SPECIAL COLLECTION: RATES AND DEPTHS OF MAGMA ASCENT ON EARTH

U-Th baddeleyite geochronology and its significance to date the emplacement of silica undersaturated magmas†

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ABSTRACT
Baddeleyite is a frequently found accessory mineral in silica undersaturated lavas. Because it is typically enriched in uranium, while having low initial lead, baddeleyite has long been a prime target for U-Pb geochronology of mafic rocks. The difficulties in retrieving small baddeleyite grains from volcanic samples and the lack of a detailed understanding of baddeleyite occurrence, however, have limited baddeleyite chronology largely to coarse-grained mafic intrusive rocks. Here, the development of U-Th in situ baddeleyite analysis using secondary ionization mass spectrometry (SIMS) is presented together with an assessment of baddeleyite occurrence in Quaternary silica-undersaturated lavas from Campi Flegrei (Naples, Italy). Samples studied comprise the pre- and post Campanian Ignimbrite (ca. 40 ka) lava domes of Cuma and Punta Marmolite, and Astroni and Accademia, respectively. The in situ sample preparation required initial identification of baddeleyite crystals from sawed and polished rock billets using scanning electron microscope (SEM) backscatter imaging and energy-dispersive X-ray analysis. U-Th baddeleyite isochron ages for intra-caldera Astroni and Accademia lava domes are 5.01±0.63 ka (MSWD = 2.0; n = 17) and 4.36±0.12 ka (MSWD = 2.9; n = 24), respectively. The ages for Punta Marmolite (62.4±1.8 ka; MSWD = 1.2; n = 11) and Cuma (45.9±1.2 ka; MSWD = 2.2; n = 11) predate the Campanian Ignimbrite. Rapid baddeleyite crystallization at the time of emplacement is supported by petrologic observations that >50% of the baddeleyite crystals documented in this study occur either in vesicles or in vesicle-rich regions of the host lavas whose textures developed over timescales of a few years to a few decades based on microlite crystal size distribution (CSD) analysis. Radiometric U-Th baddeleyite ages are mostly in agreement with previously determined K-Ar eruption ages, except for the Punta Marmolite lava dome whose U-Th baddeleyite age predates the K-Ar age by ca. 15 ka. Baddeleyite thus records eruptive emplacement with little evidence for significant pre-eruptive crystal residence, and has potential as an eruption chronometer for Quaternary silica-undersaturated volcanic rocks.

Keywords: Geochronology, baddeleyite, radiogenic isotopes, uranium series, igneous petrology, trachyte, secondary ionization mass spectrometry

INTRODUCTION
The accessory mineral baddeleyite (ZrO2) has long been recognized as an ideal chronometer for mafic and ultramafic rocks because it has an essentially infinite initial U-parent to Pb-daughter ratio (e.g., Heaman and LeCheminant 1993; Heaman 2009; Söderlund et al. 2013). Recent advances in high-spatial resolution methods (e.g., Chamberlain et al. 2010; Li et al. 2010; Schmitt et al. 2010; Ibáñez-Mejía et al. 2014) have also enabled in situ analysis of crystals too fine to be separated by conventional heavy mineral enrichment techniques (cf. Söderlund and Johansson 2002). Despite a surge in baddeleyite ages produced over the past decade (Söderlund et al. 2013), ambiguities remain about their geochronologic significance. This is in part because the chemical abrasion pre-treatment (Mattinson 2005), now the standard for zircon geochronology, appears to have little effect in enhancing concordance for baddeleyite, and consequently minor Pb-loss may go unrecognized (Riouxf et al. 2010). Unlike zircon, baddeleyite’s magmatic stability and diffusion properties have not been experimentally calibrated (cf. Cherniak and Watson 2003; Watson and Harrison 1983; Boehnke et al. 2013), and therefore comparison of high-precision U-Pb ages between coexisting zircon and baddeleyite (where available) is commonly used to constrain its age significance. In some instances, baddeleyite and zircon have yielded discordant ages (Svensen et al. 2012), but baddeleyite ages both younger and older than coexisting zircon have also been detected (e.g., Corfu et al. 2013; Sell et al. 2014; Janasi et al. 2011). Whereas inheritance is rare in baddeleyite, reflecting the tendency of baddeleyite to become obliterated under normal metamorphic or igneous conditions via reactions with silica-enriched fluids or melts to form zircon (Davidson and van Breemen 1988; Heaman and LeCheminant 1993; Söderlund et al. 2013), it has been proposed that baddeleyite predating zircon by ca. 200 ka may represent early crystallization in an evolving magma system (Sell et al. 2014), and therefore baddeleyite may not always directly date magmatic emplacement. Conflicting