Textures and high field strength elements in hydrothermal magnetite from a skarn system: Implications for coupled dissolution-reprecipitation reactions

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ABSTRACT

There is increasing evidence to suggest that high field strength elements (HFSE) could be mobile to some extent in hydrothermal fluid due to the influence of halogens (e.g., fluorine and chlorine). However, in natural hydrothermal (fluid) systems, “coupled dissolution reprecipitation” (CDR) reactions at fluid-mineral interfaces that have been emphasized in the past decade may play a key role in controlling the final textures and mineral assemblages. The influences of the CDR reactions in hydrothermal systems on HFSE enrichment or depletion at the mineral scale are enigmatic. In this study, we show that enrichment of Nb and Zr can occur in magnetite on the mineral scale formed by hydrothermal fluids at medium-to-lower temperature in a skarn system. Four stages of mineralization and alteration of magnetite have been identified in the Baishiya iron skarn deposit of the East Kunlun Mountains of China. Magnetite formed in stage 1 (S1) developed obvious oscillatory zonation, whereas that formed in stages 2 (S2) and 3 (S3) shows hydrothermal alteration and metasomatic textures, and that in stage 4 (S4) developed euhedral crystals with simple zoning. Systematic variations in the trace element compositions of different magnetite grains analyzed by EMPA and LA-ICP-MS suggest that the magnetite from S1 to S3 may have formed in a metasomatic process at relatively constant temperature, whereas the magnetite from S4 formed by re-equilibrium processes at lower temperature. The magnetite from each stage can be divided into light and dark domains based on backscattered electron images. The dark domains in the magnetite from S1 and S2 have higher Nb/Ta (8.52–27.00) and Zr/Hf (18.22–52.64) ratios and silicon contents than the light domains (0.55–5.66 and 2.54–16.43, respectively). Compared with other magnetite ores, the ores from S1 and S2 are depleted of V and Ni. This depletion may be induced by increased oxygen and co-crystallized sulfide. However, these variations are unlikely to be responsible for the enrichment of Nb and Zr in magnetite at equilibrium conditions. Conversely, the dark domains of the magnetite from S1 and S2 are porous, irregular, and/or oscillatory with quartz inclusions, indicating nonequilibrium conditions. These textural features could be attributed to the CDR reactions that are ubiquitous in skarn systems. The increased silicon concentrations in magnetite due to the CDR reactions could affect the lattice parameters of the magnetite structure, leading to an overall change in the volume of magnetite ores. The reduplicative processes of volume change, dissolution, and porosity formation within magnetite are further impoved due to an increased oxygen fugacity and co-crystallized sulfide (e.g., decreased temperature or increased sulfur fugacity) at far-from-equilibrium or local equilibrium conditions, resulting in oscillatory magnetite dark domains of S1. Ripening of the transient porosity can trap nanoscale precipitates of columbite and zircon within pores of Si-magnetite, and this precipitation could be attributed to the co-crystallized phlogopite that would incorporate fluorine from the hydrothermal fluid, and subsequently decrease the solubility of Nb and Zr in the skarn system. This scenario highlights that Nb and Zr could be scavenged and enriched in the reaction fronts (porosity) by controlling the reaction pathway at a local scale that does not reflect the overall fluid-rock interaction history of the mineral assemblage.

Keywords: Hydrothermal magnetite, skarn deposit, high field strength elements, coupled dissolution-reprecipitation reactions

INTRODUCTION

High field strength elements (HFSE) are considered to be reliable geochemical indicators because of their immobility in most geological settings. However, there is increasing evidence to suggest that they are mobile to some extent in fluid-driven systems (Gao et al. 2007; Huang et al. 2012; Jiang et al. 2005; Rapp et al. 2010; Salvi and Williams-Jones, 2006; Zhang et al. 2016). Recent experiments have further demonstrated that NaCl- and NaF-bearing aqueous fluids at hydrothermal conditions could improve HFSE mobility (Tanis et al. 2012, 2015, 2016). However, in natural hydrothermal systems, the reduplicative hydrothermal activity generally results in textural and