ENRICHMENT AND ACCOMODATION OF MANGANESE IN GRANITE-PEGMATITE

SYSTEMS. D. London[1], J. M. Evensen[1], E. Fritz[1], J. P. Icenhower[2], G. B. Morgan VI[1], and M. B. Wolf[3], [1]School of Geology & Geophysics, University of Oklahoma, 100 East Boyd Street Room 810 SEC, Norman, OK 73019 (dlondon.ou.edu), [2]Applied Geology and Geochemistry, Pacific Northwest National Laboratory, P.O. Box 999, Mailstop K6-81, Richland, WA 99352, [3]Department of Geology, Augustana College, 639 38th Street, Rock Island, IL 61201

The Mn/Fe ratio of garnet increases through the fractionation sequence from primitive S-type granites to evolved LCT pegmatites, and this trend has been cited to reflect the general increase in Mn/Fe with magmatic fractionation [1]. The distribution coefficient, $D_{Mn/Fe}^{Gt/melt}$, however, is > 1, meaning that the crystallization of garnet alone actually lowers the Mn/Fe ratio in the melt. Manganese is also compatible in biotite ($D_{Mn}^{Bt/melt} \approx$ 5) and in cordierite ($D_{Mn}^{Crd/melt} \approx$ 4), so that Mn may be depleted in partial melts where biotite, cordierite, or garnet restite is abundant (e.g., granites that originate in the field of Crd contain $\sim$ 0.1 wt% MnO, whereas Crd-absent S-types carry $\sim$ 0.9 wt% MnO). The white and dark micas probably impart most of the Mn component of anatectic melts. Though Mn is compatible in biotite, the Mn/Fe ratio of plutonic biotite is very small; i.e., the crystallization of biotite depletes melt in Fe far faster than in Mn. Manganese is incompatible in typical magmatic (schorl-foitite-olenite) tourmaline ($D_{Mn}^{Ms/melt} \approx$ 0.3), whereas Fe is very compatible. Therefore, increases in the Mn/Fe ratio of melt may commence with the crystallization of biotite but are driven by the crystallization of tourmaline.

The Little Three pegmatite dike, Ramona, CA, provided a natural test of Mn/Fe fractionation in a single igneous dike [2]. The crystallization of biotite + tourmaline gives way to tourmaline + garnet about 1/6 of the way into the dike section. Though the Mn/Fe ratio of garnet increases from the walls inward through the dike, the Mn content of tourmaline remains low and constant until the late-stage pocket zones are reached. There, spessartine disappears as mica and tourmaline compositions evolve quickly to Mn-rich lepidolite and elbaite, respectively. It is evident that the instability of spessartine results from the sudden increase in compatibility of Mn in mica and tourmaline. In the Little Three dike, the incorporation

of Mn in tourmaline is coupled with Li plus Al (elbaite component) in the ratio 1:1, giving an exchange vector of $LiMnAlFe_{-3}$ (Fe = Mg) in the octahedral Y site of the tourmaline.

To understand the interdependence of composition and temperature in promoting this coupled substitution, we have begun experiments in which tourmaline (hydroxydravite) was synthesized at 200 MPa in the presence of Li, Mn, and F – individually and in combination – and at temperatures ranging from 750° to 550° C. The Mn content of the synthetic tourmaline varies from $\sim$ 0.5 to 4.9 wt% MnO, and is positively correlated with the elbaite component (Li + Al in the Y site) and F. The exchange vector $LiMnAlMg_{-3}$ is strongly temperature dependent. When the system is saturated in Li (as eucryptite) and Mn (as spessartine), and F-rich (to $\sim$ 0.5 apfu in tourmaline), then the temperature dependence of Mn in tourmaline is expressed linearly as:

$$Wt\% \ MnO = -0.02T + 15.33$$

where T is in ° C. If Mn enters tourmaline only by the exchange vector $LiMnAlFe_{-3}$, then no tourmaline should contain more than 1 Mn apfu in the Y site, and the Mn content of the Y site should always be $\leq$ the elbaite component. Such a Mn-rich tourmaline species would have the formula $Na(LiAlMn)Al_6(BO_3)_3Si_6O_{18}(OH,F)_4$. This hypothetical species contains 7.27 wt% MnO, comparable to the maximum Mn values found in these experiments and in elbaite from the Little Three mine [2]. We suggest that the hypothetical end member "tsilaisite", $Na(Mn_{1.5}Al_{1.5})Al_6(BO_3)_3Si_6O_{18}(OH,F)_4$ [3], is unstable.

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