

SULFIDE, OXIDE, AND NITRIDE FORMATION IN CM CHONDRITES: A CONNECTION TO THE FORMATION OF TYPE II CHONDRULES INVOLVING ICES?

D. Harries¹ and M. I. F. Barth¹, ¹Institute of Geosciences, Friedrich Schiller University Jena, Carl-Zeiss-Promenade 10, 07745 Jena, Germany (Email: dennis.harries@uni-jena.de)

Introduction: Mineralogical studies of several CM and CM-like chondrites with low degrees of aqueous alteration, including Yamato (Y-)791198 [1], Queen Alexandra Range (QUE) 97990 [2,3], and Acfer 094 [4], have shown that opaque assemblages of sulfides (troilite, pyrrhotite, pentlandite, Cr sulfides), oxides (magnetite, chromite), and also nitride (carlsbergite) occur in complex associations with metallic minerals (Cr-bearing kamacite, taenite). The oxygen isotopic composition of magnetite in sulfide-oxide assemblages of Acfer 094 is similar to the bulk matrix and FeO-rich chondrules, situated at the ^{17,18}O-rich end of the CCAM array [4,5].

Several lines of evidence indicate that temperatures of formation of these assemblages were significantly above the temperatures that are inferred for aqueous alteration, and the most plausible scenario is the interaction of metallic alloys with reactive gases in nebular settings. In ice-enriched environments the reactive species could have been H₂S, H₂O, and NH₃. Carlsbergite (chromium nitride, CrN) in CM2 chondrites suggests that the nitrating agent was NH₃ [1]. A dust-enriched (hydrogen-poor) environment would have mainly provided N₂, which is much less reactive than NH₃ and probably of low abundance in dusty systems. The presence of ice in the accretion region of CM chondrites is compellingly inferred from post-accretional aqueous alteration. Hence, it seems reasonable to explore the hypothesis that ices were involved in the processing of chondritic components prior to the incorporation into the CM parent-body. FeO-rich (type II) chondrules also formed under non-canonical, oxidizing and possibly volatile-rich nebular conditions [6,7], indicating that there is a link between opaque assemblages and chondrule processing.

Material and Methods: We have further studied sulfide-oxide assemblages in Acfer 094, Y-791198 and QUE 97990 by SEM/FIB-TEM techniques. In parallel we have started to experimentally investigate gas-metal interactions in a low-pressure gas-mixing furnace (1 to 100 mbar) capable of direct and precisely controlled H₂O evaporation. Initial experiments on magnetite formation [8] have now been extended to sulfidation and nitrating, including mixed H₂O-H₂S-N₂-H₂ and H₂O-NH₃-H₂ atmospheres.

Results and Discussion: Concentric, porous polycrystalline sulfide-oxide assemblages in Acfer 094 contain variable proportions of troilite/pyrrhotite, pentlandite, and magnetite. In all three chondrites FeO-rich chondrules and chondrule-related objects (probably fragments) are frequently associated with coarse-grained sulfide assemblages of troilite/pyrrhotite and pentlandite. These also occur as individual beads in the matrix. Crystallographic orientation relationships indicate that the pentlandite formed by exsolution from an initially homogeneous monosulfide solid solution (MSS). Metal is rare in FeO-rich chondrules, very Ni-rich (up to ~30 at%), and found in direct contact with the sulfides. FeO-poor (type I) chondrules contain kamacite beads, which are Ni-poor (few at%) and altered to various degrees, either by parent-body alteration or terrestrial weathering. Several FeO-poor chondrules with overgrowths of porous, polycrystalline sulfides assemblages occur in all three chondrites. These resemble the isolated concentric sulfide-oxide aggregates in Acfer 094 and are distinct from aqueous alteration and weathering products.

We hypothesize that the formation of FeO-rich chondrules occurred in a strongly sulfidizing environment [9] and that the sulfide (±oxide) overgrowths on FeO-poor chondrules and metal grains formed in a distal region of this environment, where temperatures were not sufficient for silicate melting and sulfide homogenization (as melt or MSS). This is plausible if the ‘warm’ gas (~200 to 600 °C) was enriched with evaporated ices. Our experiments confirm that the sulfidation kinetics transit from linear (collision/adsorption-controlled) to parabolic (diffusion-controlled) as a function of pressure [10]. Atmospheres with H₂O/H₂S of up to 250 produce exclusively sulfides on Fe₉₄Ni₄Co₁Cr₁ metal at 350 to 550 °C and 10 mbar (H₂O/H₂ ≈ 50). Replacing H₂O with N₂ shows that within the linear kinetic regime (450 °C, 10 mbar) the rate of sulfidation is independent of the potentially competitive co-adsorption of water. This indicates that at ‘warm’ temperatures large partial pressures of H₂O could have gone unnoticed with respect to the formation of magnetite, if small amounts of H₂S had been present in the evaporated ices.

References: [1] Harries D. et al. (2015) *Nature Geoscience* 8:97–101. [2] Barth M. I. F. et al. (2016) *Meteoritics & Planetary Science* 51:A154. [3] Singerling S. A. et al. (2015) 46th LPSC, abstract #1059. [4] Barth M. I. F. et al. (2017) *Meteoritics & Planetary Science*, subm. [5] Kunihiro T. et al. (2005) *Geochimica et Cosmochimica Acta* 69:3831–3840. [6] Villeneuve J. et al. (2015) *Geochimica et Cosmochimica Acta* 160:277–305. [7] Grossman L. et al. (2012) *Meteoritics & Planetary Science* 47:2160–2169. [8] Harries D. (2016) *Meteoritics & Planetary Science* 51:A314. [9] Schrader D. L. et al. (2008) *Geochimica et Cosmochimica Acta* 72:6124–6140. [10] Lauretta D. S. et al. (1996) *Icarus* 122:288–315.

Acknowledgements: We gratefully acknowledge sample loan by NIPR, MWG/ANSMET, and A. Bischoff (U Münster). This work is funded by the DFG within priority program SPP 1385 (grant HA 7187/1-1). The SEM-FIB and TEM facilities at U Jena are supported by the DFG (grant LA 830/14-1 to F. Langenhorst).