

## **EBSD mapping of Cu-Fe-sulfides reveals microstructures enriched in critical/precious metals and resolves deformation histories**

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### **ABSTRACT**

Chalcopyrite ( $\text{CuFeS}_2$ ) and bornite ( $\text{Cu}_5\text{FeS}_4$ ) from the Olympic Dam Cu-U-Au-Ag deposit (South Australia) are characterized using electron backscatter diffraction (EBSD) to identify microstructures and their correlations with trace element concentrations measured by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Natural chalcopyrite is shown to be a rich source of microstructural and -textural information, preserving  $\langle 110 \rangle$  and  $\langle 001 \rangle$  crystallographic preferred orientations (CPO),  $\{110\}$  and  $\{112\}$  twin systems, grain boundary migration, foam textures, and subgrain boundaries. Selected examples of chalcopyrite illustrate different aspects of its behavior and relationship with bornite across the mineralogically zoned deposit. The oriented stress imposed by brecciation and/or fluid fluxes at Olympic Dam, alongside temperature, pressure, and strain rate, is shown to induce various microstructures preserved in chalcopyrite. Microstructures can, therefore, be used to elucidate sequential stages of low- to medium-temperature ( $<300\text{ }^\circ\text{C}$ ) ore evolution. Pyrite microstructures are already routinely used to understand higher temperature ore evolution, and the complementary microstructural study of chalcopyrite coexisting with pyrite has the potential to reveal deformational events across a more complete range of temperatures. Chalcopyrite is particularly well suited to unravel episodes of low- to medium-temperature overprinting in ore systems that lack obvious evidence for post-mineralization deformation.

EBSD mapping reveals what appears as single grains of chalcopyrite in reflected light are, in fact, aggregates composed of  $\sim 100$  individual grains. In contrast, analyzed bornite displays overwhelming crystallographic homogeneity. Rare instances of misorientation in bornite are all associated with replacement and, if correlated with EBSD analysis of coexisting chalcopyrite and its inclusions (e.g., cobaltite), can be used to discern the origin and evolution of different bornite associations. LA-ICP-MS trace element mapping of chalcopyrite aggregates indicates that grain boundaries host Pb, Bi, Ag, and Sb concentrations, with twin boundaries displaying a weaker concentration of the same elements. Bornite grain boundaries are also enriched in Pb. These observations confirm the critical role played by microstructures in Cu-(Fe)-sulfides as traps for Pb, a non-target contaminant in copper concentrates, as well as new evidence for the physical state of Ag and potential value-added critical metals like Bi and Sb. The preferential occurrence of Pb, Bi, Ag, and Sb along permeable grain boundaries may incentivize efforts to remove contaminants and/or recover by-products via leaching.

**Keywords:** Electron backscatter diffraction, Cu-(Fe)-sulfides, chalcopyrite, bornite, trace elements, microstructures, twinning, Olympic Dam