Conditions for formation of chalcopyrite in the Rumuruti chondrites

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The Rumuruti (R) chondrites

The R chondrites are a group of meteorites that are distinct from the carbonaceous, ordinary, and enstatite chondrites. Texturally, they more closely resemble the carbonaceous chondrites, with abundant matrix (3, 2) and chondrules that average 300 to 600 μm (3). Their chemistry shares characteristics with both the ordinary and carbonaceous chondrites (4). Like the enstatite chondrites, they are highly sulfidized and equilibrated at a sulfur fugacity between 1.6 and 2.8 log units above the iron-troilite buffer (4). Unlike the enstatite chondrites, though, the R chondrites are highly oxidized, recording oxygen fugacities from the fayalite-magnetite-quartz (FMQ) buffer to FMQ+3.5 log units (5). The R chondrite parent body experienced high-temperature hydrothermal alteration, which is most notably demonstrated by the presence of amphibole and biotite in the RS chondrite LAP 04840 (6), but has since been noted in other R chondrites (7, 8). Oxygen isotopes in the R chondrites are enriched in 16O, with the highest recorded δ18O values (9).

Chalcopyrite

Chalcopyrite (CuFeS2) is a common and important constituent of terrestrial ores, but very rare in meteorites. The R chondrites are the second group of chondrites (5), the other being the CK chondrites (10). Since it is not commonly observed in meteorites, its presence suggests parent body formation within a narrow range of conditions. The present study reports observations of chalcopyrite in three R chondrites, and analysis to determine the conditions in which it formed.

Table 1. Samples observed

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polishing Type</th>
<th>Remarks or parents</th>
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<tbody>
<tr>
<td>PRE 95411</td>
<td>RS</td>
<td>Metaite in which UP researchers first found chalcopyrite (4)</td>
</tr>
<tr>
<td>NWA 7514</td>
<td>RS</td>
<td>Unweathered (8)</td>
</tr>
<tr>
<td>PCA 91002</td>
<td>RS-6</td>
<td>Reports of metallic copper (11)</td>
</tr>
</tbody>
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Methods

We mapped the Cu distribution in each thin section using a Cameca SX100 electron microprobe (EMPA). The major-element compositions in the copper host grains were quantified at each location using wavelength dispersive spectrometry (WDS). A slice of the largest chalcopyrite grain in PRE 95411 (Assemblage A) was removed for transmission electron microscopy (TEM) analysis using an FEI Helios 600i focused-ion beam scanning-electron microscope (FIB-SEM) (12). We examined the FIB sections using two TEMs: a 200 km/dióios ChemiSTEM and a 200 km/dióios 2200FS. Crystal chemistry was measured with high-resolution X-ray spectrum images acquired with the large solid-angle (0.9 sr) Super-X EDS detector on the ChemiSTEM. Crystal structure was determined with the ChemiSTEM and 2200FS using selected-area electron diffraction (SAED).

Thermodynamic analyses were performed using the HSC 5 software package to apply a Gibbs free energy minimization. Stability in an aqueous system was calculated at temperatures ranging from 150°C to 2000°C for solid chalcopyrite, copper, pyrrhotite, troilite, and graphite. The measured composition of Assemblage A was compared to ternary diagrams (13) to determine the temperature of equilibrium.

Results: Occurrence of Chalcopyrite

A total of 24 grains of chalcopyrite were found: 12 grains in PRE 95411, nine grains in NWA 7514, and three grains in PCA 91002. Additionally, one grain with stoichiometry closer to cubanite was found in PCA 91002. In all three samples, chalcopyrite was found in association with pentlandite and/or pyrrhotite (Figure 2).

Results: FIB-TEM

FIB-TEM analysis of Assemblage A confirms the crystal structure of chalcopyrite, and identifies the presence of troilite (Figure 4). Microprobe analyses indicate the presence of pyrrhotite (Fe3S5), but not troilite in Assemblage A. Pyrrhotite and troilite can stably coexist below 412 C (13). Chemical mapping by EDS reveals the presence of an Fe-, Ni-, O-rich vein between the chalcopyrite and troilite grain (Figure 3). This vein is nanocrystalline at the center, and amorphous at the edges (Figure 5). Chemical maps also show a Cu- and O-rich rim around the troilite grain.

Discussion

The vein and copper rim within Assemblage A suggest that the chalcopyrite in the R chondrites is aqueous in nature. We hypothesize that Assemblage A was originally composed largely of troilite, which is the predicted nebular product. Following accretion, parent-body processing led to fluid flow that oxidized troilite to form pyrrhotite and the observed Fe-, Ni-, O-rich vein. Copper ions, either present in the solution originally or introduced at a later stage, then diffused into the pyrrhotite, forming chalcopyrite. Subsequent equilibration at 473 K may account for the close agreement between the observed assemblage and the ternary diagram. However, the coexistence of pyrrhotite and troilite within the assemblage constrains temperatures to a maximum of 412 K in equilibrium. Additionally, the amorphous character of the edges of the vein argues against significant annealing. Pentlandite may have formed simultaneously with troilite in Assemblage A, or during an episode of aqueous alteration.

Conclusions

Aqueous formation of chalcopyrite in the R chondrites is consistent with the observed mineralogy and is the most likely explanation for the Fe-, Ni-, O-rich vein and the copper rim revealed by TEM analysis. Previous studies have discussed aqueous alteration in less primitive R chondrites, with hydration occurring up to temperatures of 943 ± 6 K (6-8). Chalcopyrite in the R chondrites is evidence that the extent of aqueous processing on the R chondrite parent body was much greater than previously suggested.

Acknowledgments

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References