Na-P Concentrations in High-Pressure Garnets: A Potentially Rich, But Risky P-T Repository

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Establishing the history of HP and UHP metamorphic rocks is important for quantifying Earth dynamics. The history of these rocks defines, among other things, paleo-subduction rates, P-T paths, and the kinematics of continent-continent collision. Although the appearance of certain minerals, such as coesite, stishovite or diamond, provides unequivocal evidence of an HP or UHP component to the history of a rock, they cannot provide details of the P-T-t path a rock has experienced. However, complex solid solutions can. This reflects the fact that solid solutions have the potential to provide a continuous thermodynamically-controlled response to evolving P-T conditions. To the extent that such solid solution characteristics are preserved unmodified in a mineral throughout its history, a detailed description of the trajectory of the rock during burial and exhumation can be obtained.

Because of its common presence in UHP rocks and its diverse solid solution possibilities, garnet has become a workhorse mineral phase for deciphering P-T conditions (Axler and Ague, 2015; Liou et al., 2014). Among those of recent interest, solid solutions involving phosphate and pyrope have attracted particular attention. Brunet et al. (2006) documented that, at high pressure conditions (>8 GPa), there is continuous substitution of $Na_3Al_2(PO_4)_3$ in garnet for $Mg_3Al_2(SiO_4)_3$. Their experimental study also established that accommodation of the phosphate end member is limited. The pressure dependence of the phosphate solubility suggested the possibility that sodium and phosphate in garnet may be a potentially useful geobarometer for UHP metamorphic rocks and mantle assemblages if a co-existing buffering phosphate phase were present. In the absence of a coexisting buffer, it was still likely garnet could be utilized as an accurate monitor of phosphate activity in the mantle.

In this issue, Konzett reports on a much more detailed experimental study of this solid solution in eclogitic compositions and related partial melt formation. His experiments are consistent with previously reported results, thus confirming the solid solution series. However, the results place important caveats on the usefulness of P in garnet as a potential geobarometer. Under mid-crustal conditions, the P-end member garnet is not stable, resulting in Na-P depletion in garnets via several possible pathways. In this case, although rapid uplift may well result in preservation of the high pressure Na-P content in the garnet, slow or episodic uplift will encourage re-equilibration. Complicating this process, too, is evidence from the experiments of uptake of Mg and P in kyanite (i.e., $^{[4]}P^{[6]}Mg^{[4]}Si_{-1}{}^{[6]}Al_{-1}$). These reactions, along with decreasing solubility of $NaCa_2(AlTi)(SiO_4)_3$ in garnet, may result in coupled interactions that affect Na-P in garnet, rutile saturation and apatite formation upon decompression (e.g., Ye et al., 2000; Zhang et al., 2003). For eclogitic compositions, these results suggest that serious consideration must be given to the likelihood that Na-P in garnet, and rutile and apatite development will usually represent post-peak processes and conditions, not peak metamorphic P-T. Phase equilibria models and geobarometers relying on these phases or component concentrations will thus likely record post-peak conditions. For instances in which exchange equilibrium was not achieved, meaningless P-T values will result.

An important constraint on applying these results to existing research, however, is the inadequacy of most EMP analyses of garnets for Na and P. These components are not usually analyzed under conditions that result in highly precise and accurate concentration measurements – either long counting times and elevated beam current to achieve P accuracy result in Na volatilization or low currents and brief counting times to prevent Na loss result in low P accuracy. Given the important information that could be developed using these elements in multi-phase study of HP and UHP rocks, it would be useful to develop routine methods for EMP analyses of Na and P in garnet, kyanite and pyroxenes that generate results of sufficient precision and accuracy to be useful.

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