing of OA-bearing CAIs must therefore have happened at conditions significantly different from those during formation of RMNs and their initial incorporation into these CAIs. Processing either happened in the solar nebula or in parent bodies [13]. Nanoscale TEM investigations on the alteration assemblages and reactions are ongoing and may give answers to open questions. Details on sulfidic phases in OAs are particularly interesting, as Fe monosulfide stoichiometry strongly depends on T and fS_2 (e.g., [14]), which might haven been coupled to fO_2 (e.g., [15]).
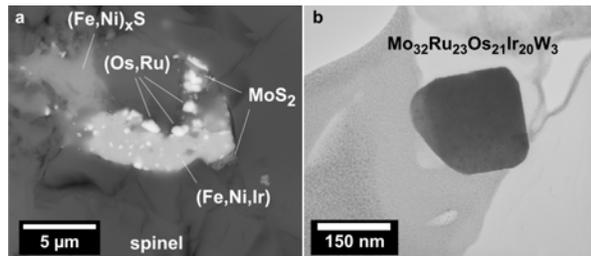

Figure 1: (a) SEM-BSE image of a heterogeneous OA in an Allende CAI. (b) TEM-BF image of a homogeneous RMN from Murchison.

Phosphorus- and Chromium-bearing Sulfides (PCS): In the second case of rather exotic, but nonetheless characteristic, metal-related mineralogy of CM chondrites, we have prepared several FIB sections of P-bearing sulfides from the CM2 chondrites Yamato (Y-)791198 and Y-793321. PCS grains occur mostly isolated in the matrix and in fine-grained rims around large objects. TEM shows that in both meteorites they are heterogeneous internally. Besides the nanocrystalline sulfide (grains <20 nm), finally identified as P-bearing pentlandite, we have found myriads of <100 nm sized flakes of chromium nitride within PCS. SAED derived d-values are consistent with cubic, NaCl structured CrN (carlsbergite). The presence of chromium and nitrogen has been confirmed by EDX and EELS. The carlsbergite flakes have thicknesses of about 3.5 nm on average and show non-random orientations. HR-TEM imaging reveals that the dominant face, i.e., the flake's plane, is the carlsbergite (100) form. It is known in metallurgy that CrN exsolving from metal alloys forms thin (100) platelets in specific orientation relationship with the host ferrite/kamacite (e.g., [16]). The orientation relationship governs the extremely thin shapes of the precipitates and causes preferred orientations. Taken together, the unusual shape and preferred alignment of carlsbergite in the sulfide grains strongly indicates that the flakes originated as precipitates in a Cr- and P-bearing, Fe,Ni alloy before sulfidation. We did not find nitrides inside

relict metal grains of Y-791198 and Y-793321, but in one case nitride crystals have been found in contact with corroded metal.

The abundance of carlsbergite and therefore high nitrogen concentrations up to 2 wt% in the PCS poses a challenging problem. N_2 partial pressures in the order of many 100 bars would be needed to reach corresponding nitrogen contents in molten Fe-Ni-Cr. This is hardly compatible with the conditions of the solar nebula. The absence of nitrides in the metal and the association with sulfides closely resembling the experimental results of [10] strongly suggests a concurrent formation during sulfidation. This in turn indicates that not only H_2 and H_2S played roles in this process, but also gas-solid interactions with volatile species such as N_2, and potentially H_2O and NH_3.

Conclusions: Metals of various composition formed or reacted within (or even beyond) the large temperature interval of 1600 to 600 K. Initially refractory metal condensates were uniform in structure and contained easily oxidizable Mo and W. Processing under yet to be constrained conditions lead to the oxidation and sulfidation of these elements and some of the dissolved Fe and Ni. At the lower temperature end, sulfidation of 'normal' chondritic Fe,Ni metals took place. The presence of nitrides in sulfidation products suggests complex interactions between volatile species and metallic solids. In both cases, the understanding of gas-solid interactions at the nanoscale offers chances to better constrain the physicochemical nebula conditions at the times when these processes took place.

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