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Enrichment of manganese to spessartine saturation in granite-pegmatite systems

## **Supplementary Material B**

### **Preparation of starting materials for experiments**

Natural minerals were crushed and then milled in an agate mortar and pestle in alcohol to a fine powder. Milled powders were placed in an oven at ~120°C for ~15 minutes to dry. Individual mixtures (bulk composition) were created by weighing individual components of natural minerals and chemical reagents to attain the target composition. Each mixture was dry milled in an agate mortar and pestle with the aim of homogenizing the mineral/reagent mixtures. The mineral/reagent mixtures were stored in glass vials in a desiccator.

### **Parameters for Rayleigh model**

**Calculation of normative mineralogy.** Two different normative mineral assemblages were calculated based on the initial composition of the average composition of 63 melt inclusions (see text for details). The normative assemblages are similar in that they all include quartz, orthoclase, and plagioclase, for which the partition coefficients for Mg, Fe, and Mn have been set to zero. The assemblages differ in that the first contains cordierite and biotite and the second contains biotite. Biotite is considered a solid-solution of phlogopite-annite in the model. Normative cordierite and biotite for the first assemblage were calculated iteratively by assigning some MnO, FeO, and MgO, and stoichiometric proportions of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and K<sub>2</sub>O, to biotite and the remainder of the mafic oxides, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> to cordierite; by this process, the residual normative corundum component approached zero. Normative biotite for the second assemblage was calculated by taking all FeO, MnO, and MgO, plus stoichiometric amounts of K<sub>2</sub>O, SiO<sub>2</sub>,

and  $\text{Al}_2\text{O}_3$ . Since biotite is a phlogopite-annite solid-solution, excess  $\text{Al}_2\text{O}_3$  is apportioned to aluminosilicate.

**Temperature and bulk partition coefficients.** Crystallization of both assemblages is modeled between 850°C and 650°C, where  $F=1.0$  at 850°C and  $F=0.01$  at 650°C. The partition coefficients were varied continuously and linearly over the temperature interval, as determined by the experiments in this study (refer to Table S8 in Supplementary Materials B for a list of Rayleigh parameters). Bulk partition coefficients,  $WD$ , were calculated by multiplying partition coefficients by the mode of the appropriate mineral (Beattie et al. 1993).

### **Caveats regarding the results of the Rayleigh model**

There are an unlimited number of scenarios involving subtle changes in the concentrations of the mafic components and the modal mineralogy as calculated from the initial melt composition, and these would lead to slight differences in the temperature and extent of crystallization that are necessary to reach saturation in spessartine-rich garnet. For instance, we intentionally excluded the impact of oxide minerals from our model. Although oxide minerals only constitute trace modal amounts in most S-type granites, we hypothesize that the crystallization of oxide minerals would result in an increase in the Mn/Fe ratio of the residual liquid. Even so, the bulk composition and mineral modes used here are typical of holocrystalline S-type granites (e.g., cordierite-biotite granite, Avila batholith, Central Spain: Pereira and Bea 1994; two-mica and biotite granites, Nepal-Tibet: Visonà and Lombardo 2002). In a study of the Hercynian cordierite-biotite granites of Central Spain, Villaseca et al. (1998) used field relationships and geochemical evidence to show that the most differentiated leucogranites represent, at minimum, the last ~30% of the initial melt. The Mn content of garnet, which is reported as an accessory mineral in many of the granitic units in the region, increases sharply

from Alm<sub>80</sub>Sps<sub>20</sub> to Alm<sub>40</sub>Sps<sub>60</sub> in the most fractionated, pegmatitic units (Villaseca and Barbero 1994).

**Solubility data for garnet.** The degree of fractional crystallization required to achieve garnet saturation depends on the saturation surface for garnet in granitic melt. However, the solubility of garnet in granitic melt, in terms of MnO content of melt, has not been systematically studied. The solubility data for garnet presented in this study stems from the dissolution of Mn-rich garnet in B-bearing, hydrous granitic melt. We hypothesize that the concentration of MnO in melt at garnet saturation would be lower in a hydrous but B-free melt of the same composition. Figure 4e shows the concentration of MnO at garnet saturation for B-rich melt (this study), F-rich melt (~ 1 wt% F: Icenhower 1995), and hydrous, but B- and F-free, granitic melt (London et al. 2012). It is clear from the data presented in Figure 4b that the solubility of MnO, at garnet saturation, is much lower in B- and F-free granitic melt. In addition, it has been shown that a decrease in the concentration of water in melt results in an increase of the activity of alumina in melt, thereby promoting the crystallization of aluminous phases at lower ASI values of the melt (Acosta-Vigil et al. 2003). We expect that the crystallization of a B-free and less hydrous melt would be to promote garnet crystallization at an F value closer to 1.0 in Figure 9.