The (chemical) potential for understanding overstepped garnet nucleation and growth

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ABSTRACT

Overstepping of porphyroblast-forming reactions has been shown to occur in regional, contact, and subduction zone metamorphism, calling into question the paradigm that metamorphic mineral reactions occur at or very close to thermodynamic equilibrium. These overstepped reactions result from the fact that nucleation and growth of new phases requires a thermodynamic driving force or a "departure" from equilibrium. We use phase equilibria modeling to elucidate the energetic consequences of over-stepped garnet nucleation and growth by comparing the chemical potentials of garnet-forming oxide components (MnO, CaO, FeO, MgO, Al_2O_3) in two sets of calculations: one in which Gibbs free energy is minimized and one in which the minimization proceeds under identical conditions but in the forced absence of garnet. We focus on 12 examples from the literature that have previously described garnet nucleation as minimally overstepped (garnet nucleation at the *P-T* of initial garnet stability) or garnet nucleation as more substantially overstepped (garnet nucleation at *P-T* conditions greater than initial garnet stability). For a small *P-T* interval above nominal garnet-in reactions, differences in the chemical potentials between the two calculations are commonly minimal. In all tested examples calculated using two versions of the THERMOCALC thermodynamic data set, the chemical potential of Al_2O_3 ($\mu_{Al_2O_3}$) diverges between garnet-bearing and garnet-absent calculations at greater *P-T* conditions than that of MnO, CaO, FeO, and MgO. The *P-T* interval between thermodynamic garnet-in and the point at which $\mu_{Al_2O_3}$ differs substantially between the two sets of calculations appears to be a function of bulk-rock MnO content, reemphasizing the role that small quantities of MnO play in the apparent stability of garnet in calculated phase equilibria. These results highlight the importance of considering multiple thermodynamic data sets, the location of the garnet-in curve, and the abundance of mineral phases in the discussion of overstepped metamorphic reactions. The results have implications for determining kinetic barriers to crystal nucleation and growth and considering the most appropriate way of defining "garnet-in" for samples that have experienced overstepping.

Keywords: Garnet nucleation, overstepping, thermodynamic modeling, chemical potential, pseudosections