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Titanium substitutions in garnet at magmatic, granulite facies, and high-pressure granulite facies conditions

JAY J. AGUE[1,2,*], DUNCAN S. KELLER[3,†], MICHAEL R. ACKERSON[4], AND MEGAN HOLYCROSS[5]

[1]Department of Earth and Planetary Sciences, Yale University, PO Box 208109, New Haven, Connecticut 06520-8109, U.S.A.
[2]Division of Mineralogy and Meteoritics, Yale Peabody Museum, Yale University, PO Box 208118, New Haven, Connecticut 06520-8118, U.S.A.
[3]Department of Earth, Environmental and Planetary Sciences, Rice University, 6100 Main Street, Houston, Texas 77005, U.S.A.
[4]Department of Mineral Sciences, Smithsonian National Museum of Natural History, Washington, D.C. 20560, U.S.A.
[5]Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, New York 14850, U.S.A.

ABSTRACT

Crystallographically oriented lamellar to acicular rutile ± ilmenite inclusions in garnet may record important information about the pressure (*P*), temperature (*T*), and petrotectonic evolution of the lithosphere. However, reading this record requires a robust understanding of titanium (Ti) substitution mechanisms and solubility in garnet. To this end, we examine the Ti substitution systematics revealed by 87 garnet analyses from previously published experimental studies relevant for granulites, high-pressure granulites, and deep crustal magmatic rocks. The experimental *P-T* conditions range mostly between 850–1230 °C and 1.0–2.7 GPa; four 3.2 GPa, 1075–1150 °C ultrahigh-*P*, ultrahigh-*T* examples are also included. We find that normalizing garnet formulas based on two octahedral sites per 12 O atoms provides better Fe^{3+} estimates than the standard 8-total-cation scheme. The Fe^{3+} must be constrained as both it and Ti substitute on octahedral sites. Graphical analysis reveals that the main substitutions are Tschermak-Ti (${}^{VI}Ti^{4+} + {}^{IV}Al^{3+} \leftrightarrow {}^{VI}Al^{3+} + {}^{IV}Si^{4+}$) and andradite (${}^{VI}Al^{3+} \leftrightarrow {}^{VI}Fe^{3+}$), with lesser but nonetheless important contributions by andradite-Ti (${}^{VI}Ti^{4+} + {}^{IV}Al^{3+} \leftrightarrow {}^{VI}Fe^{3+} + {}^{IV}Si^{4+}$) and alkali-Ti (${}^{VI}Ti^{4+} + {}^{VIII}(Na^{+},K^{+}) \leftrightarrow {}^{VI}Al^{3+} + {}^{VIII}M^{2+}$). Here, ${}^{VIII}M^{2+}$ denotes dodecahedrally coordinated divalent cations (Ca, Fe^{2+}, Mg, Mn). We also posit a small role for Ti substitution coupled to dodecahedral vacancies. These inferences were independently tested using a Monte Carlo modeling procedure developed herein that quantitatively reproduces both the nature and extent of the observed substitutions. We also compared the experimental data with a representative suite of natural garnet analyses. In general, the natural garnets have far lower Ti and alkali (Na ± K) contents than the experimental ones. We attribute this to Ti and alkali loss in nature during exhumation and cooling by processes including diffusion and interface-coupled dissolution-reprecipitation. Some fraction of the lost Ti can be hosted by exsolved precipitates of crystallographically oriented rutile ± ilmenite. However, in many cases, these are absent, and the Ti must have left the garnet structure entirely. The lost alkalis may be hosted by exsolved amphibole or mica precipitates, but these are relatively uncommon, suggesting that alkalis are typically transferred from garnet to the matrix or to non-precipitate inclusions.

Keywords: Garnet, titanium, substitution, granulite, high-pressure granulite, eclogite, ultrahigh-temperature, magma