IRON NITRIDE IN METAL OF THE PRIMITIVE CHONDRITE ACFER 094: EXTREME NEBULAR NITROGEN PROCESSING?

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Introduction: Nitrogen is a commonly volatile and atmophile element crucial for the development of life and protective atmospheres on habitable, geologically active planets such as the Earth. Its abundance, speciation, and transport in the solar protoplanetary disk and within early-formed planetesimals appear to be governed by a number of complex processes arising from nitrogen's variable mineralogical and chemical binding states – ranging from refractory nitrides to highly volatile ices/gases to organic compounds.

Our recent studies revealed the presence of carlsbergite (CrN) in sulfide inclusions and in one kamacite grain of primitive CM2 chondrites, suggesting the presence of reactive, metastable ammonia (NH_3) released from ices in the processing regions of these chondritic components [1,2]. These observations prompted us to search for evidence of reactive gas-metal interactions in one of the most primitive carbonaceous chondrites known – Acfer 094 [3,4] – in order to better understand the pathways of volatiles from the protoplanetary disk to the terrestrial planets. In particular, we systematically searched for nitrogen-bearing phases in sulfide and metal grains.

Material and Methods: We studied a thin section of Acfer 094 (PL93022) by field-emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectroscopy (EDX) imaging, specifically targeting metal grains. Elemental distribution maps revealed µm-sized nitrogen anomalies in at least two of more than 30 metal grains studied. So far, one of these grains was sectioned by focused ion beam (FIB) preparation and studied by transmission electron microcopy (TEM) using selected area electron diffraction (SAED) and EDX.

Results: FE-SEM backscatter electron images of the 50 µm large, roughly spherical grain revealed a set of slightly darker, lamella-like structures at the site of the nitrogen anomaly. FIB sectioning confirmed the lamellar structure, and SAED-derived lattice d-values identified the inclusion as cubic $(Fe,Ni)_4N$ (roaldite [5]). The roaldite lamella is at least 12-14 µm long, 0.3 µm wide and surrounded by defect-rich, probably martensitic kamacite, which contains ~6 at% Ni, <0.5 at% Co and Cr. TEM-EDX spectra of the lamella qualitatively show the presence of nitrogen and a low to non-detectable concentration of carbon. The Fe/Ni ratio of roaldite is indistinguishable from that of the bordering kamacite. The roaldite lamella appears to be a platelet-shaped precipitate and is accompanied by octahedral inclusions of chromite (<1 µm) in the surrounding metal.

Discussion: To our knowledge this is the first report of roaldite from a chondritic meteorite. The formation of CrN and Fe_4N in Cr- and Ni-bearing Fe-rich alloys requires intense nitrogen activities [1,6]. A rough estimate of the volume ratio of the roaldite lamella and the total grain volume indicates a bulk nitrogen content on the order of 10 ppm N if the nitrogen had been dissolved in the metallic phase (potentially more if other roaldite lamellae within this grain went unnoticed). This is low compared to N concentrations on the order of 100 to 1000s ppm estimated for CrN-bearing grains [1,2], but in general similar to N concentrations in iron meteorites of typically 10-30 ppm [e.g., 6 and ref. therein].

Equilibrium thermodynamics indicate that both the N content of iron meteorites and chondritic metal as well as the stable coexistence of roaldite and Fe,Ni alloy in a gas of solar composition would require N_2 pressures orders of magnitude larger than reasonably anticipated for the solar protoplanetary disk. At 10^{-3} bar at most 0.08 ppm N would dissolve in Fe,Ni alloy, and the equilibrium between kamacite and roaldite would require N_2 partial pressures on the order of 400-4000 bar at 300-800 K [6]. The incorporation of nitrogen into reactive fluids or metallic melts of planetesimals may be explained by the decomposition of organic compounds at elevated pressures and temperatures. Our current understanding is that Acfer 094 never experienced such parent-body activity [4]. Thus, the high nitrogen activities required to stabilize nitrides in a nebular setting demand non-equilibrium chemistry [6], which we hypothesize to involve metastable NH_3 released from evaporated ices at nebular pressures [1]. The formation of Fe_4N requires much larger nitrogen activities than CrN, indicating that the enrichment of NH_3 relative to H_2 and H_2O must have been extreme. This possibly requires the fractionation of NH_3 from H_2O as otherwise oxidation instead of nitridation would have occurred.

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