Oxygen-fugacity evolution of magmatic Ni-Cu sulfide deposits in East Kunlun: Insights from Cr-spinel composition

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Abstract

In this study, we use Cr-spinel as an efficient indicator to evaluate the oxygen fugacity evolution of the Xiarihamu Ni-Cu deposit and the Shitoukengde non-mineralized intrusion. Oxygen fugacity is calculated using an olivine-spinel oxybarometer, with spinel Fe3+/ΣFe ratios determined by a secondary standard calibration method using an electron microprobe. Cr-spinel Fe3+/ΣFe ratios of the Xiarihamu Ni-Cu deposit vary from 0.32 ± 0.09 to 0.12 ± 0.01, corresponding to magma fO2 values ranging from ΔQFM+2.2 ± 1.0 to ΔQFM-0.6 ± 0.2. By contrast, those of the Shitoukengde mafic-ultramafic intrusion increase from 0.07 ± 0.02 to 0.23 ± 0.04, corresponding to magma fO2 varying from ΔQFM-1.3 ± 0.3 to ΔQFM+1.0 ± 0.5. A positive correlation between fO2 and Cr-spinel Fe3+/ΣFe ratios suggests that the Cr-spinel Fe3+/ΣFe ratios can be used as an indicator for magma fO2. The high fO2 (QFM+2.2) of the harzburgite in the Xiarihamu Ni-Cu deposit suggests that the most primitive magma was characterized by relatively oxidized conditions, and then became reduced during magmatic evolution, causing sulfur saturation and sulfide segregation to form the Xiarihamu Ni-Cu deposit. The evolution trend of the magma fO2 can be reasonably explained by metasomatism in mantle source by subduction-related fluid and addition of external reduced sulfur from country gneisses (1.08–1.14 wt% S) during crustal processes. Conversely, the primitive magma of the Shitoukengde intrusion was reduced and gradually became oxidized (from QFM-1.3 to QFM+1.0) during crystallization. Fractional crystallization of large amounts of Cr-spinel can reasonably explain the increasing magma fO2 during magmatic evolution, which would hamper sulfide precipitation in the Shitoukengde intrusion. We propose that the temporal evolution of oxygen fugacity of the mantle-derived magma can be used as one of the indicators for evaluating metallogenic potential of Ni-Cu sulfide deposits and the reduction processes from mantle source to shallow crust play an important role in the genesis of magmatic Ni-Cu sulfide deposits.

Keywords: Oxygen fugacity, Cr-spinel, ultramafic rocks, Ni-Cu sulfide deposit, East Kunlun

Introduction

Sulfur (S), occurring as either sulfide (S2−), sulfate (SO42−) in silicate melts, or sulfite (S4+2−) in volcanic gases, is a complex but key element in magmatic systems (e.g., Carroll and Rutherford 1988; Symonds et al. 1994; Jugo et al. 2010). The behavior of chalcophile and siderophile elements (e.g., Ni, Cu, Au, Pt, and Pd) in magma is dictated by S as sulfide, and sulfide saturation exerts a primary control on the genesis of metaliferous deposits, especially for Ni-Cu-platinum group element (PGE) deposits (Imai et al. 1993; Sillitoe 1997; Clemente et al. 2004; Mungall et al. 2005; Li and Ripley 2009; Taranovic et al. 2016). Jugo (2009) declared that sulfur speciation is strongly controlled by the oxidation state of magma, often expressed in terms of oxygen fugacity (fO2). Transition from sulfide to sulfate in silicate melts occurs over a narrow fO2 interval, and sulfide and sulfate in magma correspond to low (<QFM) and high oxygen fugacity (>QFM+2) conditions, respectively, where QFM is the quartz-fayalite-magnetite buffer (e.g., Carroll and Rutherford 1987; Mavrogenes and O’Neill 1999; Matjuschkin et al. 2016; Jugo 2009; Sun 2020). The sulfur solubility under the latter condition is an order of magnitude higher than that under the former one (Jugo 2009; Jugo et al. 2010). Therefore, sulfur saturation leading to sulfide segregation is more likely to occur in reduced magma than in oxidized magma (Liu et al. 2007; Jugo 2009; Naldrett 2011; Brennan and Caciagli 2000; Tomkins et al. 2012). However, several Ni-Cu deposits appear to have formed in a relatively oxidized environment (>QFM), such as the Heishan and Mirabela deposits (Xie et al. 2014; Barnes et al. 2013). In addition, from partial melting in the mantle to emplacement in the shallow crust, the redox state of the parental magma would have undergone significant changes. In this regard, the fO2 at a certain stage of magmatic evolution cannot be used as an index of Ni-Cu mineralization (Mungall et al. 2006; Thakurta et al. 2008; Tomkins et al. 2012). Therefore, identifying the temporal changes in magma fO2 is crucial for understanding the Ni-Cu mineralization mechanism.

Spinel often crystallizes throughout magmatic evolution and is relatively refractory and resistant to alteration compared to other minerals (e.g., olivine and pyroxene) (Barnes and Roeder 2001; Kamenetsky et al. 2001). Spinel oxybarometry, based on phase equilibrium between olivine, orthopyroxene, and spinel, provides one window into the oxygen fugacity of the upper mantle and related mantle-derived magma (Bryndzia and Wood 1990; Ballhaus et al. 1991). Obtaining accurate spinel Fe3+/ΣFe ratios is especially important as minor changes in the activity of