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

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A R T I C L E   I N F O

Article history:
Received 24 July 2014
Received in revised form 14 October 2014
Accepted 21 October 2014
Available online 29 October 2014

Editor: K. Mezger

Keywords:
Chevkinite
Uranium-series geochronology
Ion microprobe
Yellowstone
La Primavera
Rhyolite

A B S T R A C T

Application of 238U–230Th 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 238U–230Th 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 238U–230Th 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 238U–230Th dating of chevkinite via ion microprobe analysis may be used to date crystallization and chemical evolution of silicic magmas.

1. Introduction

High-resolution 238U–230Th 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 [Ce4(Ti, Fe2+, Fe3+)5O8(Si2O7)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 238U–230Th geochronology. Magma reservoirs associated with calderas that erupt the largest volumes of silicic magma assemble and evolve over timescales of 105 to 106 years (Costa, 2008; Gelman et al., 2013). Hence, the 238U–230Th system with its ability to date crystallization ages over 103–104 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 238U–230Th 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 238U–230Th 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 Lowenstein, 2005).

This paper describes ion microprobe 238U–230Th 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 40Ar/39Ar geochronology. Chevkinite microphenocrysts from pre- and post-caldera lavas from La Primavera yield model 238U–230Th 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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http://dx.doi.org/10.1016/j.chemgeo.2014.10.020
0009-2541/Published by Elsevier B.V.
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 $^{230}$Th/$^{234}$U 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 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., 2002). The solubility of chevkinite in peralkaline and metaluminous silicic 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 to $^{238}$U during crystallization make young chevkinite ideal for $^{230}$U–$^{238}$U disequilibrium dating. In chevkinite, quadrivalent Th and U are accommodated in the A-site according to the general formula:

$$A_4B_2C_2D_2Si_4O_{22}$$

where A = rare earth element (REE), Ca, Th, U; B = Fe$^{2+}$; C = Ti, Al, Zr, Nb, Mg, Mn, Fe$^{3+}$, 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:

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

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

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

(Vlach and Gualda, 2007) where REE = rare earth elements, A = A site, C = C site, and $M_4$ = 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.% ($\text{Ce}_2\text{O}_3$ (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 $>760 \, ^\circ\text{C}$ (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).
1.2. Chevkinite in La Primavera and Yellowstone rhyolites

Chevkinite-bearing rhyolites have erupted from La Primavera, Mexico, and Yellowstone, USA, calderas (Fig. 1). La Primavera is a Quaternary caldera located next to Guadalajara, Jalisco, Mexico, along the western segment of the Trans-Mexican volcanic arc (Fig. 1). Multiple eruptions of porphyritic to aphyric high-silica rhyolite between ca. 140 and 30 ka generated a series of rhyolitic domes and coulees that are exposed over an ~500 km² area (Mahood, 1980; Walker et al., 1981). This volcanism was punctuated by the explosive eruption of ~40 km³ of rhyolite at ca. 95 ka, generating La Primavera caldera and the compositionally zoned Tala Tuff ignimbrite (Mahood, 1981; Mahood and Drake, 1982). La Primavera rhyolites contain ≪1% modal chevkinite (Michael, 1988) that occurs as microphenocrysts in groundmass glass, typically associated with clusters of clinopyroxene, fayalite, zircon, and Fe–Ti oxides, and inclusions in major phases (Fig. 2).

Voluminous high-silica rhyolites characterize silicic volcanism associated with the Yellowstone hotspot. At Yellowstone caldera, multiple episodes of intracaldera volcanism have occurred since explosive eruption of the Lava Creek Tuff and caldera formation at ca. 640 ka (Christiansen, 2001; Lanphere et al., 2002). The youngest episode of caldera volcanism erupted more than 600 km³ of rhyolite, primarily as lava, between ca. 170 ka and ca. 75 ka (Christiansen et al., 2007). These rhyolites compose the Central Plateau Member (CPM) of the Plateau Rhyolite and cover much of the caldera floor (Christiansen and Blank, 1972; Christiansen, 2001). Age-correlated changes in the trace element and isotopic composition of CPM glasses and minerals, as well as geothermometry, suggest open-system evolution of a cooling magma reservoir that was periodically replenished with new rhyolite (Vazquez et al., 2009; Watts et al., 2012; Stelten et al., 2013).

In Yellowstone rhyolites, chevkinite occurs as microphenocrysts in groundmass glass and inclusions in clinopyroxene and fayalite, and like La Primavera chevkinite it is typically associated with clusters of mafic oxide and silicate phenocrysts (Fig. 2).

2. Samples and analytical methods

Using standard heavy liquid techniques, chevkinite and zircon were separated from two samples of ca. 125 ka precaldera Rio Salado dome and one hand sample of the ca. 85 ka postcaldera Arroyo Ixtahuatonte dome at La Primavera caldera (Fig. 1). Single chevkinite crystals were separated from the ca. 115 ka West Yellowstone flow at Yellowstone caldera. These West Yellowstone flow chevkinite crystals are from the same sample used by Vazquez and Reid (2002) for $^{238}$U–$^{230}$Th ion microprobe dating of zircon. Individual crystals of chevkinite and zircon were cast in epoxy and indium mounts for ion and electron microprobe analysis. The smallest (<100 μm) chevkinite and zircon crystals were embedded in indium metal in order to prevent the generation of $^{232}$Th$^{16}$O$^{12}$C$^{2+}$ when the primary ion beam partly overlaps onto epoxy surrounding a Th-bearing matrix and interferes with $^{230}$Th$^{16}$O$^{+}$ (Schmitt et al., 2006). The positive mass defect of $^{230}$Th and high mass resolution analysis ensures that any $^{115}$In$^{16}$O$^{+}$ derived from primary beam overlap of the surrounding indium is well resolved from $^{230}$Th$^{16}$O$^{+}$. Prior to analysis, mounts were washed in soapy water and finally rinsed with dilute HCl acid. The mounts were coated with a thin (~10 nm) layer of gold to create a conducting surface for ion microprobe analysis.

Ion microprobe analyses of chevkinite and zircon were performed with the Stanford-USGS SHRIMP-RG and UCLA CAMECA ims 1270 high-resolution ion microprobes. For SHRIMP-RG analyses, chevkinite was analyzed with a 12–18 nA $^{18}$O$^{-}$ primary beam with 10 kV acceleration.
focused to an ~40 μm diameter spot on sample surfaces. For CAMECA ims 1270 analyses, chevkinite and zircon were analyzed with a 20–80 nA 16O− primary beam with 12.5 kV acceleration and focused to an ~40 μm diameter spot. Samples were pre-sputtered for 10 to 60 s before the start of each analysis. Positive secondary ions were extracted and accelerated into the mass analyzers at 10 kV potential and measured at mass resolutions (m/Δm) at 10% peak height of ~4500 (ims 1270) and ~9000 (SHRIMP-RG). Peak hopping using a single electron multiplier was employed for all chevkinite analyses except for one session (ims 1270) during which measurements were performed by static multi-collection using a Faraday cup for 232Th16O+ and electron multipliers for other masses. Cross-calibration of collectors during multi-collection was performed using measured versus the natural 238U/235U ratios. Secondary ions of 230Th16O+, 232Th16O+, and 238U16O+ were used for age calculations instead of their corresponding metal species because oxide secondary ion yields for chevkinite are 8–10 times greater than for their corresponding metals. Centering of the 230Th16O+ peak was guided using a persistent 16Ndt16O+ guide peak and 230Th16O+ secondary ions. Precisions, and detection limits of the electron microprobe analyses are provided in Appendix A.

3. Results

The U–Th isotope composition of La Primavera and Yellowstone chevkinite and zircon and their host rocks are listed in Tables 1 and 2, and representative compositions from electron microprobe measurements are listed in Table 3. Complete results from electron microprobe analyses are tabulated in Appendix A. All analyzed crystals yield 232Th/238U ratios indicating decay-chain disequilibrium, with 230Th/238U activity ratios of ~3 to ~6 (300 to 600% excesses). Individual chevkinite crystals analyzed with both SHRIMP-RG and CAMECA ion microprobes yield results that agree at the 95% confidence interval, despite sampling somewhat different intra-crystal domains after re-polishing of sample mounts between the analytical sessions (Table 1). Host rocks for La Primavera rhyolite yield 230Th activity excesses of 10–12% relative to 238U. Model ages for chevkinite and zircon from 231U–230Th disequilibrium are calculated as described in Reid et al. (1997), and range from ca. 50 ka to ca. 145 ka for La Primavera rhyolite, and ca. 115 ka to ca. 290 ka for Yellowstone rhyolite. Dates from chevkinite–zircon isochrons (Fig. 4) are calculated from error-weighted least-squares regression according to Mahon (1996). Reported uncertainties for isochron and mean model ages are expanded to account for scatter as represented by MSWD (mean square of weighted deviates; Wendt and Carl, 1991) and number of data as described by Ludwig and Titterington (1994). La Primavera and Yellowstone chevkinite crystals contain ThO2 concentrations of ~0.5 to ~2.0 wt.% with Th/U between ~30 and ~50. Chevkinite from the pre- and post-caldera La Primavera rhyolites yield a restricted range of major and minor element compositions relative to those from the West Yellowstone flow.

4. Discussion

4.1. Crystalization ages from 230U–238Th dating of volcanic chevkinite

Dates derived from U–Th disequilibrium in chevkinite of typical microphenocryst size (~50 and < 300 μm radius) in volcanic rocks will reflect crystallization if diffusion of U and Th is slow at the temperatures and timescales associated with magma chamber evolution. To date, experimental limits on U and Th diffusion in chevkinite are not established. An order-of-magnitude estimate of diffusion rate may be derived from the empirical relation between diffusivity and the ionic porosity of a mineral (Fortier and Giletti, 1989; Dahl, 1997). Ionic porosity is the proportion of a mineral’s unit cell volume that is unoccupied by ions, with larger porosities being associated with higher rates of diffusion than for smaller porosities (Fortier and Giletti, 1989; Dahl, 1996, 1997). Following Dahl (1996) and Zhang (2008), an ionic porosity of 0.33 is calculated for chevkinite using observed compositions (Table 3), unit-cell data (Liziero, 2008), and effective ionic radii (Shannon, 1976). The relation between experimental diffusion parameters (Cherniak et al., 1997; Van Orman et al., 1998; Cherniak, 2005; Cherniak and Pyle, 2008) and
Table 1
U–Th isotope data and model ages for La Primavera and West Yellowstone chevkinite.

<table>
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<tr>
<th>Sample</th>
<th>Crystal #</th>
<th>(238U)/(232Th)</th>
<th>1 s.e.</th>
<th>(230Th)/(232Th)</th>
<th>1 s.e.</th>
<th>Model age (ka)</th>
<th>+1σ</th>
<th>−1σ</th>
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**Analysis name contains prefix of 1270 or RG to denote measurement using CAMECA ims 1270 or SHRIMP-RG ion microprobes, respectively. Italicized analyses are excluded from isochron regressions. Decay constants used for activity ratios: λ128 = 9.1765 × 10⁻⁹ year⁻¹ (Cheng et al., 2013); λ232 = 4.9475 × 10⁻¹⁰ year⁻¹; λ230 = 1.55125 × 10⁻¹⁰ year⁻¹ (Jaffey et al., 1971; Steiger and Jäger, 1977). Model ages calculated using chevkinite–white rock isochrons assuming secular equilibrium between ²³⁸U and ²³⁴U; see text for details.**

Ionic porosity for various minerals (Dahl, 1996) suggests that diffusion rates for Th and U in chevkinite are on the orders of 10⁻¹⁷ to 10⁻¹⁸ m²/s, respectively, at 850 °C. At these rates, a tabular chevkinite crystal with a 20 µm half-thickness would experience ≤0.6% fractional loss over the maximum timescale of 300 k.y. (Crank, 1975) that is resolvable by ion microprobe ²³⁵U–²³⁸Th dating (cf. Reid et al., 1997). Monazite and allanite share similar ionic porosities (0.31–0.33; Dahl, 1997) to chevkinite, and yield ²³⁸U–²³⁵U and ²³⁵Th–²³⁰Th ages that indicate retention of U and Th at the temperatures and timescales (10⁷–10⁸ yr) associated with silicic magmatism (e.g., Copeland et al., 1988; Oberli et al., 2004). Accordingly, chevkinite dates derived from ²³⁸U–²³⁴Th disequilibrium are likely to reflect crystallization rather than cooling. Dates derived from other elements that diffuse relatively quickly in chevkinite (e.g., He) yield cooling ages rather than crystallization ages (Min et al., 2006).
of precise internal isochrons (Fig. 4). This limited ability to generate internal isochrons also exists for volcanic allanite with its analogously high Th/U (e.g., Vazquez and Lidzbarski, 2012), and contrasts with the typical variable Th/U of volcanic zircon. Accordingly, the derivation of precise isochron ages using chevkinite will almost always require one or more coeval phases with lower Th/U. Model ages for crystallization of individual chevkinite may be derived, but require an assumption about initial Th-isotope composition during crystallization. In this study, initial Th-isotope composition is delimited by $^{238}U - ^{230}Th - ^{232}Th$ analyses of glassy whole rocks.

### 4.3. Timing of chevkinite crystallization in La Primavera and Yellowstone rhyolite

#### 4.3.1. La Primavera chevkinite and zircon

The combined analyses of chevkinite in both samples of the Rio Salado rhyolite yield an uncertainty-weighted mean model age $117 \pm 7$ ka ($n = 30/30, MSWD: 2.3, 95\%$ confidence). The limited number ($n = 5$) of Arroyo Ixtahuatonte chevkinite is insufficient to generate a precise age, but combining chevkinite with coexisting zircon and whole rock yields an isochron age of $86 \pm 15$ ka ($n = 13, MSWD = 4.2, 95\%$ confidence), or $93 \pm 7$ ka ($n = 11/13, MSWD = 1.5, 95\%$ confidence). The whole rock compositions lie on this regression (Fig. 4), suggesting that chevkinite and zircon co-crystallized over the same brief interval. These ages are indistinguishable from $121 \pm 13$ ka ($n = 5, MSWD = 5.3, 95\%$ confidence) if two young outliers are excluded (Fig. 4). These ages for Arroyo Ixtahuatonte yield an uncertainty-weighted mean model age $117 \pm 7$ ka ($n = 30/30, MSWD: 3.2, 95\%$ confidence), or $121 \pm 13$ ka ($n = 5, MSWD: 2.3, 95\%$ confidence) if several apparent outliers are omitted.

### Table 3

Representative compositions of chevkinite from La Primavera (LP), Yellowstone (WY) rhyolite, and Pakistani pegmatite (Arondu).

<table>
<thead>
<tr>
<th>Analysis</th>
<th>LP001B-2</th>
<th>LP008gr2-4</th>
<th>WY-CHV-1.1</th>
<th>WY-CHV-2.1 Arondu-Chip1-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>20.45</td>
<td>19.88</td>
<td>20.44</td>
<td>21.14</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>17.16</td>
<td>17.59</td>
<td>18.32</td>
<td>18.91</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.26</td>
<td>0.27</td>
<td>0.26</td>
<td>0.27</td>
</tr>
<tr>
<td>FeO</td>
<td>10.92</td>
<td>11.49</td>
<td>10.79</td>
<td>10.42</td>
</tr>
<tr>
<td>MnO</td>
<td>0.25</td>
<td>0.25</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>MgO</td>
<td>0.02</td>
<td>0.03</td>
<td>0.23</td>
<td>0.37</td>
</tr>
<tr>
<td>CaO</td>
<td>2.79</td>
<td>2.91</td>
<td>2.90</td>
<td>3.06</td>
</tr>
<tr>
<td>ThO$_2$</td>
<td>0.88</td>
<td>0.57</td>
<td>1.30</td>
<td>1.27</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>12.09</td>
<td>13.18</td>
<td>11.37</td>
<td>11.53</td>
</tr>
<tr>
<td>Ce$_2$O$_3$</td>
<td>21.90</td>
<td>22.76</td>
<td>21.17</td>
<td>21.26</td>
</tr>
<tr>
<td>Pr$_2$O$_3$</td>
<td>1.84</td>
<td>1.68</td>
<td>2.16</td>
<td>2.25</td>
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<tr>
<td>Nd$_2$O$_3$</td>
<td>7.33</td>
<td>6.80</td>
<td>7.65</td>
<td>7.67</td>
</tr>
<tr>
<td>Sm$_2$O$_3$</td>
<td>0.86</td>
<td>0.60</td>
<td>0.96</td>
<td>0.85</td>
</tr>
<tr>
<td>Gd$_2$O$_3$</td>
<td>0.55</td>
<td>0.36</td>
<td>0.68</td>
<td>0.64</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>0.51</td>
<td>0.32</td>
<td>0.66</td>
<td>0.68</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>0.46</td>
<td>0.65</td>
<td>0.53</td>
<td>0.32</td>
</tr>
<tr>
<td>Nb$_2$O$_5$</td>
<td>0.94</td>
<td>0.58</td>
<td>1.01</td>
<td>0.66</td>
</tr>
<tr>
<td>Total</td>
<td>99.19</td>
<td>99.94</td>
<td>99.28</td>
<td>100.82</td>
</tr>
</tbody>
</table>

Concentrations determined via electron microprobe. Analytical details provided in Appendix A.
from the 84 ± 4 ka (2σ) K–Ar age for coexisting sanidine (Mahood and Drake, 1982).

The highly evolved nature and isotopic compositions of La Primavera rhyolites suggest derivation via extensive fractional crystallization of mantle-derived magma and/or melting of lower crustal mafic rocks (Mahood and Halliday, 1988). Highly evolved rhyolites that are crystal-poor, such as those erupted from La Primavera and Yellowstone calderas, are often attributed to fractionation of crystal-poor magma from a crystal-rich reservoir of magma “mush” (e.g., Hildreth, 2004; Macdonald, 2012). The indistinguishable U–Th and K–Ar ages for both Rio Salado and Arroyo Ixtahuatonte rhyolites suggest a geochemically brief interval of crystallization prior to eruption, in turn relatively short residence of eruptible magma following its fractionation from a crystal-rich parent. Alternatively, crystallization may have occurred after an episode of magma heating that fully resorbed preexisting chevkinite and zircon, although there is no apparent geochemical or petrographic evidence for heating or magma mixing. Zircon saturation temperatures (Boehnke et al., 2013) based on bulk rhyolite composition and reported Zr concentrations (Mahood, 1981) are 840 °C and 860 °C for Rio Salado and Arroyo Ixtahuatonte rhyolites, respectively, which effectively match an apparent eruption temperature of ~850 °C from Fe–Ti oxides (Mahood, 1981). These near-identical zircon saturation and eruption temperatures are consistent with the dating results indicating a geologically short interval for chevkinite + zircon crystallization prior to eruption.

4.3.2. West Yellowstone flow chevkinite and zircon

Chevkinite crystals from the West Yellowstone flow yield model crystallization ages ranging from ca. 115 ka to ca. 290 ka (Table 1; Fig. 5). This range of ages matches the range of model crystallization ages for zircon from the same hand sample (Fig. 5). Vazquez and Reid (2002) interpreted this range of zircon ages to reflect the protracted cooling and crystallization to near-solidus conditions at ca. 120 ka in the voluminous magma reservoir that fed the CPM rhyolites, with ages greater than ca. 200 ka likely representing antecrysts or inherited domains. The overlapping intervals of crystallization for chevkinite and zircon suggest persistence of the thermochemical conditions required for saturation of both minerals in post-caldera rhyolite at Yellowstone.

Chevkinite saturation temperatures for the West Yellowstone flow rhyolite are ~800 °C based on the model of Boehnke et al. (2013), with pyroxene–fayalite and Fe–Ti oxide phenocryst compositions yielding temperatures of 845–860 °C (Vazquez et al., 2009). Only the youngest chevkinite model age overlaps the 114 ± 2 ka eruption age derived by 40Ar/39Ar dating of sanidine (Christiansen et al., 2007). Dating of near eruption growth on the chevkinite crystals is likely to require ion microprobe sampling of unpolished rim surfaces of individual crystals in the same manner that has been used for other accessory minerals (e.g., Schmitt et al., 2011; Vazquez and Lidzbarski, 2012).

4.4. Age-compositional relations of La Primavera and Yellowstone chevkinite

Differentiation of metaluminous silicic magma and/or increasing peralkalinity typically results in crystallization of chevkinite with higher La, Ce, Mn, Fe, and Nb concentrations, and lower Al, Ti, Mg, Ca, and MREE concentrations (Macdonald et al., 2002, 2009). The compositions of La

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**Fig. 4.** Isochron diagrams with 236U–230Th–232Th (activity) compositions of chevkinite and zircon from La Primavera rhyolite. Ellipses represent 2σ analytical uncertainties. Open ellipses are data excluded from isochron calculation (Table 1). Calculated dates are given at the 95% confidence level.

**Fig. 5.** Th/U versus 236U–230Th model crystallization age for West Yellowstone flow chevkinite (blue circles) and zircon (gray circles). Zircon data are from Vazquez and Reid (2002) with ages recalculated using 230Th decay constant of Cheng et al. (2013). Concentrations of Nb, Zr, and Mg in West Yellowstone chevkinite are from electron microprobe analyses and are correlated to their respective U–Th age. 40Ar/39Ar eruption age of ca. 115 ka (Christiansen et al., 2007) is denoted by vertical dashed line.
Primavera and Yellowstone chevkinite follow this general trend and are consistent with increasing magnitude of differentiation and/or peralkalinity of their host rocks. West Yellowstone chevkinitehas lower average Th/U, Mg/Fe, Fe and Th, and higher average Mn, Zr, and Nb with decreasing age (Fig. 5). These trends mimic the general trend of groundmass glass compositions for rhyolites erupted over the same ca. 115 ka–260 ka interval (Vazquez et al., 2009), as well as a general decrease in Th/U between the interiors and rims of West Yellowstone zircon from the same sample (Fig. 5). The most evolved, i.e., lowest Mg, chevkinite crystals from the West Yellowstone flow are similar in composition to those occurring in the ca. 640 ka Lava Creek Tuff (Fig. 6), but they are 100’s of k.y. younger.

The La Primavera pre-caldera Rio Salado and post-caldera Arroyo Ixtahuatonte chevkinite appear to lie along the same general compositional trend defined by the West Yellowstone rhyolite, with some overlap in compositions (Fig. 6). Based on major element chemistry, the weakly peralkaline host rhyolites from La Primavera are broadly comparable to those of West Yellowstone, but based on trace elements, La Primavera rhyolites are even more evolved (Rb/Sr = 100–250 and [Sr] = 0.5–1.5 ppm) than post-caldera rhyolites at Yellowstone (Rb/Sr = 2–140 and [Sr] = 2–85 ppm) (Mahood and Halliday, 1988; Halliday et al., 1991; Vazquez and Reid, 2002). Rio Salado and Arroyo Ixtahuatonte rhyolites are nearly identical in bulk and trace element composition, reflecting compositional rebound of the La Primavera magmatic system in the ca. 95–85 ka interval after the caldera-forming eruption of the compositionally zoned Tala Tuff magma (Mahood, 1981). Rio Salado rhyolite primarily differs from Arroyo Ixtahuatonte rhyolite by having higher Rb, Y, and U, lower Zr concentrations, and slightly lower peralkalinity (Mahood, 1981). Chevkinite in both rhyolites mirrors the overall similarities and distinctions in terms of major and trace element concentrations between the whole rocks, with lower Zr and La, and higher Y in chevkinite from the older Rio Salado rhyolite. Concentrations of Nb are significantly different between the Rio Salado and Arroyo Ixtahuatonte chevkinite, but their relative Zr/Nb is consistent with that for the two rhyolites (cf. Mahood, 1981). These geochemical characteristics are consistent with reorganization and renewed differentiation of the subcaldera magma reservoir by addition of new rhyolite from deeper levels in the magmatic system immediately after evacuation of the Tala Tuff magma chamber (Mahood, 1981).

5. Summary and conclusions

High Th concentrations and large magnitude Th/U fractionation during crystallization from rhyolitic magma make volcanic chevkinite amenable to $^{230}$Th/$^{238}$U disequilibrium dating via secondary ion mass spectrometry. Ion microprobe measurements of chevkinite microphenocrysts from rhyolite lavas erupted before and after formation of La Primavera caldera yield U–Th crystallization ages that are similar to their respective sanidine K–Ar ages of ca. 125 ka and ca. 85 ka, indicating a geologically brief interval between magma crystallization and volcanic eruption. Chevkinite from post-caldera rhyolite at Yellowstone caldera yield U–Th dates between ca. 115 ka and ca. 300 ka, which matches the range of crystallization ages from coexisting zircon. The typically restricted range in Th/U for related volcanic chevkinite thwarts the generation of precise chevkinite-only isochrons, but combination with zircon and/or major phases with relatively low Th/U can produce mid- to late-Pleistocene isochron dates with precision of ~5%. The major and minor element compositions of chevkinite from La Primavera and Yellowstone rhyolites are consistent with the relative degrees of differentiation and/or peralkalinity of their host magmas, and can be keyed to their respective U–Th crystallization ages to resolve the age-compositional evolution of rhyolitic magma.

Acknowledgments

The U.S. Geological Survey and National Science Foundation award GEO-0503609 supported this research. The ion microprobe facility at UCLA is partly supported by a grant from the Instrumentation and Facilities Program, Division of Earth Sciences, National Science Foundation. We are grateful to Cristo Ramirez for the assistance during sample collection at La Primavera. We thank Brad Ito, George Jarzebinski, Frank Kyte, and Robert Oscarson for their technical assistance and instrument maintenance, and also Andy Calvert, Calvin Miller, and Anonymous for their manuscript reviews.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2014.10.020.

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