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 (CuFeS\textsubscript{2}) and bornite (CuFeS\textsubscript{2}) 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 pK\textsubscript{s}, of H\textsubscript{2}S(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 chalcopyrite, 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

**INTRODUCTION**

Chalcopyrite and bornite are the most abundant Cu-bearing sulfides and are the primary Cu minerals in a wide range of ore deposits from moderate temperature sedimentary exhalative (SEDEX) deposits, through Fe oxide Cu gold (IOCG) deposits, to high-temperature porphyry Cu deposits and skarns (Robb 2005). Whatever the ore deposit type, chalcopyrite and bornite are essentially hydrothermal minerals, formed from Cu-rich saline hydrothermal fluids. Much of our knowledge of the phase relations in the Cu-Fe-S system is based on experimental studies undertaken using the classic dry sealed tube technique, which serve to inform our understanding of subsolidus processes, but may not provide an accurate view of controls on mineral formation under hydrothermal conditions (see Fleet 2006; Vaughan and Craig 1978).

There have been very few experimental studies on chalcopyrite or bornite formation under hydrothermal conditions relevant for ore formation. Barnard and Christopher (1966a, 1966b) recrystallized crushed chalcopyrite grains in pure water and in Cl-rich solutions at temperatures between 400 and 500 °C, and observed that chalcopyrite recrystallized in Cl-rich solutions but not in pure water. This result is consistent with the poor stability of the Cu(I) aqua ion in aqueous solutions ( disproportionation to Cu(II) and Cu(0)), and the importance of Cl-complexing for the transport of Cu(I) in hydrothermal solutions (Brugger et al. 2007; Etschmann et al. 2010). Kojima and Sugaki (1985) studied the phase relations in the Cu-Fe-Zn-S system between 300 and 500 °C under hydrothermal conditions by the recrystallization of chalcopyrite, bornite, and other sulfides in a 5 m NH\textsubscript{4}Cl solution. These authors did not report the direct synthesis of chalcopyrite or bornite hydrothermally. Seyfried and Ding (1993) conducted a...