Comment on “Rapid cooling and cold storage in a silicic magma reservoir recorded in individual crystals”

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Rubin et al. (Reports, 16 June 2017, p. 1154) proposed that gradients in lithium abundance in zircons from a rhyolitic eruption in New Zealand reflected short-lived residence at magmatic temperatures interleaved with long-term “cold” (<650°C) storage. Important issues arise with the interpretation of these lithium gradients and consequent crystal thermal histories that raise concerns about the validity of this conclusion.

Rubin et al. (1) proposed that gradients in lithium concentration recorded in zircons from the 131H + 10 CE Kaharoa eruption (2) reflect diffusive modification of initially sharp step changes in lithium abundance. On the basis of diffusive modeling, they construed the gradients to reflect histories for the grains studied that could not have involved more than ~40 years above the rheological lockup temperature (750°C) or more than a total of ~150 to 1200 years above the solidus (650°C to 700°C). Such a scenario was linked to prolonged “cold” (3) storage of the crystals and their host rocks, and as such was used to propose a short-lived history for the Kaharoa material as an eruptible magma. Such a scenario, although plausible in principle, is contradicted in this example by two key lines of evidence.

First, there is a mismatch between the natural scenarios modeled by Rubin et al. and the conditions under which the apparent diffusion characteristics for lithium in zircon used to undertake the modeling were obtained (4, 5). Rubin et al. report lithium abundances in their zircons typically in principle, is contradicted in this example by two key lines of evidence.

Second, there is a flaw in the logic used to match the inferred diffusion profiles in the zircons with the thermal history of the grains. Rubin et al. infer from textural information and U-Th disequilibrium model ages that the interior parts of their zircon crystals grew, incorporating a sharply defined step in the concentration of lithium. The time scales they then infer from diffusion modeling of the lithium profiles are then used to propose that the relevant parts of the crystal incorporating the lithium profile were held for all but a tiny fraction of their histories at temperatures at which they infer lithium diffusion to have been ineffective (e.g., a maximum of 1200 years at 650°C). The flaw in this logic is that between the crystal cores and the rims there has been growth of further, additional zircon, which demands (given the oscillatory and sector-zoned nature of the crystals under cathodoluminescence: figs. S1 and S2 of (1); (11, 12)) growth from a melt. The paradox is then that for the crystal to grow over the prolonged time scales indicated by the U-Th disequilibrium model ages given by Rubin et al. (1, 11) and others (12, 13), the zircon has to have been maintained in a melt (i.e., above the solidus) for much of that time (e.g., (12, 13)). Of all the minerals present in rhyolites such as the Kaharoa (2), zircon is the one that is most mediated by diffusion to the growing crystal; the low supersaturations would require either substantial melt flow relative to the crystal or long enough time to diffuse to the nucleus for growth to occur. One cannot freeze a diffusive profile in an inner growth zone and at the same time immerse the crystal exterior in a melt to permit it to grow larger to the sizes reported (1, 11–13).

In summary, we would contend that (i) the diffusion parameters used by Rubin et al. are inappropriate for the lithium concentrations reported by them in the Kaharoa zircons; (ii) the proposed lithium diffusion profiles represent near-equilibrium concentration profiles controlled by partitioning for charge balancing within the zircon structure; and (iii) the thermal histories proposed are wholly incompatible with evidence (1, 11–13) for extended growth times of the zircons from melts. There is great potential in the use of lithium (both elemental and individually as 6Li and 7Li isotopes) as a geospeedometer in volcanic systems [e.g., (14, 15)], but diffusion modeling must first take into account of compositional controls in the host minerals concerned [e.g., (6, 7, 14)] before time scales can be inferred with confidence.

REFERENCES AND NOTES

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