Forum Reply

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New Ti-in-quartz diffusivities reconcile natural Ti zoning with time scales and temperatures of upper crustal magma reservoirs

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The accuracy of diffusion chronometry is entirely dependent on experimental calibrations of diffusivity. Corroboration of experimental diffusivities using natural systems is thus extremely valuable. For Ti-in-quartz, this would mean finding systems where (1) time scales relevant for quartz crystallization are independently well-constrained, and (2) Ti profiles have been measured in quartz, then determining diffusion time scales using the experimental diffusivities. Gualda and Pamukçu (2020) have carried out such an exercise and concluded that the Cherniak et al. (2007) diffusivities are compatible with geological observations, whereas those of Jollands et al. (2020), are not; however, in the examples that they provide, conditions 1 and/or 2 are not met.

Firstly, Gualda and Pamukçu suggest that time scales derived using the new diffusivities are inconsistent with fast quartz growth during decompression. This is valid if quartz growth is indeed due to decompression, which is debatable. Blundy and Cashman (2001) used experimental phase equilibria to show that quartz should be resorbed during decompression of hydrous rhyolitic melt, and Evans et al. (2016) suggested that the Bishop Tuff quartz rims relate not to decompression but to a recharge event. In the latter case, acceptable time scales could plausibly be much longer than those associated with decompression.

Secondly, considering time scales from melt inclusion faceting, it is notable that the Gualda et al. (2012) study begins with the caveat that the "kinetics of melt inclusion faceting has not been treated in detail" and that their model constitutes a "simplified treatment" only. To our knowledge, the model has not been experimentally validated. Melt inclusion faceting, while potentially a powerful tool, does not currently provide well-constrained time scales to which others can be compared.

Thirdly, crystal size distributions (CSDs) apparently yield time scales in line with those determined from Ti-in-quartz profiles using the Cherniak et al. (2007) diffusivities. In this case, there is circular logic. Extracting time scales from CSDs requires a growth rate. Both Gualda et al. (2012) and Pamukçu et al. (2020) extract growth rates from Ti-in-quartz diffusion profiles using the data set of Cherniak et al. (2007). CSDs in the Gualda et al. (2012) and Pamukçu et al. (2020) studies therefore do not provide an independent constraint to evaluate differing Ti-in quartz diffusivities.

Fourthly, turning to Oruanui, it is indeed the case that the Ti-in-quartz profiles of Pamukçu et al. (2020), fitted using the Cherniak et al. (2007) diffusivities, give a <3 k.y. time scale. This is consistent with the time interval between eruptions determined by radiocarbon dating (e.g., Wilson et al., 2005). Applying the Jollands et al. (2020) diffusivities to the Pamukçu et al. (2020) data, after accounting for effects of beam convolution, ~50% of the time scales are over 3 k.y.. Approximately 90% are <40 k.y., the time associated with assembly of the system, although this may relate to spatially distinct magma volumes (Charlier et al., 2005). Considering Fe-Mg diffusion in opx, Allan et al. (2017) presented time scales that supported this 3 k.y. limit, when using their preferred $D_{Fe\text{-}Mg}$. However, they also showed that ~75% of Fe-Mg profiles yield time scales of >3 k.y. when using the Dohmen et al. (2016) diffusivities. The caveat is that $D_{Fe\text{-}Mg}$ has not been experimentally determined at X_{Fe} relevant for Oruanui opx. If in fact it is the case that 3 k.y. is a true upper limit, apparently 'too long' Ti profiles and hence time scales would most likely result from initial Ti concentration-distance profiles inherited from natural crystal growth, which are not perfect step functions.

Finally, a number of Gualda and Pamukçu's statements are inaccurate: (1) Cooper and Kent (2014) present no Ti-in-quartz data, thus the Jollands et al. (2020) diffusivities cannot be applied to their study. (2) Flaherty et al. (2018) also presented no Ti-in-quartz data. (3) Shamloo and Till (2019) did not present Ba, Sr in sanidine, and Ti-in-quartz time scales in mutual agreement; rather, their Ba time scales were up to ~250x longer than their Sr time scales, with Ti intermediate. (4) The Jollands et al. (2020) experiments were broadly similar to those of Cherniak et al. (2007) but the exact nature of the experiments (specifically, the bulk Ti content) and the analytical techniques used, were different.

In summary, Gualda and Pamukçu have not shown inconsistency between the Jollands et al. (2020) diffusivities and independently well-constrained time scales. Their arguments do not justify the conclusion that our data set is incompatible with the weight of geological evidence.

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