Altered Primary Iron Sulfides in CR and CM Carbonaceous Chondrites: Formation by Dissolution and Pseudomorphic Replacement

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Introduction

Potential primary sulfides:
- pyrrhotite (Fe₇Ni₃S₈, αpo)
- pentlandite (Fe₉Ni₃S₈, ρn)

Formation mechanisms:
- Crystalization: cooling of sulfide melts produced during chondrule formation event [1-5]
- Sulfidization: Fe-Ni metal + H₂S = (Fe₇Ni₃)S₈ ([Fe,Ni]S₈)

What are the effects, mechanisms, and conditions of alteration of primary pyrrhotite and pentlandite?

Altered primary sulfides textural groups:
- Porous, pyrrhotite-pentlandite (4P) grains
- Located in CM chondrite matrix and type IA chondrules
- Grains of po with Mn alteration textures exhibiting extensive porosity that appears crystallographically controlled (Fig. 2)
- Show different degrees of pitting of po resulting in progressively more Mn-like compositions (Figs. 2-5)
- Pyrrhotite-pentlandite intergrowth altered (PPI alt) grains
- Located in CM and CR chondrites matrix and type IA chondrules
- Altered grains of po with Mn alteration textures (Fig. 6)
- Po altering to porous magneto(pyrrhotite-pentlandite) (phy) or phyllosilicates (phyllosilicates) (phyllosilicates)
- Sulphide-rimmed metal altered (SRM alt) grains
- Located in CM chondrule type IA chondrules

Results

Formation mechanisms:
- NOT terrestrial alteration: increase in degree of alteration of bulk sample correlates with increase in proportion of altered grains (Fig. 8)
- 4P grains = dissolution
- Crystallographic orientation of pitting
- Preferential pitting of pyrrhotite grains
- Complete partial to complete alteration of po/metal varies grain by grain
- Reaction volume calculations agree with presence/absence of pores/fractures (Table 2, Fig. 9)

Formation conditions:
- Effects in T, pH, O₂, and/or arf shift stability fields (Fig. 10)
- Could vary so drastically within same sample due to microchemical environments and/or brecciation

Discussion

Figures and Table

Fig. 1. BSE images of primary iron sulfides in CRs and CMs (a-c) represent po-pn intergrowth (PPI) grains whereas (d) represent sulfide-rimmed metal (SRM) grains. Images are from the following samples: (a) CM QUE 97990, (b) CR EET 90242, (c) CM Murchison, (d) CR QUE 99177, (e) CR EET 90242.

Fig. 2. BSE images of 4P grains from CMs (a-d) Mighei, (e, f) Murray showing increasing, moving downwards, pitting of po. Remnant po patches are visible in (a-d). Crystallographic orientation of pitting is excellent in (a-d).

Fig. 3. Elemental-normal plots (wt %) for 4P grains. Textured regions denote envelopes for primary sulfides from [4]. Samples are color-coded according to degree of alteration (warmer to cooler colors indicating increase in degree of alteration). Error bars are 1σ.

Fig. 4. 4P grain compositions plotted on an Fe-Ni-S ternary diagram (in at%). The legend for the samples is the same as in Fig. 3. Phase fields and tie-lines are from [9]. Note how all 4P grains plot between po and pn with compositions closer to the pn field: x = troilite, hpo = hexagonal pyrrhotite, mpo = monoclinic pyrrhotite, py = pyrite, po = pentlandite, aew = awaruite.

Fig. 5. TEM x-EDS maps of 4P grains from CMs (a) QUE 97990, (b) Mighei. The Fe and Ni maps of (a) clearly show the pn lamellae, which are Ni-rich and Fe-poor in comparison to the adjacent po. The lamellar regions in (a) do not appear to be compositionally distinct from the po. The Fe and Ni maps of (b) show less distinct pn lamellae. The preferential pitting of po is more extensive in (b) and has resulted in a greater proportion of remnant pn, hence the greater abundance of Ni-rich regions.

Fig. 6. BSE, HAADF (a-d) and HAADF-STEM (c-f) images of 4P grains in po. Alteration of po/metal in (a-e) CR Murchison and (b-d) CR Renazzo. Different mag textures (mottled and smooth) are shown. In the HAADF STEM images, the gap between po and mottled mag results in a greater proportion of remnant pn, hence the greater abundance of Ni-rich regions.

Fig. 7. BSE (a-c) and HAADF STEM (d) images of SRM grains from CR Renazzo. Grains are located on chondrule rims (intermediate between type I and IA), altering to mag in both po and mottled mag, indicating the presence of cracks oriented perpendicular to the boundary. An SAED pattern is shown for the mag confirming the identification of the Fe-oxide phase as magnetite.

Fig. 8. Bar plot illustrating the relative proportions of unaltered (warm colors) and altered (cool colors) primary sulfides in the CR and CM chondrules. Samples are listed in order of increasing degree of alteration of the bulk sample moving from left to right. Note the decrease in unaltered grains (PPI & SRM) in both groups with increasing alteration.

Fig. 9. Graphical representation of mgo/mgo ratios for PPI alt grains in CR Renazzo and CM Murray and Murchison. The vertical dashed line indicates the two-phase model. The theoretical value of 0.815. Nearly all grains agree with this value.

Fig. 10. Lop₂⁻/vpx diagram, created using Geochemist’s Workbench, for po interacting with Fœ⁻⁻ bearing aqueous fluid. Solid and thick dashed lines are for 70°C. Thick dashed lines show changing a mgo. In aqueous solution, light dashed lines are for T = 100°C and a mgo = 10⁻⁴. An increase in T shifts and expands the stability fields. An increase in a mgo shifts stability fields to lower pH. Lighter colors represent regions for positions that result in a phase change with a change in one of the conditions (T, pH, a mgo).

Table 1. Textural groups, proportions, sizes, and locations of altered primary sulfide grains and sulfd-metal assemblages by sample. Samples of the same meteorite group are listed in order of increasing degree of aqueous alteration. That CR QUE 99177 is not listed as it does not contain any altered primary grains.

<table>
<thead>
<tr>
<th>Meteorite Group</th>
<th>Sample</th>
<th>Textural Group</th>
<th>Relative %</th>
<th>Size Range (μm)</th>
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Table 2. Volume changes for pseudomorphic replacement of PPI alt and SRM alt grains. Equations are listed below. A ratio less than 1 indicates a molar deficit in the reaction and can result in the formation of pores. A ratio greater than 1 indicates a molar excess in the reaction and can result in the formation of fractures/cracks.

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<tr>
<th>Phase</th>
<th>Molar Volume Gain (cm³)</th>
<th>Equation (1)</th>
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<th>Equation (3)</th>
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References