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The Ti-saturation surface for low-to-medium pressure metapelitic biotites: Implications for geothermometry and Ti-substitution mechanisms

DARRELL J. HENRY,[1,*] CHARLES V. GUIDOTTI,[2] AND JENNIFER A. THOMSON[3]

[1]Department of Geology and Geophysics, Louisiana State University, Baton Rouge, Lousianna 70803, U.S.A.
[2]Department of Geological Sciences, University Of Maine, Orono, Maine 04469, U.S.A.
[3]Department of Geology, Sci 130, Eastern Washington University, Cheney, Washington 99004, U.S.A.

ABSTRACT

The Ti content of biotite can serve as a geothermometer for graphitic, peraluminous metapelites that contain ilmenite or rutile and have equilibrated at roughly 4–6 kbar. The relationship between Ti-content, temperature, and Mg/(Mg + Fe) value was calibrated empirically using an extensive natural biotite data set (529 samples) from western Maine and south-central Massachusetts in combination with the petrogenetic grid of Spear et al. (1999). The calculated Ti-saturation surface is curved such that for a given Mg/(Mg + Fe) value, Ti concentration increases as a function of temperature in a nonlinear fashion, and for a given temperature Ti concentrations decrease with an increase in Mg/(Mg + Fe). The fit to the Ti-saturation surface can be reformulated as the geothermometric expression: $T = \{[\ln(\mathrm{Ti}) - a - c(X_{\mathrm{Mg}})^3]/b\}^{0.333}$, in which T is temperature in degrees Celsius, Ti is the number of atoms per formula unit (apfu) normalized on the basis of 22 O atoms, X_{Mg} is Mg/(Mg + Fe), $a = -2.3594$, $b = 4.6482 \times 10^{-9}$ and $c = -1.7283$. The calibration range for this expression is $X_{\mathrm{Mg}} = 0.275$–1.000, Ti = 0.04–0.60 apfu, and $T = 480$–800 °C. Precision of the Ti-in-biotite geothermometer is estimated to be ±24 °C at the lower temperature range and improves to ±12 °C at higher temperatures. Application of the Ti-in-biotite geothermometer to ilmenite- or rutile-bearing, graphitic, peraluminous metapelites equilibrated at 3–6 kbar is generally consistent with independent temperature determinations, but with some deviations that represent local reequilibration. Consequently, the Ti systematics in biotite can also serve as the basis of a very sensitive indicator of chemical equilibrium, or lack thereof. Application of the geothermometer to metapelites not containing the requisite mineral assemblages can lead to minor-to-significant errors in estimated temperatures.

Biotite Ti-substitution mechanisms are controlled by several factors. Based on the biotite calibration data set, magnesian biotites ($X_{\mathrm{Mg}} > 0.65$) incorporate Ti in accordance with the exchange vector $\mathrm{TiAl_2R_{-1}Si_{-2}}$, where R is the sum of the divalent cations Mg + Fe + Mn. This substitution mechanism is primarily a response to misfit of the octahedral and tetrahedral layers in magnesian biotites. Intermediate biotites ($X_{\mathrm{Mg}} < 0.65$), particularly at higher temperatures, exhibit enhanced Ti concentrations, most consistent with the Ti-deprotonation $\mathrm{TiO_2R_{-1}(OH)_{-2}}$ exchange vector. Dominance of Ti-deprotonation substitution is largely a function of reduction of H_2O activity at higher metamorphic grades. Supplementary biotite data from metaluminous amphibolites and mafic granulites, metamorphosed isothermally with variable H_2O activities, reveal that low-Al biotite incorporates significantly higher concentrations of Ti relative to peraluminous biotite as a result of a combination of the exchange vectors $\mathrm{TiO_2R_{-1}(OH)_{-2}}$ and $\mathrm{RSiAl_{-2}}$ substituting in roughly an 8:1 ratio.