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Silicate melt inclusions in the Qiushuwan granitoids, northern Qinling belt, China: Implications for the formation of a porphyry Cu–Mo deposit as a reduced magmatic system

Lili Wang *, Dehui Zhang, Lu Tian

School of Earth Sciences and Resources, China University of Geosciences (Beijing), Beijing 100083, China

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ABSTRACT

Melt inclusions (MIs) in quartz from granitoids in the northern Qinling belt were studied using microthermometry and laser Raman spectroscopy. The total homogenization of melt inclusions occurs in a mean range between 1050 and 1100 °C. Laser Raman experiments reveal H_2O, C_2H_6, C_4H_6 and CH_4 as the dominant volatile compounds. Our results provide insights into the temperatures of magma crystallization and the dominantly reducing environment during the early magmatic stage. Based on ore mineralogy, and on the volatile species content in the MIs, we evidence firstly that the Qiushuwan porphyry Cu–Mo deposit in the Qinling–Dabie–Sulu orogenic belt was derived from a reduced magmatic system, emplaced at relatively deep domains more than 10 km deep, and secondly, that the magmas that are responsible for the generation of Qiushuwan were either derived from an inherently reduced source, or reduced during ascent and emplacement. The mechanism might have involved the assimilation of sedimentary material with minimal crustal interaction. The parental magmas likely underwent reduction essentially by loss of all of their SO_2 by degassing, as evidenced by the low S content in melt inclusions. These reduced materials provided adequate sulfur source for the formation of the porphyry Cu–Mo deposits with obvious zonation, which plays a key role in the mineralization; finally, we conclude that the reduced environment and the relatively deep domain of magma emplacement probably limited the extent of mineralization, generating only a relatively small Cu–Mo deposit in Qiushuwan, located within the northern Qinling accretionary belt.

1. Introduction

Many of the important Cu, Mo, and Au deposits around the world are associated with porphyry systems (Patrick and Marco, 2010; Richards, 2003). Recent studies (e.g., Smith et al., 2012; Sun et al., 2013) show that porphyry deposits are formed in either oxidized or reduced environments, as can be seen on the basis of the mineralogy of the host pluton, ores and associated alteration assemblages, and the nature of hydrothermal alteration. The classic model of Burnham and Ohmoto (1980) for ore mineralization involves fluids that are relatively oxidized, with higher temperature and higher f_{O_2} value varying between the hematite–magnetite (HM) and nickel–nickel oxide (NNO) oxygen buffers, and also hosts a large number of primary magnetite, hematite, and sulfates associated with oxidized Type-I granitoids (Smith et al., 2012; Sun et al., 2013). Experiments (e.g., Candela and Bouton, 1990) also showed that the high oxygen fugacity of magmas can improve the differentiation index of Mo residual fluid (Mo in fluid over Mo in silicate melt). Similar phenomena have been observed for porphyry

* Corresponding author.
E-mail address: lilywang.gsf@cugb.edu.cn (L. Wang).

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copper deposits in eastern Tibet (Liang et al., 2006), and it has been widely accepted fact that porphyry Cu–Mo–Au deposits are usually related to fluids derived from highly oxidized magmas (e.g., Han et al., 2013; Li et al., 2012, 2014). Therefore, many workers (e.g., Han et al., 2013; Li et al., 2012) consider that the progressive increase in zircon Ce/Ce* or oxygen fugacity of the magmas resulted in the progressive extraction of Mo, leading to the accumulation of this metal in porphyry and eventually forming giant Mo deposits. In marked contrast to the models on highly oxidized fluid systems, several other typical porphyry Cu–Mo–Au deposits show evidence of having formed from relatively reduced ore fluids with lower f_{O_2} less than or equal to the QFM buffer (quartz–fayalite–magnetite), and lack of primary hematite and sulfate minerals, but with abundant reduced mineral assemblages, such as chalcopyrite, molybdenite, pyrite, sphalerite, galena, and hypogene pyrrhotite (e.g., Gao et al., 2014; Rowins, 2000; Smith et al., 2012); in addition to H_2O, the ore fluids in these deposits contain significant amounts of CO_2 and CH_4.

The East Qinling–Dabie orogenic belt hosts the largest Mo ore deposits in the world, with measured reserves of 802.4 Mt of Mo metal (Mao et al., 2011). The majority of the Mo deposits in this orogenic belt are associated with granite porphyries (Chen et al., 2014; Mao et al., 2008, 2011; Zhu et al., 2010). However, the redox states of these granitoids and their significance to metallogenesis have not been fully investigated. The redox states of melts and fluids could influence the behavior of the metallogenic components, such as Mo, Cu and Au, etc., during magma evolution (Candela, 1997). Silicate melt inclusions (MIs) are small (~1 to 300 μm) droplets of silicate melt that are trapped within phenocryst minerals in magmatic rocks. They are glassy or crystalline, and are found within both extrusive and intrusive rocks. Since many MIs form at high pressures and are enclosed within relatively robust phenocryst hosts, they may also preserve the traces of volatile elements that normally escape from magmas during degassing, even though the bulk magma decompresses to surface pressure during eruption. The careful analysis of quenched MIs can provide important information on the history of magma evolution and the role of volatile compounds (Anderson et al., 2000; Chesner and Luhr, 2010; Lowenstern, 1995). Quartz is one of the best minerals for inclusion studies because of its transparent and simple composition, which allows minimal chemical exchange with the included melt (Chesner and Luhr, 2010). In this study, we investigate melt inclusions in quartz from ore-bearing granitoids in the northern Qinling belt using microthermometry and laser Raman spectroscopy. Our results provide insights into the temperatures of magma crystallization and the role of volatiles.

2. Regional geology

The Qinling–Tongbai–Hong'an–Dabie–Sulu orogenic belt was developed through the Paleozoic convergence between the South China and North China cratons involving a series of tectonic processes including subduction–accretion–collision (Wu and Zheng, 2013, and references therein). Arc–continent collision and continent–continent collision dominated during the Early Mesozoic in the Dabie–Sulu orogens. The Qinling Orogen is considered to have evolved from the closure of the northernmost Paleo-Tethys Ocean and finally through the Mesozoic collision between the North China Craton and the blocks separated from Gondwana, such as the Yangtze Craton (Fig. 1A and B; Chen et al., 2009; Deng et al., 2013; Dong et al., 2011; Li et al., 2012; Wang and Shu, 2012; Wu and Zheng, 2013; Zhang et al., 2012). The Qinling Orogen is divided into four major tectonic units as follows: the Huaxiong block, which is the reactivated southern margin of the North China Craton; the northern Qinling accretionary belt; the southern Qinling orogenic belt; the foreland fold-thrust belt (e.g., the Songpan fold-thrust belt) along the northern margin of the Yangtze Craton. These four tectonic units are separated by the San-Bao, Luanchuan, Shang-Dan, Mian-Lue, and Longmenshan faults (Fig. 1B). In a recent synthesis, Deng et al. (2013) identified that among the 25 Mo deposits in the Eastern Qinling Molybdenum Belt (EQMB), 22 occur in the Huaxiong Block, with the remaining three small deposits being located within the northern Qinling accretionary belt (Fig. 1C).

The northern Qinling accretionary belt is bound to the south by the Shang-Dan fault, and to the north by the Luanchuan fault, which is considered as the southern boundary fault of the North China Craton (Chen et al., 2004). The main lithostratigraphic units of the northern Qinling belt include the Qinling Group, the Erlangping Group, and the Kuanping Group from south to north (Deng et al., 2013; Zhang et al., 2011). The Qinling Group, distributed between Zhu-Xia fault and Shang-Dan fault, is composed of gneisses, amphibolites, and marbles, and was mostly metamorphosed to amphibolite facies, and partly to granulite facies with ages ranging from the Neoproterozoic to the Early Paleozoic (Deng et al., 2013; Zhang et al., 2011). The protoliths of these rocks are commonly interpreted as being dominated by volcanic and sedimentary rocks formed in a Neoproterozoic–Ordovician volcanic arc (Hu et al., 1988; Zhang et al., 2001, 2009). The Erlangping Group, located to the north of Qinling Group and to the south of Kuanping Group, and separated by faults, is composed of an ophiolite unit, of metamorphosed clastic sedimentary rocks and carbonates, where the ophiolite unit includes ultramafic rocks, mafic lavas, and a small amount of radiolarian cherts (Dong et al., 2010; Zhang et al., 2011). The Kuanping Group to the north of the Erlangping Group is composed of highly deformed greenschist facies rocks, the protoliths of which comprise mainly basic volcanic rocks, clastic rocks and carbonates with Meso-Neoproterozoic ages (Zhang et al., 2001). All these three tectono-stratigraphic units in the northern Qinling area were accreted to the North China Craton before Devonian, and intruded by Late Paleozoic to Mesozoic granitoids (Chen et al., 2004; Hu et al., 1988).

3. Deposit geology

The Qiushuwan Cu–Mo porphyry–skarn deposit was the first Mo deposit to be discovered in the northern Qinling accretionary belt in the 1980s, and the deposit was formed in the Late Jurassic (ca. 148 Ma), associated with the Yanshanian orogeny, as estimated from Re–Os dating