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Constrains from magmatic and hydrothermal epidotes on crystallization of granitic magma and sulfide mineralization in Paleoproterozoic Malanjkhand Granitoid, Central India



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ABSTRACT

The Paleoproterozoic Malanjkhand Granitoid (MG) pluton in the Central India was studied to constrain the depth of emplacement, upward magma transport rate, and quantification of physicochemical condition of sulfide deposition. In this study, the magmatic and hydrothermal epidotes are of two varieties, reported from a mineralized granitoid. In the MG, composition of magmatic epidotes (pistachite – Ps: 21.6–31.1 mole%) and hydrothermal epidotes (Ps: 22.6–31.1 mole%) are overlapping in terms of mole percent of pistachite component. It does not provide any significant discrimination between the two varieties. Presence of oscillatory zoning in magmatic epidotes indicates that there was cyclic change in the oxygen fugacity or bulk composition of granitic magma during crystallization.

Al-in-hornblende barometry indicates that the MG crystallized under 2–5.6 kbar pressure and high oxidation state (FMQ-HM) conditions, inferred from Fe/(Fe+Mg) ratio in hornblende (0.36–0.51) over wide range of temperature (800–650 $^{\circ}$ C). Partial dissolution of epidote indicates an average 6 years time that corresponds to upward transport rates 0.45 km/year for magma migration in the crust. Rapid upward magma migration in most cases was probably through dyke mechanism, which is also the most appropriate model to understand the emplacement of granitic magma responsible for the formation of Malanjkhand pluton.

In the Malanjkhand ore deposit, hydrothermal epidotes associated with major sulfide phases (chalcopyrite and pyrite) suggest that they equilibrated with the mineralizing ore fluid. Hydrothermal epidotes were formed over a wide range of temperature (147–424 °C). From mineral–fluid equilibria modeling it was inferred that low to moderate temperature, moderate to high $f_{\rm O_2}$ (>HM buffer) and low $f_{\rm S_2}$ conditions were favorable for formation of hydrothermal epidotes. Interaction between hydrothermal epidote with mineralizing ore fluid in the wall rock would raise the $\log(a_{\rm Ca^{2+}}/a_{\rm H^+}^2)$ ratio that brings a fall in pH values, followed by potassic alteration, which promotes the deposition of sulfide ores at Malanjkhand. Sulfide mineralization in the MG represents a unique Paleoproterozoic granite ore system.

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1. Introduction

Epidote is a hydrous rock forming silicate mineral reported from various plutonic rocks such as tonalite, dacite, diorite (Schmidt and Poli, 2004), granite-granodiorite (Sial et al., 2008), gabbro (Korinevskii, 2008), volcanic rocks, calcareous sediments, and geothermal environments (Bird and Spieler, 2004). It is also reported as metamorphic mineral and extending its stability from

lower greenschist to amphibolite, blueschist, and eclogite facies rocks (Poli and Schmidt, 2004). Chemical composition of the epidotes depends on various factors such as bulk composition, temperature, pressure, pH, fugacities of CO₂, S₂, and O₂ (Arnason et al., 1993; Schmidt and Poli, 2004; Bird and Spieler, 2004). It occurs in granitic rocks as single holocrystalline grain, euhedral crystal, where the cenotypal appearance indicates magmatic origin (Schmidt and Poli, 2004; Korinevskii, 2008). Magmatic epidotes are formed at a pressure of about 10 kbar and sometimes are stable above 3 kbar pressures at relatively low-temperature (Schmidt and Thompson, 1996). It crystallizes before biotite within a narrow range of temperature in granitic magma (Schmidt and Poli,

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2004). Presence of magmatic epidote in granitic rock indicates that the hydrous magma is crystallized at high oxidation state in greater depth or at high pressure (Dawes and Evans, 1991), and is emplaced in the upper crust due to rapid transportation (Brandon et al., 1996). Epidotes occur in veins and cavities along with secondary mineral phases such as altered biotite, chlorite, pyrite, chalcopyrite, magnetite, and hematite indicating its hydrothermal origin (Bird et al., 1988; Bird and Spieler, 2004). A physicochemical environment with low to moderate temperature and high oxidation state is more favorable for the formation of hydrothermal epidotes. It is very sensitive to redox conditions and aqueous speciation in hydrothermal fluid. The composition of hydrothermal epidotes is influenced by a wide range of octahedral substitution Al³+–Fe³+ in low-pressure hydrothermal systems in order to become stable (Bird and Spieler, 2004).

Formation of granitic plutons through incremental addition of multiple pulses of magma from contrasting sources partially preserves the primary heterogeneities (Bea, 2010; Clemens et al., 2010; Brown, 2013). Heterogeneities in granitic magma from largescale (exposed outcrop) to micro-scale (individual mineral grains) promote investigations to constraint the petrogenesis and crystallization evolution of mineral grains (Gagnevin et al., 2008). Slow cooling rate during crystallization of granitic magma promotes continuous exsolution of H₂O and growth of equant mineral grains (Nabelek et al., 2010). The crystallization sequence of minerals in granitic magma is strongly dependent upon the upward transport rate (Brandon et al., 1996; Petford et al., 2000) and emplacement mechanism during pluton formation (Whitney, 1988; Hutton et al., 1990). The timescale of magma crystallization and ore deposition (Shinohara et al., 1995; Lowenstern et al., 2000), multiple events of the magmatic-hydrothermal fluid-rock interaction in the formation of significant large ore deposits (Ballard et al., 2001), may be shorter compared to the total time span of pluton formation (Halter et al., 2004). Granite related ore systems represent one of the most complex processes of magma crystallization and multiple episodes of hydrothermal activities. It can be also influenced by various physicochemical factors such as magma composition, oxidation state, crystallization history, ascent rate, exsolution of volatile phases, depth of emplacement, and so on (Candela, 1997). The post-magmatic multiple episodes of hydrothermal activities may easily overprint the texture and chemistry of the existing magmatic and hydrothermal mineral assemblages (Schaltegger et al., 2005). Post-emplacement tectonic stresses develop extensive fault and fracture network in granitic plutons, and allow circulation of hydrothermal fluid (Marques et al., 2010). Infiltration of hydrothermal fluid along the fracture network and micro-cracks favors dissolution-precipitation processes and the subsequent formation of hydrothermal or secondary minerals (Nishimoto and Yoshida, 2010). Typical hydrothermal epidote-group minerals also occur in granitic rocks (Bird and Spieler, 2004; Vlach, 2012). Therefore, it is difficult to understand the crystallization sequences of epidotes in granitic rocks, and they need a systematic study. Investigation of the sequence of magma crystallization reactions and proper identification of hydrothermal mineral assemblages in granitic rocks could reveal the physicochemical conditions of pluton formation. Epidote is well recognized as one of the common silicate minerals present in the granitic rocks, formed during magmatic crystallization and hydrothermal alteration processes. Phase equilibria studies of magmatic and hydrothermal mineral assemblages would provide a better opportunity to constrain the history of granite evolution and related ore mineralization (Marks et al., 2003).

The present study deals with two varieties of epidotes (magmatic and hydrothermal types) found in a Paleoproterozoic mineralized granitoid, located in the Central India and their fundamental contributions to the granite related ore system. The objective is divided into three parts: (1) petrographic and mineral

chemical discrimination between magmatic and hydrothermal epidotes; (2) investigating the crystallization trends of magmatic epidotes, evaluating the depth of epidote formation and estimation of transport rate of granitic magma; and (3) constraining the physicochemical conditions of hydrothermal epidotes formation and sulfide deposition at the Malanjkhand. For this purpose, five samples from the mineralized zone (mine pit) and seven samples from outside the mineralized zone were selected from the MG. Primarily, we have attempted to constrain the *P-T* conditions for crystallization of magmatic epidotes during the granite emplacement and contextualize the significance of hydrothermal epidotes during sulfide mineralization in a granite related ore system.

2. Geological setting

The Bastar or Bhandara craton dominantly occupies the Central India, bordered by the Pranhita-Godavari Rift in the South, the Mahanadi Rift in the northeast, the Satpura Mobile Belt in the North, the Eastern Ghats Mobile Belt in the East, and Deccan Traps cover in the West (Naqvi and Rogers, 1987). It consists of mainly Precambrian granites and basement granitic gneisses, supracrustal sequences, mafic dyke swarms and sedimentary basins (Meert et al., 2010). The Malanjkhand and Dongargarh granitoids are two prominent units of Precambrian/Paleoproterozoic granitoids (Pandit and Panigrahi, 2012). Supracrustal sequences are part of the Dongargarh supergroup (Nandgaon and Khairagarh group), Sakoli Group and Sausar Group (part of Central Indian Tectonic Zone, i.e. CITZ). Multiple episodes of Precambrian mafic magmatism formed dyke swarms, mafic volcanic rocks and mafic dykes (French et al., 2008; Srivastava and Gautam, 2009). There are two major sedimentary basins (Chhattisgarh and Indravati Basin) and other six minor basins in the Bastar Craton. The ENE-WSW striking CITZ divides the Precambrian Indian Peninsula into two parts, i.e. northern and southern crustal blocks (Radhakrishna and Naqvi, 1986; Acharyya, 2003; Naganjaneyulu and Santosh, 2010; Bhowmik et al., 2012; Mandal et al., 2013).

The MG situated along the southern boundary of CITZ (Fig. 1a), hosts one of the largest copper deposit in India (Sikka, 1989; Sarkar et al., 1996; Panigrahi and Mookherjee, 1997; Bhargava and Pal, 1999; Stein et al., 2004). It is comprised of coarse-grained hornblende-biotite bearing granite-granodiorite and emplaced as a single episode of early Paleoproterozoic (ca. 2.48 Ga) felsic magmatism in the Central India exposed over ~1400 km² area (Panigrahi et al., 2004, 2009). Two subordinate units of leucogranite are found with sporadic occurrences at Birsa (close to copper mines) and Devgaon (~12 km south of the mine pit) within the Malanjkhand batholith (Fig. 1b). They are considered as a separate phase of granitic activity, which provide a Rb-Sr whole rock isochron age ~2.11 Ga (Panigrahi et al., 1993), rendering uncertain their origin and emplacement. Amphibolitic enclaves in MG are one of the common features in which modal hornblende is >60%. This suggests mixing of mafic and felsic magma in various proportions within a dynamic magma chamber resulting in the formation of granitic magma and emplacement at shallow crustal level (Kumar et al., 2004; Kumar and Rino, 2006). However, Re-Os model ages (~2.49 to 2.44 Ga) of molybdenites obtained from the Malanjkhand deposit are interpreted as discrete deformation episodes and molybdenite formation (Stein et al., 2004, 2006) which overlap with the zircons ages (\sim 2.48 Ga) possibly due to the extent or episodic hydrothermal activities (Panigrahi et al., 2006, 2008, 2013). Further, microstructural studies as well as the anisotropy of magnetic susceptibility reveal that emplacement of MG and tectonic evolution of CITZ was synchronous during the Neoarchean/Paleoproterozoic era (Majumder and Mamtani, 2009a,b). Recently, Pandit and Panigrahi (2012) suggested that the origin of the Palaeoproterozoic granitoids

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