Titanium diffusion profiles and melt inclusion chemistry and morphology in quartz from the Tshirege Member of the Bandelier Tuff

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Abstract

Many rhyolites contain quartz crystals with relatively Ti-rich rims and Ti-poor cores, with a sharp interface between zones, attributed to partial dissolution followed by overgrowth following a heating event due to mafic recharge of the system. Quartz crystals in the compositionally zoned, high-silica rhyolite Tshirege Member of the Bandelier Tuff erupted at 1.26 Ma from the Valles caldera, New Mexico, show a range in zoning styles with Ti-rich rims becoming more abundant upward in the ignimbrite sheet among progressively less evolved magma compositions. Here we compare times between quartz overgrowth and eruption obtained by applying Ti diffusion coefficients to Ti concentration profiles in Tshirege Member quartz crystals with those from cathodoluminescence (CL) brightness profiles and show that panchromatic CL provides only a crude proxy for Ti in quartz in this unit. Titanium concentrations are measured to detection limits of ~1.2 ppm with small analytical errors (<5%) using MAN backgrounds, blank corrections, and oblique corrected transects to resolve diffusion-relaxed zone boundaries as thin as ~10 μm. Timescales derived from Ti profiles using the widely applied Ti-in-quartz diffusion coefficients of Cherniak et al. (2007) range from 60 to 10,000 years, suggesting heating and mobilization events at different times prior to the eruption. However, the use of the newer Ti diffusivities reported by Jollands et al. (2020) yields timescales up to three orders of magnitude longer, including results that are geologically unreasonable for the Bandelier system. We suggest that assumptions commonly made in diffusion modeling, specifically about the form of the Ti zoning profile prior to diffusive relaxation, may be invalid.

Melt inclusions in the Ti-poor cores of late-erupted quartz are chemically akin to early erupted melt compositions, while adhering and groundmass glasses more closely reflect the composition of the host pumice. Heating and mobilization events identified from quartz Ti zoning are thus linked to overall compositional zoning of the tuff, which may have been produced by repeated episodes of melting of a crystal cumulate cognate to the early-erupted, evolved rhyolite. Quartz-hosted melt inclusion faceting suggests the development of a crystal mush over a minimum time frame of 1000–10,000 years prior to the recharge events that produced the erupted Tshirege magma at 1.26 Ma.

Keywords: Caldera, cathodoluminescence, diffusion, inclusion, melt, quartz, tuff, volcano

Introduction

Diffusion modeling of element concentration profiles in crystals is a fruitful way of extracting timescales of processes occurring at elevated temperatures in geologic systems. The approach relies on some assumptions, such as starting conditions for the diffusion episode and that the concentration profiles being modeled are indeed the result of ionic diffusion. In studies of volcanic systems, diffusion profiles can help determine the residence times of crystals in magma based on compositional zoning of the minerals of interest. Diffusion modeling can also be used to determine the time elapsed between an identifiable event in the history of a crystal (e.g., overgrowth on a resorption surface) and eruption (Costa and Dungan 2005; Morgan and Blake 2006; Wark et al. 2007; Costa et al. 2008; Till et al. 2015). Timescales deduced from the diffusive blurring of an overgrowth boundary can provide insights on how magma systems respond to disturbance, such as rejuvenation and heating by magmatic recharge, shortly before an eruption. This approach has yielded estimates of short activation timescales (<1–1000 years) preceding past catastrophic silicic caldera-forming “super-eruptions” (Wark et al. 2007; Matthews et al. 2012; Till et al. 2015; Gualda and Sutton 2016; Cooper et al. 2017). Smaller, much more frequent eruptions may also have activation timescales of <1 years, for example, Calbuco volcano, 2015 (Arzilli et al. 2019).

In rhyolitic volcanic systems, quartz is a widely used target for diffusion modeling because quartz crystals are usually large and of effectively constant major element composition. Trace element substitutions, particularly that of Ti4+ for tetrahedral Si4+ in the quartz structure (Götze 2012; Leeman et al. 2012),