Uranium scavenging during mineral replacement reactions†

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**ABSTRACT**

Interface coupled dissolution-reprecipitation reactions (ICDR) are a common feature of fluid-rock interaction during crustal fluid flow. We tested the hypothesis that ICDR reactions can play a key role in scavenging minor elements by exploring the fate of U during the experimental sulfidation of hematite to chalcopyrite under hydrothermal conditions (220–300 °C). The experiments where U was added, either as solid UO$_2$(s) or as a soluble uranyl complex, differed from the U-free experiments in that pyrite precipitated initially, before the onset of chalcopyrite precipitation. In addition, in UO$_2$(s)-bearing experiments, enhanced hematite dissolution led to increased porosity and precipitation of pyrite+magnetite within the hematite core, whereas in uranyl nitrate-bearing experiments, abundant pyrite formed initially, before being replaced by chalcopyrite. Uranium scavenging was mainly associated with the early reaction stage (pyrite precipitation), resulting in a thin U-rich line marking the original hematite grain surface. This “line” consists of nanocrystals of UO$_2$(s), based on chemical mapping and XANES spectroscopy. This study shows that the presence of minor components can affect the pathway of ICDR reactions. Reactions between U- and Cu-bearing fluids and hematite can explain the Cu-U association prominent in some iron oxide-copper-gold (IOCG) deposits.

**Keywords:** Uranium, scavenging, IOCG deposits, experiment, sulfidation reaction, interface coupled dissolution-reprecipitation reactions

**INTRODUCTION**

Iron oxide-copper-gold (IOCG) deposits, such as Olympic Dam (OD) and Prominent Hill in South Australia, are important sources of copper, uranium, gold, and silver. Uranium is always enriched in South Australian IOCG ores, acting as a penalty element or a resource depending on grade and distribution. OD is characterized by a relatively oxidized mineral assemblage; magnetite-pyrite precipitated at the periphery of the deposit, and hematite dominates in the ores, with a barren hematite body forming the core of the deposit. Copper minerals show an increase in Cu:S ratio toward the core of the deposit: chalcopyrite dominates at the periphery, followed by bornite and finally chalcocite. Brattrud et al. (2007) suggested that the mineralogical zoning at OD and the stable isotopic (O, S) composition of ore minerals is consistent with a two stage model, whereby a hot, highly saline fluid (>30 wt% NaCl; >400 °C) sourced from a granitic magma formed a low-grade, relatively reduced, magnetite-chalcopyrite orebody, which was later remobilized and upgraded by interaction with meteoric, oxidized fluids.

Although OD is the world’s largest U deposit in terms of metal endowment, no specific study on the genesis of U mineralization has been conducted (Cuney 2009). Leaching of U from the wall rocks and reaction of the U-bearing hydrothermal fluids with the Fe-oxide and Cu-sulfide mineralization is assumed to be responsible for U enrichment in some IOCG deposits by a factor of 10 to 40 relative to the fresh host rocks (Hitzman et al. 1992; Hitzman and Valenta 2005). In contrast to the Cu-bearing minerals, the U-bearing minerals do not show a clear zonation pattern at OD. Uranium minerals occur throughout the Cu-enriched zone; uraninite is associated mainly with Cu-Fe sulfides and hematite; brannerite and coffinite are associated mainly with sulfides, quartz, and sericite (Ehrlig et al. 2012).

The importance of fluid-mediated interface coupled dissolution-reprecipitation (ICDR) reactions in geological processes has been emphasized over the past decade (Putnis 2009; Putnis and John 2010). These reactions are key to understanding ore formation processes, grade control, and the evolution of ore textures, e.g., alteration of pentlandite in the cementation zone (Tennefjall et al. 2006); replacement of magnetite and pyrrhotite by Fe-sulfides (Qian et al. 2010); hematite by chalcopyrite and bornite (Zhao et al. 2014); scavenging of bismuth and gold during ICDR reactions (Tooth et al. 2011); or reactions involving Au-Ag-tellurides (Okrugin et al. 2014; Zhao et al. 2009, 2013).