TECHNICAL RESPONSE

VOLCANOLOGY

Response to Comment on "Rapid cooling and cold storage in a silicic magma reservoir recorded in individual crystals"

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In a recent paper, we used Li concentration profiles and U-Th ages to constrain the thermal conditions of magma storage. Wilson and co-authors argue that the data instead reflect control of Li behavior by charge balance during partitioning and not by experimentally determined diffusion rates. Their arguments are based on (i) a coupled diffusion mechanism for Li, which has been postulated but has not been documented to occur, and (ii) poorly constrained zircon growth rates combined with the assumption of continuous zircon crystallization.

We thank Wilson and co-authors for their interest in our recent paper and welcome the opportunity to further discuss our results. Wilson *et al.* (*1*) bring up points that we had considered but had not expanded on in the original paper (*2*). Their comments underscore the importance of our method (combining diffusion modeling and dating in the same crystal domains) for constraining thermal histories to develop a better understanding of magmatic processes.

The conclusions in our paper (*2*) are the logical result of combining our measured Li data with the available experimental data on Li diffusion (*3*, *4*). As we discussed (*2*), if the current diffusion data are shown not to be relevant to the conditions of zircon storage in nature, our conclusions would indeed need to be reexamined. However, there are as yet no data (either experimental or observational) conclusively documenting a diffusion mechanism in zircon that is different from the experimental results. Wilson *et al.* base most of their criticism on a recent paper (*5*) that we did not cite because it was not yet published at the time of our study. However, Tang *et al.* (*5*) do not present direct evidence for a slow [controlled by rare-earth elements and yttrium (REE+Y)] diffusion or partitioning mechanism in zircon. Instead, they hypothesize multiple modes of diffusion based on measurements of Li in complexly zoned zircon crystals, together with additional assumptions of thermal histories and mineral growth arguments, and subsequently develop a theoretical model to examine the potential effects of multiple diffusion modes. Similarly, although Wilson *et al.* hypothesize that coupling of Li diffusion to slower-diffusing elements may be important (*1*), they do not present or cite data showing a correlation of Li with REE+Y or other elements that may be involved in coupled diffusion. Furthermore, if there is a slow diffusion mechanism that is the result of a particular ratio of REE to Li in a zircon (*5*), there is no way at present to assess the conditions under which this slow diffusion mechanism would become dominant.

Wilson *et al.* (*1*) also argue, on the basis of the difference in age between the Kaharoa zircon cores and rims, that growth of the zircon requires extended residence at relatively high temperatures. However, this argument does not consider the full range of estimated zircon growth rates and implicitly assumes that growth was continuous between the core and the rim. Growth rates of zircon are not well constrained, with estimates ranging from 10^{-11} to $<10^{-17}$ cm/s (corresponding to $<10^{-3}$ to >1 μm/year) (*6*–*9*). These values are likely to be underestimates because they do not consider the effect of Cl and F as network modifiers that increase the Zr diffusivity in the melt (*10*), which in turn increases growth or dissolution rates of zircon [e.g., (*6*)]. The Li peaks that we modeled are located between ~5 and ~30 μm from the surfaces of the crystals; thus, crystallization of the zircon rimward of the Li peaks at these growth rates could have occurred within years to decades, consistent with our diffusion results. In addition, growth hiatuses are common in Kaharoa zircon crystals (*11*) and have been observed in other magmatic systems (*12*), and any gaps in crystallization or variations in crystallization rate will have the effect that average growth rates (*7*) underestimate the times of more rapid crystallization. In fact, one implication of our observations when compared to theoretical studies is that crystal growth in nature may typically be highly punctuated, with periods of very rapid growth interspersed with periods of very slow or no crystallization, consistent with models that suggest that most zircon growth occurs at high temperatures after a thermal input (*13*). This type of punctuated crystallization could also provide an explanation for the shapes of the Y profiles noted by Wilson *et al.* (*1*): The deviation of Y concentration gradients in our crystals from a step function may reflect rapid crystallization and growth entrapment of Y (*14*) rather than a diffusion time scale. The lack of correlation between Y (or any other element) and Li that we noted in our zircon (*2*) indicates that the Y concentration gradients and the Li concentration gradients did not form during the same growth episodes, and the shapes of the different concentration profiles may reflect fundamentally different processes. Elements with different diffusivities will respond differently to rapid crystallization, such that profiles of relatively fast-diffusing elements such as Li may dominantly reflect diffusion after crystallization, whereas those of slow-diffusing elements such as REE+Y may dominantly reflect entrapment processes during crystallization.

Studies of Li in zircon offer opportunities for further refinement of our understanding of the thermal history of magma during crustal storage. Although further experimental and/or observational data are necessary to clarify what controls the partitioning and diffusion of Li in zircon, the implications of the data that we presented (*2*) for magmatic systems require us to revisit our views of subvolcanic magmatic processes. Indeed, other recent results support for a model of dominantly cold storage and rapid remobilization of magmas in the shallow crust. For example, diffusion studies in major phases typically indicate rapid assembly of erupted magma bodies [e.g., (*15*)]. Recent numerical modeling studies suggest that physical behavior of crystal-melt systems may be much more complex than typically assumed, with both "jamming" of crystals producing elastic behavior at low crystal fractions and mobilizing magmas at very small strain rates even at high crystal fractions (*16*)—which suggests in turn that remobilization from a solid or near-solidus state may be more feasible than previously thought. Other recent work shows that thermal pulses related to injection of new magma into a shallow magma reservoir are highly localized in both space and time (*17*), indicating that crystals may not record thermal perturbations from all (or even most) injection events. Understanding of these systems will require further experimental work to document the behavior of Li in zircon, combined with additional numerical studies that may reveal the dynamics of crystal-melt systems, as well as

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fundamental observational studies of how these behaviors manifest in natural magmatic systems. We (and no doubt many others) will continue exploring this behavior, and we look forward to continued discussions of the results in the literature.

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