

## Textural and Compositional Studies of Sulfide-Metal Assemblages in CR Chondrites: Evidence for Nebular Sulfidization and Parent Body Oxidation

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The CR chondrites are some of the most primitive meteorites available for study and often contain sulfide-metal assemblages, which consist of phases that readily react to secondary processes such as heating or aqueous alteration [e.g., 1]. As such, these sulfide-metal assemblages have the potential to indicate if their host rock experienced any secondary processing and to reveal the conditions and mechanism of such processes. Parent body alteration mechanisms and conditions are currently poorly constrained, making further studies of alteration essential for a more robust understanding of early solar system processes.

A population of sulfide-metal assemblages in chondrites likely formed by sulfidization in the solar nebula [e.g., 2]. In this scenario, Fe,Ni-metal grains condensed from a cooling gas and, at lower temperatures, reacted with H<sub>2</sub>S gas to form troilite (FeS). Experimental studies by [3, 4] have shown that this process can replicate the textures and compositions observed in chondritic sulfide-metal assemblages. In the CR chondrites, we previously observed sulfide-metal assemblages, referred to as sulfide-rimmed metal (SRM) grains [5], on the rims of type I chondrules (those that contain Mg-rich silicates and Fe,Ni metal). The SRM grains are characterized by an Fe,Ni-metal core rimmed with pyrrhotite (Fe<sub>1-x</sub>S) that often contains submicron-scale pentlandite ((Fe,Ni)<sub>9</sub>S<sub>8</sub>). For sulfide-metal assemblages that occur on chondrule rims, it is necessary to invoke a formation mechanism involving migration of immiscible metal melts from chondrule interiors to rims where interaction with H<sub>2</sub>S gas in the nebula promoted sulfidization [6]. In the present study, we aim to analyze the textures and chemical compositions of both unaltered and altered SRM grains on a submicron scale in order to evaluate the effects of the alteration processes and the likely environment where the alteration took place (i.e., solar nebula or asteroidal parent body).

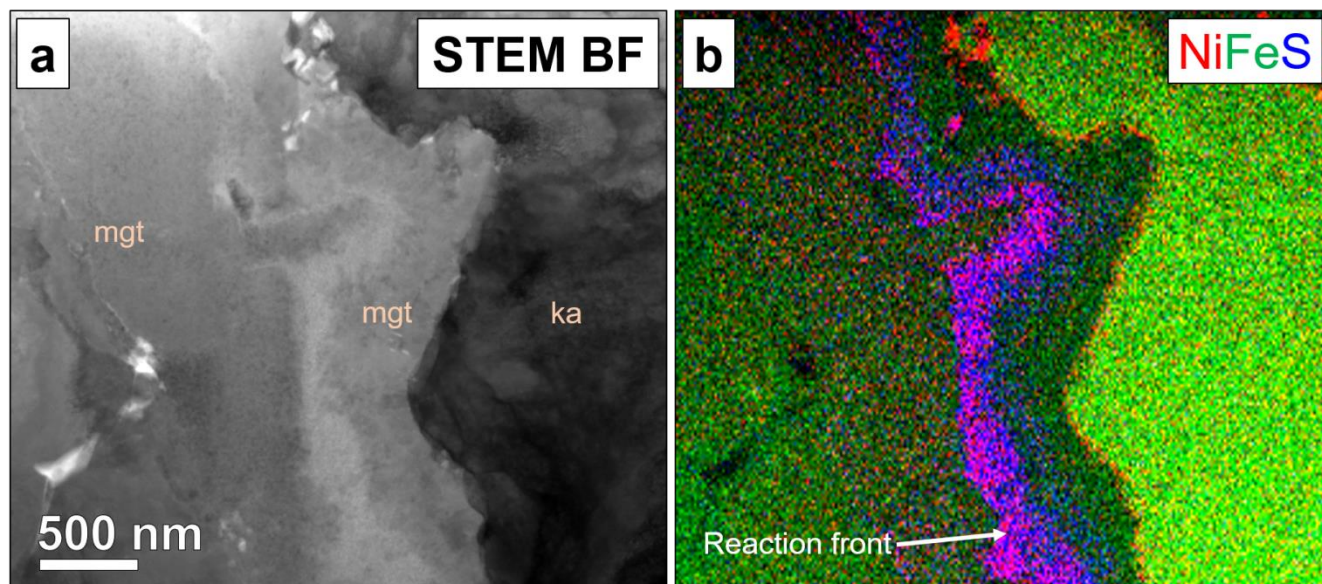
We used SEM and TEM to analyze 3 grains—1 unaltered SRM grain (EET 92042 C3S1) and 2 altered SRM grains (Renazzo C4S4 and Renazzo C10S3). A FEI Quanta 3D Dualbeam FIB-SEM at UNM was used for SEM analyses, including BSE imaging, and to prepare FIB sections of the grains. A JEOL JEM 2100 S/TEM at Virginia Tech was used to collect BF S/TEM and ADF STEM images, SAED patterns, and EDS data at 200 kV.

The unaltered SRM grain EET C3S1 is located on a type I chondrule rim, measures 270 μm × 60 μm in size, has an elongate shape, and has sulfide rims measuring <10 μm to 20 μm in thickness. The phase assemblage includes kamacite (Fe metal with low-Ni content), taenite (Fe metal with high-Ni content), pyrrhotite, and pentlandite. All of these phases have textures inconsistent with alteration and are considered primary phases that formed in the solar nebula. In our TEM analyses of EET C3S1, we found that the metal was predominantly Ni-poor (kamacite); however, along one pyrrhotite-metal interface we

observed Ni-rich metal (taenite), which ranged in thickness from 780 nm to 1590 nm. In their experiments, [7] noted Ni-enrichments in the metal adjacent to pyrrhotite produced by sulfidization. In terms of the crystallinity, the metal occurs as mostly elongated, micron-sized grains, whereas the pyrrhotite appears to be monocrystalline. Orientation relationships between the sulfide and the metals are  $[001]_{\text{troilite}}//[111]_{\text{kamacite}}$  and  $[001]_{\text{troilite}}//[110]_{\text{taenite}}$ .

The altered SRM grain Renazzo C4S4 is located near a void that likely contained a plucked chondrule. The grain measures  $70 \mu\text{m} \times 30 \mu\text{m}$  in size, has an elongate shape, and has sulfide rims measuring  $<10 \mu\text{m}$  to  $20 \mu\text{m}$  in thickness. The other altered SRM grain Renazzo C10S3 is located on a type I chondrule rim, measures  $260 \mu\text{m} \times 50 \mu\text{m}$  in size, has an elongate shape, and has sulfide rims measuring  $<10 \mu\text{m}$  to  $50 \mu\text{m}$  in thickness. The phase assemblage of the altered SRM grains includes kamacite, magnetite ( $\text{Fe}_3\text{O}_4$ ), pyrrhotite, pentlandite, and phyllosilicates (C10S3 only). In our TEM analyses of both grains, we found that the magnetite-metal interfaces often have thin regions ( $\sim 50 \text{nm}$ ) of Ni-rich metal (Fig. 1b). The magnetite is polycrystalline and contains Ni,S-rich materials, some of which appear to be discrete phases (pyrrhotite and pentlandite), while others appear more diffuse and define reaction fronts similar in shape to the magnetite-metal interfaces (Fig. 1b). Both altered SRM grains also appear to contain lower Z-contrast phases within the metal cores, observed in BSE images on the SEM; however, TEM analyses on FIB sections that bisected these regions did not reveal the presence of any phases within the metal. It is possible that these lower Z contrast regions are surficial in nature, but further work is needed to determine their identity and relation to the SRM grains, namely if they are laboratory artifacts or intrinsic to the sample itself.

Based on textural considerations, we argue that the magnetite and phyllosilicates are secondary in origin and formed on the CR parent body from aqueous alteration. The magnetite likely formed by the oxidation of metal by the reaction:  $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 2\text{H}_2$ . The occurrence of the magnetite along the edges of the metal in the SRM grains is consistent with infiltration of fluid produced by the melting of water ice that accreted on the CR parent body. The presence of the Ni-rich metal along the magnetite-metal interface is likely a reaction product of the oxidation of kamacite. Additionally, the presence of Ni,S-rich reaction fronts in the magnetite argues for Ni and S mobility and may imply that this grain experienced two separate alteration events. The phyllosilicates only occur along magnetite-sulfide interfaces, implying that the aqueous alteration of sulfides in association with magnetite in some way promotes the formation of phyllosilicates. This behavior was also observed in altered sulfides in CM1 chondrites and requires the introduction of a Mg,Si-bearing fluid [8]. Further detailed thermodynamic and kinetic calculations on the potential reactions involved in the formation of these secondary phases will provide further constraints on parent body conditions during alteration [9].



**Figure 1.** STEM bright field (a) and Ni-Fe-S RGB composite EDS map (b) of the magnetite-metal boundary in the altered SRM grain Renazzo C4S4. The Ni-rich metal is visible as the red region along the boundary in (b). A Ni,S-rich reaction front within the magnetite is indicated with the white arrow in (b). This SRM grain did not contain any phyllosilicates. Mgt – magnetite, ka – kamacite.

#### References:

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