Article:

Title: Cold storage in a heat wave?

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Abstract: Rubin et al. (Research Report, 16 June 2017, aam8720) 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. Significant issues arise with the interpretation of these lithium gradients and consequent crystal thermal histories that raise concerns about the validity of this conclusion.

One Sentence Summary: Lithium gradients in zircon crystals reflect partitioning behavior to ensure local charge balance, not short-lived diffusion episodes.

Main Text: Rubin et al. (1) proposed that gradients in lithium concentration recorded in zircons from the 1314±10 CE Kaharoa eruption (2) reflected diffusive modification of initially-sharp step changes in lithium abundance. Based on diffusive modeling, they considered that the gradients reflected 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° 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, whilst plausible in principle, is contradicted in this example by two key lines of evidence.

First, there is a mismatch between the natural scenarios modelled by Rubin et al. and the conditions under which the apparent diffusion characteristics for lithium in zircon used to undertake the modelling were obtained (4,5). Rubin et al. report lithium abundances in their zircons typically of tens of parts per billion (ppb), yet the diffusion experiments on which the modelling is based (4,5) involved abundances of hundreds of parts per million (ppm), 3-4 orders of magnitude higher than in the natural grains (1). The relevance of this discrepancy is that at the ppb level, movement of 1^+ charged lithium in the zircon lattice will be heavily controlled by the requirement for charge balance, and will be locked especially to the position and/or movement of 3^+ ions such as yttrium and the rare-earth elements (REE) (6, 7). Any elemental gradients in lithium at the ppb level are thus much more likely to be controlled by local charge balancing in the crystal and to bear no relationship to the diffusion rates used by Rubin et al. (1) that were measured (4) under lithium loadings of hundreds of ppm in a natural zircon (Mud Tank). This Mud Tank zircon used in the diffusion experiments (4, 5) contains only between 26 and 71 ppm total yttrium plus REE (8, 9), and ~35 ppb naturally-occurring lithium (4, reporting Ushikubo, pers. comm.), set against 100-600 ppm (4) or up to ~1000 ppm (5) lithium introduced into the crystals during diffusion experiments. In contrast, the content of yttrium alone in the Kaharoa zircons varies from ~40 to ~14,000 ppm (1, supplementary material), yet the peak lithium concentrations are at most ~350 ppb and mostly <50 ppb (1). We would contend that the distributions of lithium in the zircons described by Rubin et al. (1) are primarily controlled by local factors associated with charge balancing in the zircon lattice, consistent with the findings of (6, 7). Support for our alternative interpretation is given by the fact that the shapes (widths, slopes, and relative compositional contrasts) of peaks in the abundances of yttrium (1, supplementary Figs. S1, S2) are similar to those of lithium in the same grain. Such a

correspondence would, if the hypothesis of Rubin et al. were correct and yttrium and lithium had independent diffusion, imply that the diffusivity of lithium and yttrium in these grains was of a similar magnitude. Such a conclusion is wholly implausible on available data (4-8). That the positions of peaks in lithium are not always correspondent with peaks in yttrium is not necessarily an issue, as charge balancing in zircon can span several different ionic species, including the REE, phosphorus and hydrogen with, for example, hydrogen abundances often being a factor of local yttrium, REE and phosphorus contents (10).

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 modelling 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: 1, supplementary Figs. S1 and S2; 11, 12) growth from a melt. The paradox is then that for the crystal to grow over the prolonged timescales 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 like the Kaharoa (2), zircon is the one that is most mediated by diffusion to the growing crystal – the low supersaturations would require either significant melt flow relative to the crystal or significant 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 (a) the diffusion parameters used by Rubin et al. are inappropriate for the lithium concentrations reported by them in the Kaharoa zircons; (b) the proposed lithium diffusion profiles represent near-equilibrium concentration profiles controlled by partitioning for charge balancing within the zircon structure; and (c) that 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 ^{6}Li and ^{7}Li isotopes) as a geospeedometer in volcanic systems (e.g. 14, 15), but diffusion modelling has to first take account of compositional controls in the host minerals concerned (e.g. 6, 7, 14) before timescales can be inferred with confidence.

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