Nanostructural Analysis of a Sulfide Assemblage in an R-Chondrite Meteorite via large solid-angle EDS

M.S Thompson¹, K.E Miller¹, T.J Zega¹, D.S Lauretta¹

¹Department of Planetary Sciences, Lunar and Planetary Laboratory, University of Arizona, 1629 E. University Blvd, Tucson, AZ 85721 USA

Introduction: Rumuruti chondrites (R chondrites) are a well-established and distinct group of meteorites that represent some of the most highly oxidized and sulfidized samples we have in our collections [1,2]. These meteorites are composed of olivine with high Fe and Ni content, pyroxene and abundant sulfide assemblages including pyrrhotite (Fe₁₋ₓS), pentlandite (Fe,Ni)₉S₈, and rare meteoritic components such as chalcopyrite (FeCuS₂) and reports of pyrite (FeS₂) [3]. Analysis of the crystal structure and chemistry of the minerals within these meteorites can provide insight into the evolution of volatile-rich material in the early solar system. Here we report measurements of a sulfide assemblage by transmission electron microscopy (TEM) and large solid-angle EDS enabled by in situ lift out with a focused-ion-beam scanning-electron microscope (FIB-SEM).

Samples and Methods: Prior electron microprobe analysis indicated a rare troilite (FeS)-chalcopyrite (CuFeS₂) assemblage, with an unknown phase occurring between them in the PRE 95411 R3.8 chondrite. We used an FEI Helios 600i FIB-SEM to create an electron-transparent cross section of the assemblage for detailed investigation. The FIB section was analyzed using a 200 keV FEI Osiris ChemiSTEM equipped with a high brightness X-FEG, Super-X quad-annular SDD detector, and both high-angle annular-dark-field (HAADF) and bright-field (BF) scanning-based TEM (STEM) detectors.

Results: SAED patterns confirm that the sulfide phases are single crystals of troilite and chalcopyrite measuring 3 to 4 µm in diameter. Both HAADF and BF imaging reveal linear structures that transect the interior of the sulfide grains (Figure 1). HAADF shows that the veins have, on average, darker contrast than the host sulfides suggesting lower atomic number. X-ray mapping with the quad SDD detector shows that the linear structures are composed primarily of O, Fe, and Ni, with high concentrations of Cu at the interface between the linear feature and the sulfide crystals (Figure 2). There are localized concentrations of Cu and Fe within the linear features. SAED shows that the bulk of the linear structure is amorphous, but the Cu-and Fe-rich domains are nanocrystalline.

Discussion: Troilite is thermodynamically predicted to be the primary sulfide to condense from a gas of solar composition [4] and synthesis experiments show that it can form under canonical nebular conditions [5]. The TEM data on troilite suggest it is a single crystal and chemically pure, consistent with thermodynamic predictions. In comparison, the chalcopyrite is not a thermodynamically predicted condensate. We hypothesize that the chalcopyrite identified in the PRE 95411 chondrite formed through aqueous-phase processes on its parent body.

The linear features we observe in the PRE 95411 chondrite bear a remarkable chemical and microstructural similarity to veins reported in the Orgueil CI chondrite [6]. Specifically, they are rich in an amorphous Fe-Ni-O bearing material and show Cu concentrated at the boundary between
sulfide crystals and the vein. The similar morphology and chemistry of these features to those observed in Orgueil suggest that they too are veins and likely formed via in situ alteration on the PRE 95411 parent body. The exact chemical pathway for producing the veins is not clear. However, their Cu-Fe rich nanocrystalline sub-domains and Fe-Ni-O bearing ground mass argue both for varied fluid chemistry and rates of crystallization. Moreover, their transection of the troilite and the chalcopyrite argue for multiple stages of alteration. The cross-cutting veins formed later, presumably under oxidizing conditions from a Fe-Ni rich solution. The Cu enrichment seen at the margins likely resulted from the leaching of Fe from the sulfide crystals and its relative immobility during alteration [e.g., 6]. Until this finding there has been very limited evidence of aqueous alteration visible in the R chondrite samples. This is among the most substantial and direct observations for this type of alteration in a low-petrologic grade R chondrite sample. Moreover, the similarity between the structure and chemistry of the veins in PRE 95411 and Orgueil suggests a similar mechanism may be operating on multiple parent bodies.

References:
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Figure 1: a) HAADF image of FIB lift out showing cross section of sulfide assemblage with visible transecting veins, b) close up DF image of veins adjacent to chalcopyrite grain.

Figure 2: HAADF image, O, Fe, Cu, Ni and mixed element maps from the Super-X EDS detector. Note the concentration of Cu towards the interface of the vein and sulfide grain.