Uptake and oscillatory zoning of REE in titanite: effects of thermal cycling and bulk composition

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Titanite (ttn) is an important accessory phase in igneous rocks owing to its affinity for REE and U. Ttn crystals in volcanic and plutonic rocks show extreme REE contents (10^3-10^4 times chondrite) and intense oscillatory zoning (Fig. 1B), with measured *D* values (crystal/glass) on the order of 10^3 for MREE. Experiments in mafic systems, however, yield *D*~10. We have performed experiments doped with Y (MREE analog) and La in the systems ttn-albite and ttn-basalt under static, declining, and oscillatory T conditions in order to understand uptake of REE and the origin of zoning.

Surprisingly, Y and La are barely compatible in ttn in the ttn-albite system (*D*~1), but are more strongly compatible (*D*~10) in ttn-basalt. This suggests that the coupled substitution is more complicated than $Ca^{2+} + Ti^{4+} = 2(REE,Y)^{3+}$ and involves another cation; e.g., $2Ca^{2+} + Ti^{4+} = 2(REE,Y)^{3+} + Fe^{2+}$. In thermally cycled experiments in ttn-basalt, oscillatory rims grow on low-REE seed crystals, with the number of zones equal to the number of thermal cycles (Fig. 1A). Constant-T or linear cooling experiments do not produce oscillatory zoning.

Thermal cycling promotes annealing and growth of crystals, including crystals that begin growth late in the crystallization sequence. Such cycling, which is likely unavoidable in magmatic systems, may promote coarsening of ttn and production of oscillatory zoning, and exert strong control on trace-element uptake.

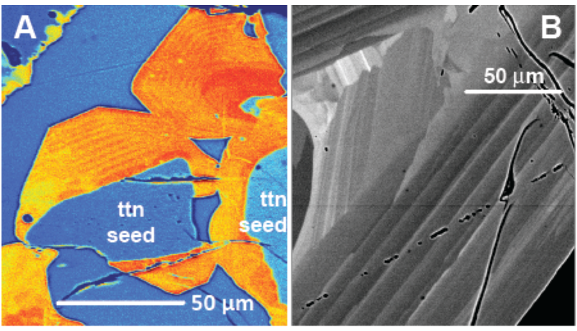

Figure 1: Backscattered electron images of ttn; brightness scales with (REE,Y) concentration. (A) Y- and La-enriched 10-cycle rims grown on ttn seeds in 10-cycle ttn-basalt experiment (T=1220±10 °C, 48-min. period). (B) Complex oscillatory zoning in natural ttn in Half Dome Granodiorite.