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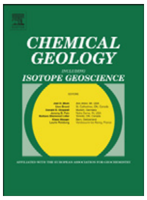

^{238}U–^{230}Th dating of chevkinite in high-silica rhyolites from La Primavera and Yellowstone calderas

Jorge A. Vazquez [a,*], Noel O. Velasco [b], Axel K. Schmitt [c], Heather A. Bleick [a], Mark E. Stelten [d]

[a] United States Geological Survey, 345 Middlefield Road, Mail Stop 910, Menlo Park, CA 94028, USA
[b] Department of Geological Sciences, California State University—Northridge, 18111 Nordhoff Street, Los Angeles, CA 91330, USA
[c] Department of Earth, Planetary, and Space Sciences, University of California—Los Angeles, 595 Charles Young Drive East, Los Angeles, CA 90095, USA
[d] Department of Geology, University of California—Davis, One Shields Avenue, Davis, CA 95616, USA

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ABSTRACT

Application of ^{238}U–^{230}Th disequilibrium dating of accessory minerals with contrasting stabilities and compositions can provide a unique perspective on magmatic evolution by placing the thermochemical evolution of magma within the framework of absolute time. Chevkinite, a Th-rich accessory mineral that occurs in peralkaline and metaluminous rhyolites, may be particularly useful as a chronometer of crystallization and differentiation because its composition may reflect the chemical changes of its host melt. Ion microprobe ^{238}U–^{230}Th dating of single chevkinite microphenocrysts from pre- and post-caldera La Primavera, Mexico, rhyolites yields model crystallization ages that are within 10's of k.y. of their corresponding K–Ar ages of ca. 125 ka to 85 ka, while chevkinite microphenocrysts from a post-caldera Yellowstone, USA, rhyolite yield a range of ages from ca. 110 ka to 250 ka, which is indistinguishable from the age distribution of coexisting zircon. Internal chevkinite–zircon isochrons from La Primavera yield Pleistocene ages with ~5% precision due to the nearly two order difference in Th/U between both minerals. Coupling chevkinite ^{238}U–^{230}Th ages and compositional analyses reveals a secular trend of Th/U and rare earth elements recorded in Yellowstone rhyolite, likely reflecting progressive compositional evolution of host magma. The relatively short timescale between chevkinite–zircon crystallization and eruption suggests that crystal-poor rhyolites at La Primavera were erupted shortly after differentiation and/or reheating. These results indicate that ^{238}U–^{230}Th dating of chevkinite via ion microprobe analysis may be used to date crystallization and chemical evolution of silicic magmas.

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1. Introduction

High-resolution ^{238}U–^{230}Th dating of accessory minerals with contrasting stabilities and compositions (e.g., allanite and zircon) can provide a unique perspective on magmatic evolution by placing the thermochemical changes of silicic magma within a framework of absolute time. Chevkinite-(Ce), a titanosilicate $[Ce_4(Ti, Fe^{2+}, Fe^{3+})_5O_8(Si_2O_7)_2]$ that typically has elevated Th concentrations and occurs in peralkaline and metaluminous rhyolites as microphenocrysts and inclusions in major phases, may be particularly useful as a chronometer of crystallization and differentiation in magma chambers because its composition may reflect the chemical changes of its host melt and it is amenable to ^{238}U–^{230}Th geochronology. Magma reservoirs associated with calderas that erupt the largest volumes of silicic magma assemble and evolve over timescales of 10^3 to 10^5 years (Costa, 2008; Gelman et al., 2013). Hence, the ^{238}U–^{230}Th system with its ability to date crystallization ages over 10^3–10^4 year intervals is optimized for resolving the crystallization history of magmas at young calderas (see reviews by Cooper and Reid, 2008; Schmitt, 2011). Pioneering studies using ^{238}U–^{230}Th disequilibrium to date crystallization of accessory minerals employed multi-grain analysis (e.g., Fukuoka and Kigoshi, 1974; Pyle et al., 1988) with unavoidable uncertainty about the age variation between and within single crystals. The advent of ion microprobe ^{238}U–^{230}Th geochronology greatly reduced this uncertainty by dating domains within single crystals, allowing unique insight into the timing of accessory mineral crystallization relative to eruption (e.g., Reid et al., 1997), intra-crystal age distribution (e.g., Storm et al., 2011), crystal growth rates (e.g., Schmitt et al., 2011) and the magnitudes of inheritance and antecrystic recycling (e.g., Bacon and Lowenstern, 2005).

This paper describes ion microprobe ^{238}U–^{230}Th dating of chevkinite from Pleistocene rhyolites erupted from La Primavera and Yellowstone calderas (Fig. 1), both of which have protracted volcanic histories that are delimited by K–Ar and ^{40}Ar/^{39}Ar geochronology. Chevkinite microphenocrysts from pre- and post-caldera lavas from La Primavera yield model ^{238}U–^{230}Th crystallization ages that are consistent with crystallization ages for coexisting zircon, and which match or are within 10's of k.y. of their corresponding K–Ar ages of ca. 125 ka and ca. 85 ka. When combined, associated chevkinite and zircon crystals yield isochron ages

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[*] Corresponding author. Tel.: +1 650 329 5240.
E-mail addresses: jvazquez@usgs.gov (J.A. Vazquez), axelk@argon.ess.ucla.edu (A.K. Schmitt), hbleick@usgs.gov (H.A. Bleick), mestelten@ucdavis.edu (M.E. Stelten).

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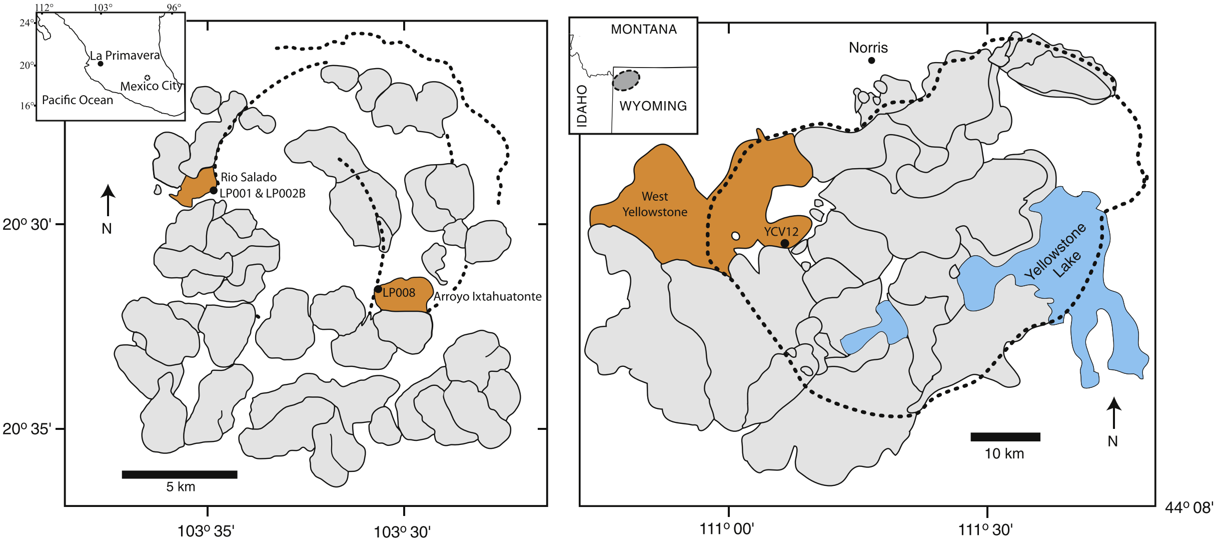

Fig. 1. Locations of La Primavera and Yellowstone calderas with individual post-caldera lava flows outlined as gray fields. Sampled rhyolite lavas are plotted in orange. Dashed lines are caldera faults. Maps after Mahood (1981) and Christiansen (2001).

with ~5% precision due to the nearly two order difference in Th/U between both minerals. Chevkinite microphenocrysts from the post-caldera West Yellowstone flow at Yellowstone caldera yield model ages that range up to approximately 200 k.y. before their $^{40}Ar/^{39}Ar$ eruption age of ca. 115 ka, and that match the range of crystallization ages recorded by coexisting zircon. When keyed to composition, the chevkinite ages reveal secular variation of crystal composition that is likely to reflect the compositional evolution of host magma. These results demonstrate that ion microprobe U–Th dating of single chevkinite crystals may resolve the time-compositional chronology for differentiation of rhyolitic magma.

1.1. Compositions and crystallization of chevkinite-(Ce) in silicic magmas

Chevkinite occurs as microphenocrysts or inclusions in major phases in a range of evolved silicic volcanic rocks including trachyte and comendite (e.g., Cameron and Cameron, 1986; Novak and Mahood, 1986; Michael, 1988; Scaillet and Macdonald, 2001; Macdonald et al., 2002; Heumann and Davies, 2002; Troll et al., 2003; Johnson et al., 1989) as well as evolved "A-type" rhyolites (e.g. Young and Powers, 1960; Izett and Wilcox, 1968; Johnson et al., 1989; Mills et al., 1997; Macdonald and Belkin, 2002; Min et al., 2006; Cubukcu et al., 2007). Plutonic equivalents such as syenites and granitoids from a variety of tectonic settings may also contain chevkinite (e.g., Lowenstern et al., 1997; Robinson and Miller, 1999; Verplanck et al., 1999; Schmitt et al., 2000; Ridolfi et al., 2003; Bacon et al., 2007; Vlach and Gualda, 2007).

Chevkinite in silicic volcanic rocks may contain several weight (wt.) % ThO_2 with Th/U ratios up to ~60 (Macdonald et al., 2002, 2009). Like allanite, the high concentration of Th and a large excess of ^{230}Th relative to ^{238}U during crystallization make young chevkinite ideal for ^{238}U–^{230}Th disequilibrium dating. In chevkinite, quadrivalent Th and U are accommodated in the A-site site according to the general formula:

$$A_4BC_2D_2Si_4O_{22}$$

where A = rare earth element (REE), Ca, Th, U; B = Fe^{2+}; C = Ti, Al, Zr, Nb, Mg, Mn, Fe^{3+}, Fe^{2+} and D = Ti (Macdonald and Belkin, 2002), with the most abundant REE being La, Ce, Pr, Nd, and Sm. In chevkinite, charge balancing for REE incorporation follows:

$$\left(Ca^{2+}\right)_A + \left(Ti^{4+}\right)_C = \left[(REE,\ Y)^{3+}\right]_A + \left(M^{2+,3+}\right)_C$$

(McDowell, 1979; Green and Pearson, 1988) and:

$$\left(Ca^{2+}\right)_A + \left(Ti^{4+}\right)_C + \left(Zr^{4+}\right)_C = \left[(REE,\ Y)^{3+}\right]_A + \left(M^{2+,3+}\right)_C$$

(Vlach and Gualda, 2007) where REE = rare earth elements, A = A site, C = C site, and M_C = Fe, Al, Mg, Zr, Nb, P, and K (McDowell, 1979; Macdonald and Belkin, 2002). Concentrations of light rare earth elements (LREEs) typically range between 9–25 wt.% $(Ce, La)_2O_3$ (Macdonald et al., 2002, 2009), giving chevkinite some of the highest observed crystal/melt partition coefficients for LREE (Macdonald et al., 2002; Troll et al., 2003). Heavy rare earth element concentrations in chevkinite are typically 1–3 orders of magnitude lower than LREE (Macdonald et al, 2002). Hence, crystallization and fractionation of chevkinite may be apparent from LREE concentration trends in suites of silicic magmas related by fractional crystallization even if crystals are a small minority of the crystal mode (e.g., Cameron and Cameron, 1986; Parker and White, 2007). Variation in the composition of igneous chevkinite may reflect magmatic evolution, with distinctions between phenocryst and groundmass crystals of plutonic rocks (McDowell, 1979) and in some cases within single crystals (Macdonald and Belkin, 2002; Vlach and Gualda, 2007).

The solubility of chevkinite in peralkaline and metaluminous silicic magma is not yet established by a comprehensive set of experiments. The importance of temperature, magma composition, oxygen fugacity, and concentrations of essential structural constituents, in this case LREE and Ti concentrations, in host melt are underscored by phase-equilibrium experiments on peralkaline rhyolites from East Africa (Scaillet and Macdonald, 2003) and REE-doped silicic compositions (Green and Pearson, 1988), as well as theoretical considerations (Bacon, 1989) and observed suites of rocks (e.g., Vlach and Gualda, 2007). Crystallization of chevkinite in metaluminous magma appears to occur at a more restricted temperature range than for crystallization in peralkaline magmas. Chevkinite-bearing metaluminous rhyolites typically yield crystallization temperatures that are >760 °C (e.g., Izett and Wilcox, 1968; Vazquez et al., 2009). At lower temperatures, allanite is the stable LREE-rich phase (e.g., Hildreth et al., 1984). In contrast, peralkaline silicic magmas containing chevkinite yield Fe–Ti oxide and two-pyroxene temperatures between ~700 °C and ~1000 ° C (e.g., Novak and Mahood, 1986; Scaillet and Macdonald, 2003; Troll et al., 2003).