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Compositions of biotite, amphibole, apatite and silicate melt inclusions from the Tongchang mine, Dexing porphyry deposit, SE China: Implications for the behavior of halogens in mineralized porphyry systems

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ABSTRACT

The Dexing deposit, located in the Circum-Pacific ore belt, is the largest porphyry copper deposit in eastern China. It is composed of 3 separate plutons, which host three mines: Tongchang, Fujiawu and Zhushahong mines. The porphyritic granodiorite samples studied in this investigation were collected from the Tongchang ore-forming pluton of this giant deposit. This paper presents electron microprobe analyses of biotite, apatite, amphibole, plagioclase, potassium feldspar and rehomogenized glassy melt inclusions from the Tongchang porphyritic granodiorites. Petrographic observations of the samples are consistent with portions of the granodioritic magma represented by our samples being overprinted by potassic hydrothermal fluid which variably altered these minerals.

All of the studied micas are Mg-rich biotites. The biotites are separated into altered magmatic and secondary types based on their petrographic and geochemical characteristics. The phlogopite components of the secondary biotites are typically higher than those of the altered magmatic biotites, and the X_{Mg} values of all biotites correlate negatively with Cl contents, consistent with the Mg–Cl avoidance principle. The X_{Mg} values also correlate negatively with ($K_2O + Na_2O + BaO$), FeO and TiO_2 for both generations of biotites. The calculated log ($fH_2O/fHCl$) values (for 690 K) of the coexisting potassic fluids, which are determined from the altered magmatic biotite compositions, range from 4.43 to 4.67, and are very similar to those of other major porphyry deposits. However, the log(fH_2O/fHF) and log($fHF/fHCl$) values for the same batch of hydrothermal fluids are significant higher and lower than those of these other porphyry deposits, respectively.

The Cl concentrations of amphiboles and melt inclusions range from 0.18 to 0.32 wt.% and 0.15 to 0.44 wt.%, respectively. Most apatites trapped in biotite and plagioclase phenocrysts display a bimodal Cl distribution: 0.19 to 1.35 wt.% and 1.48 to 3.73 wt.%. Similarly, the S contents of the apatite also show a distinct bimodal distribution reflecting the effects of variable anhydrite saturation during evolution of the Tongchang melt and variable dissolution of anhydrite by saline aqueous fluids. The Cl contents of the apatites from the Tongchang system are typically higher than those of other studied porphyry deposits. Furthermore, the Cl contents of the melt inclusions are at or very near the Cl saturation levels (0.36 to 0.46 wt.% at 850 °C and 50 MPa and 0.42 to 0.54 wt.% at 850 °C and 200 MPa) for these melt compositions at shallow crustal pressures. These findings suggest that the area of the granodioritic magma represented by our samples, and perhaps the bulk of the Tongchang granodioritic magma was rich in Cl. The melt inclusion compositions are consistent with a high-salinity, hydrosaline liquid being exsolved directly from the granodioritic melt directly. This high-salinity hydrosaline liquid was likely very efficient at dissolving, transporting and precipitating ore metals in the mineralizing magmatic–hydrothermal system.

1. Introduction

The giant Dexing porphyry copper deposit is an important source of copper and, to a lesser extent, molybdenum and gold for China (Zhu et al., 1983; Zhang et al., 2013). In evolving magmatic porphyry systems,

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hydrothermal fluids exsolve from crystallizing intermediate-felsic melts due to first and/or second boiling, and these processes determine the styles of mineralization and hydrothermal alteration of the deposits (Burnham, 1979; Cline and Bodnar, 1991; Cline, 1995; Halter and Webster, 2004; Weis et al., 2012; Wilkinson, 2013; Hurtig and Williams-Jones, 2015; Spencer et al., 2015). Previous studies show that halogens in silicate melt can strongly influence the evolution of magmatic and magmatic–hydrothermal systems (Ulrich et al., 1999; Aiuppa et al., 2009; Bao et al., 2014; Kodêra et al., 2014). The characteristics of the Dexing deposit hydrothermal fluids have been studied and determined to be Cl rich based on fluid inclusions (Pan et al., 2009, 2012), but more information is required to understand how the Cl-bearing magmatic fluids exsolved and how they affected the compositions of the hydrous minerals.

Magmatic biotite, a common gangue mineral in porphyry systems, readily exchanges OH, F and Cl in the hydroxyl site with coexisting melts and hydrothermal fluids (Munoz, 1984; Selby and Nesbitt, 2000). Prior research on porphyry deposits has used biotite chemistry to trace the composition and evolution of magmatic–hydrothermal fluids (Beane, 1974; Jacobs and Parry, 1979; Munoz, 1984; Selby and Nesbitt, 2000; Ayati et al., 2008; Boomeri et al., 2009, 2010; Afshooni et al., 2013; Einali et al., 2014; Parsapoor et al., 2015), and we have expanded this approach to include data from coexisting amphiboles, apatites and rehomogenized glassy silicate melt inclusions. Following on the thermodynamic development of the partitioning of F–Cl–OH between biotite and hydrothermal fluids (Zhu and Sverjensky, 1991, 1992), Munoz (1992) formulated relevant relations to determine halogen fugacity ratios of the melt or aqueous fluid coexisting with biotite based on biotite compositions. Based in part on the identification of magmatic fluid inclusions by Pan et al. (2009), the calculation of fugacity ratios and applying those to magmatic and hydrothermal fluids is appropriate. Using the halogen compositions of biotites, we calculate the $\log(fH_2O/fHF)$, $\log(fHF/fHCl)$ and $\log(fH_2O/fHCl)$ ratios of the potassic fluids from Tongchang porphyry. These fluids contained abundant copper as shown by the existence of chalcopyrite-bearing fluid inclusions in potassium feldspar-quartz veins (Pan et al., 2009). We also compare these results to other porphyry deposits to distinguish and interpret the unique halogen characteristics of the hydrothermal fluids of the Tongchang mine, Dexing porphyry Cu–Mo–Au deposit.

Previous research on the Dexing porphyry Cu–Mo–Au deposit concentrated on the petrogenesis, petrography, and geochemistry of its three constituent plutons (He et al., 1999; Wang et al., 2006; Liu et al., 2012; Hou et al., 2013; Zhou et al., 2012, 2013; Zhang et al., 2013; Wang et al., 2015). To date, the role of magmatic volatiles in the ore-forming processes of this system has not been studied comprehensively. Audétat and Pettke (2003) and Audétat et al. (2008) proposed, generally, that whether or not intermediate- to high-silica plutons are mineralized depends primarily on the salinity of the exsolved fluids which contribute significantly to the efficiency of metal extraction from the coexisting silicate melt. High-salinity hydrothermal fluids with high contents of complexing ligands (chlorine) are more efficient at extracting the metals residing in the silicate melt than low-salinity fluids (Candela and Piccoli, 1995; Aiuppa et al., 2009; Zajacz et al., 2011; Bao et al., 2014). For most porphyry systems, high-salinity fluids are thought to form through the immiscible condensation of brine from a low-salinity Cl-bearing vapor that had exsolved directly from the silicate melt (Burnham, 1979; Hedenquist and Lowenstern, 1994; Bodnar et al., 2014). However, other studies show that such high-salinity aqueous fluids can also exsolve directly from the silicate melt (Cline and Bodnar, 1994; Webster, 2004). In this study, we will evaluate the likelihood and the consequences of the direct exsolution of high-Cl hydrosaline liquids (with or without low-salinity vapor) from the Tongchang granodioritic magmatic system.

2. Geological setting and deposit geology

The Dexing porphyry copper deposit is located in the South China craton which is composed of the Yangtze and Cathaysia blocks (Fig. 1; Zhu et al., 1983). Li and McCulloch (1996) proposed that the South China craton was formed by a collision between Yangtze and Cathaysia at ca. 970 Ma. These two blocks are separated by the Jiangshan–Shaoxing (Jiang–Shao) fault system (Fig. 1), a major Neoproterozoic suture in southern China. The reactivation of the Jiang-Shao suture, during the Mesozoic, formed the NE-trending Gan–Hang rift system (Gilder et al., 1991).

There has been abundant magmatism in the South China craton, primarily during three magmatic pulses: 183–168, 160–140 and 140–90 Ma (Fig. 1; Hou et al., 2013). The older magmatic rocks (183–168 Ma) are dominantly alkalic and tholeiitic basalts. Bimodal volcanic rocks, and A-type granites and syenites also formed during this period. In contrast, the intermediate aged magmatism is expressed as granitoid rocks (160–140 Ma) and is closely associated with W–Mo (Mao et al., 2004), Sn–W and Nb–Ta (Wang et al., 2003; Zhang et al., 2004; Hua, 2006) mineralization. As shown in Fig. 1, the most widespread magmatic activity occurred during the period from 140 to 90 Ma. A belt of volcanic–intrusive complexes formed along the coast and 260 granitic intrusions were emplaced making up the Lower–Middle Yangtze River metallogenic belt.

The Dexing copper ore deposit consists of three porphyritic plutons: Tongchang (middle), Fujiawu (southeast) and Zhushahong (northwest), which host three separate mines (Fig. 2). The Neoproterozoic Shuangqiaoshan group country rocks (metamorphic volcanic and sedimentary rocks and epizonal metamorphic rocks) were intruded by these three ore-forming granodiorite porphyries. The wall rocks are characterized by extensive hydrothermal alteration. The main alteration types are potassic, phyllic, argillic and propylitic, which is similar to the typical alteration types of porphyry deposits summarized by Sillitoe (2010). Five samples of sole, ore-forming porphyritic granodiorite pluton that hosts the Tongchang mine of the Dexing porphyry deposit were evaluated as part of this study (Fig. 2). We consider the samples to be representative of the bulk of this pluton because the sample locations span most of the porphyritic granodiorite pluton core.

3. Experimental and analytical methods

3.1. Sample preparation

Doubly-polished thick sections were prepared commercially and grain mounts were made with the objective of identifying amphibole, potassium feldspar and plagioclase phenocrysts and different generations of biotites, apatites and melt inclusions (MI) enclosed in the biotite, plagioclase and quartz phenocrysts. The epoxy-based, biotite and plagioclase grain mounts were polished to a depth in the phenocrysts that allowed access to the interiors of the host minerals and to apatite inclusions at the polished surfaces.

The crystallized MI required rehomogenization prior to investigation. We were concerned that, during rehomogenization of crystallized MI in the separated quartz phenocrysts, some of the groundmass materials attached to the phenocrysts might melt which would degrade the optical transparency of the quartz crystals. So, the quartz phenocrysts were soaked in cold dilute hydrofluoric acid for 22 h to dissolve the attached materials. Afterward, the quartz grains were rinsed, dried and then loaded into an open palladium–silver capsule and heated at temperatures of 790–910 °C and 100 MPa for 5–8 h during multiple runs in an internally heated pressure vessel (IHPV) at the American Museum of Natural History (AMNH), New York. If the MI in the heated grains were not fully homogenized at a given temperature, a new batch of quartz phenocrysts was heated at 100 MPa and at 30 °C higher temperature. Once the appropriate range in homogenization temperatures was determined, all additional quartz phenocrysts were heated to these temperatures directly in the IHPV and held for 8 h. After the heating process, the quartz phenocrysts were mounted, ground and polished to search for glassy MI. Multiple steps of polishing and searching were