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Local equilibrium in polymetamorphic gneiss and the titanium substitution in biotite

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ABSTRACT

Secondary metamorphic biotite grew with sillimanite and garnet at the expense of cordierite during a Pan-African metamorphic event overprinting Grenville age granulite-facies metapelites at the western margin of the Namaqualand Metamorphic Complex, South Africa. Fe-Mg exchange thermometry and average pressure calculations constrain the conditions of the overprinting metamorphism to about 660 °C at 6 kbar. Biotite compositions reflect chemical equilibrium in local domains defined by partly to completely pseudomorphed cordierite grains. They show a continuous range of Ti content from 0.0 to 4.5 wt% TiO_2 depending on the proximity of the domain to a source of Ti such as ilmenite. Thus, they allow an assessment of the Ti substitution that is independent of metamorphic grade variation. Significant correlations between Ti and microprobe analysis total indicate that Ti is accommodated largely through a deprotonation substitution $Ti^{4+} + 2O^{2-} + H_2 \rightarrow M^{2+} + 2OH^-$ (where M^{2+} is a divalent octahedral cation) rather than by substitutions involving octahedral vacancies. Ti shows a positive correlation with K, and strong negative correlations with octahedral Al and the sum of divalent cations. Ti content also varies with molar Mg/(Mg + Fe) in biotite (X_{Mg}), because the process of cordierite replacement involves the mass transfer of Fe into cordierite domains. However, the above trends are also shown by a set of analyses with uniform X_{Mg}. In detail, the correlations depend on the method of formula recalculation. If the deprotonation substitution is dominant, normalization should not be made to a constant number of oxygen atoms. A statistical treatment of biotite analyses normalized to 14 tetrahedral and octahedral cations per formula unit suggests that the introduction of Ti involves deprotonation of two OH groups per Ti, and that the replacement of some octahedral Al by Ti is balanced by increases in K and/or Si in other sites. An appropriate Ti-biotite end-member may be $K_2[Mg_4Ti_2]Al_2Si_6O_{24}$, rather than the vacancy-bearing end-members proposed in other studies. In view of the fact that even Ti-free biotite appears to contain a small proportion of octahedral vacancies, a suitable recalculation scheme for microprobe analyses may involve normalizing to 22 + Ti O atoms (neglecting H_2O).