Resolving silicic magma evolution by in situ $^{230}$Th-$^{238}$U dating of zircon and allanite

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The age distribution and chemical heterogeneity of accessory phases are important archives of the thermal and compositional evolution of silicic magmas. For example, the inheritance of basement-derived zircon in silicic magmas is well-known and demonstrates that pre-existing crust has been consumed during magma genesis. One corollary of this is that ages obtained on zircon aggregates will be skewed to older values when inherited zircons are inadvertently included in mineral separates. In order to more fully exploit the record of accessory phase crystallization and to apply it to young lavas, we used the ims 1270 secondary ion mass spectrometer to develop the first in situ analyses of $^{238}$U-$^{230}$Th disequilibria in zircon (Reid et al., 1997) and allanite (a LREE-epidote). Individual spots yield uncertainties of better than 10 ka on <100 ka zircons and allanites, and better than 15% on ages of up to 200 ka in zircon and 350 ka in allanite. Th and U diffusion rates in zircon and probably allanite are relatively slow, even at magmatic temperatures, such that ages determined in this fashion are likely to be predominantly those of crystallization. The ion microprobe affords a relatively rapid method of analysing spatially restricted crystal domains, thus enabling the episodicity and duration of crystallization to be investigated.

Analytical techniques

We measure ratios between the oxides of $^{238}$U, $^{232}$Th, and $^{230}$Th sputtered from grain mounts by an O$^-$ primary ion beam. U/Th in zircon is high so that the accuracy of ages depends on the UO$^+$/ThO$^+$ relative sensitivity factor, whereas U/Th in allanite is nearly zero and ages are more sensitive to uncertainties in the inherited ('common') $^{230}$Th/$^{232}$Th. The relative ionization efficiency of $^{230}$Th$^{16}$O$^+$ with respect to $^{232}$Th$^{16}$O$^+$ also affects the absolute accuracy of ages and is likely to be more significant when interpreting younger crystal ages. Relative U-Th sensitivity factors for zircon have been obtained by reference to time-integrated Pb isotope signatures in concordant zircons; relative U-Th sensitivity factors and $^{230}$Th/$^{232}$Th ionization efficiencies for allanite have been determined with respect to thermal ionization mass spectrometry (TIMS) analyses of nominally homogeneous grains. To delimit the effect of the common Th correction, we use glass and whole rock $^{230}$Th/$^{232}$Th values obtained by TIMS analyses. The two ages constrained in this fashion differ most in cases where a significant fraction of the allanite, a major host of Th in rocks where it occurs, are older than the age of eruption. $^{230}$Th$^{16}$O intensities are low (<5 cps); to ensure that molecular interferences at $^{238}$U are well-resolved, we confirmed that relatively old zircons and allanites yield isotopic analyses within error of secular equilibrium (i.e. $^{230}$Th$^{16}$O/$^{238}$U$^{16}$O = 1.69 × 10$^{-5}$).

Results

Ages for zircon and allanites from rhyolites associated with Toba (Indonesia) and Long Valley (western USA) calderas have been determined. The mineral ages are within error of or older than independent estimates for the age of eruption, as expected if molecular interferences at $^{230}$Th are well-resolved. The relatively precise mean age, $11 ± 1$ ka (MSWD = 1.0), of allanites from a sparsely porphyritic Mono Craters rhyolite is older than ages for stratigraphically younger (≤3.8 ka) rhyolites. Allanite crystallization may have occurred relatively quickly, close to the time of eruption. For the other rhyolites studied (e.g. Fig. 1), most of the allanite and zircon crystallized somewhat (few to tens of ka) to significantly (more than 200 ka) before eruption. The broad ranges of ages require two or more episodes of accessory phase crystallization. In general, petrographic evidence suggests that where allanite and
Fig. 1. Comparison of ages obtained on zircon and allanite from 0.65 ka South Deadman dome, Long Valley, plotted with respect to \((238\text{U})/(232\text{Th})\). Relative ages of allanite and zircon generally support the inference that allanite saturation occurs at somewhat lower temperature than that of zircon saturation, which is approximately 800°C for these rhyolites.

In keeping with this, allanite ages tend to be younger than but nevertheless overlap those of zircon. Solubility considerations suggest that the magmas must have attained \(T = 800°C\) by the time zircon crystallized. Collectively, our results indicate a protracted interval of accessory phase crystallization in silicic magmas prior to eruption.

References