

## **Experimental study of the formation of chalcopyrite and bornite via the sulfidation of hematite: Mineral replacements with a large volume increase**

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### **ABSTRACT**

Chalcopyrite ( $\text{CuFeS}_2$ ) and bornite ( $\text{Cu}_5\text{FeS}_4$ ) are the most abundant Cu-bearing minerals in hydrothermal Cu deposits, forming under a wide range of conditions from moderate-temperature sedimentary exhalative deposits to high-temperature porphyry Cu and skarn deposits. We report the hydrothermal synthesis of both chalcopyrite and bornite at 200–300 °C under hydrothermal conditions. Both minerals formed via the sulfidation of hematite in solutions containing Cu(I) (as a chloride complex) and hydrosulfide, at pH near the  $\text{pK}_a$  of  $\text{H}_2\text{S}(\text{aq})$  over the whole temperature range. Polycrystalline chalcopyrite formed first, followed by bornite.

Assuming that Fe behaves conservatively, the transformation of hematite to chalcopyrite involves a large increase in volume (~290%). The reaction proceeds both via direct replacement of the existing hematite and via overgrowth around the grain. Chemical exchanges between bulk solution and hematite are enabled by a network of micrometer-size pores. However, in some cases the chalcopyrite overgrowth develops large grain sizes with few apparent pores and in these cases fluid transport may have been via a network of fractures. Similarly to the replacement of hematite by chalcopyrite, bornite forms via the replacement of chalcopyrite. The reaction has a large positive volume (~230%), and proceeds both via chalcopyrite replacement and via overgrowth.

This study shows that replacement reactions can proceed via coupled dissolution-reprecipitation even where there is a large volume increase between parent and product mineral. This study also provides further evidence about the controls of reaction pathways onto the final mineral assemblage. In this case, the host initial fluid was undersaturated with respect to Fe-bearing minerals. Upon slow release of Fe at the surface of hematite, a mineral assemblage of chalcocite, bornite, and finally chalcopyrite is expected. However, in practice chalcocite did not nucleate on the surface of hematite. Rather relatively slow nucleation of bornite enabled high concentrations of Fe to build up near the dissolving hematite, so that chalcopyrite (high-sulfidation experiments) or chalcopyrite+pyrite (low sulfidation) crystallized first.

**Keywords:** Hematite, chalcopyrite, bornite, mineral replacement, hydrothermal experiment