Deciphering a million-dollar reaction – the mineral replacement of chalcopyrite by digenite/covellite

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Copper-iron-sulfides constitute an economically important class of minerals with applications ranging from construction to energy storage. Chalcopyrite ($CuFeS_2$) is the most important primary mineral mined for copper extraction[1]. Hydrometallurgical leaching of chalcopyrite is commonly hampered by the formation passivation layers, whereas conventional extraction via smelting is energy-intensive and generates toxic by-products. The metathesis of chalcopyrite has recently emerged as an alternate mineral processing method, which upgrades the primary chalcopyrite to high-grade, easily leachable secondary copper sulphides (e.g., digenite $Cu_{1.8}S$, chalcocite Cu_2S) via fluid-driven reactions (copper-rich acidic medium) under mild hydrothermal conditions (180˚C-300˚C). Chalcopyrite metathesis involves the removal of Fe^{2+}/Fe^{3+} into solution and the uptake of Cu^{2+} from the solution. Chalcopyrite metathesis is essentially a mineral replacement reaction, which takes place via a coupled-dissolution reprecipitation (CDR) reaction mechanism. We have undertaken a systematic *in-situ* and *ex-situ* investigation of this mineral replacement reaction using synchrotron radiation and rapid quench laboratory experiments. *In-situ* synchrotron diffraction experiments reveal the formation of szomolnokite ($FeSO_4.H_2O$) at high temperature, and the retrograde formation of djurleite ($Cu_{1.96}S$). *In-situ* XAS measurements reveal fast reduction of Cu^{2+}(aq) to Cu^{+}(aq), and show dissolution of Fe in the form of Fe^{2+}(aq) during mineral replacement at high-temperatures. Focused ion beam-backscattered electron imaging revealed the presence of a complex, multi-scale network of porosity along the grain boundaries between the two mineral phases, which controls the reaction kinetics and mechanism. A better geochemical understanding of the mineral replacement of chalcopyrite by digenite/chalcocite can pave the way for economical hydrometallurgical processes for copper extraction in the future, as well as constrain mineral formation in Nature.

References

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