Titanium in muscovite, biotite, and hornblende: Modeling, thermometry, and rutile activities of metapelites and amphibolites

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ABSTRACT

Reactions involving the $^{VI}$Ti$^{IV}$Al$^{IV}$Al$^{IV}$Si exchange in muscovite, biotite, and hornblende were calibrated thermodynamically using a set of experimental and natural data in rutile- plus quartz- coesite-bearing assemblages. The specific respective reactions are

\[ K(Al_3)(AlSi_3)O_{10}(OH)_2 + TiO_2 = K(AlTi)(AlSi_3)O_{10}(OH)_2 + SiO_2 \] (R1)

\[ K(\square MgAl)Si_3O_{10}(OH)_2 + TiO_2 = K(\square MgTi)AlSi_3O_{10}(OH)_2 + SiO_2 \] (R2)

\[ Ca_2Mg_3Al_4Si_2O_{22}(OH)_2 + 2TiO_2 = Ca_2Mg_3Ti_2Al_4Si_2O_{22}(OH)_2 + 2SiO_2, \] (R3)

Ideal mixing on octahedral or octahedral plus tetrahedral sites and a non-ideal van Laar solution model yield the best regression results for thermodynamic fit parameters, with $R^2$ values of 0.98–1.00. Isopleths of the equilibrium constant ($K_{eq}$) show minimal pressure dependencies of $<1$ °C/kbar, implying that the equilibria are poor barometers. Model reproducibility of the ideal portion of the equilibrium constant ($K_{id}$) is excellent (ca. ±0.1 to 0.3, 2σ), but the absolute value of the combined term $\Delta S + K_{id}$ is quite small (absolute values from 0 to 4), so calibration residuals propagate to temperature errors $>\pm50–100$ °C. Whereas the consistency of a mica or hornblende composition with a known $T$ can be evaluated precisely, Ti chemistry in these reactions is sensitive to composition and does not resolve $T$ or $P$. Although the activity of TiO$_2$ in rutile [$a(rt)$] was also evaluated using both the garnet-rutile-ilmenite-plagioclase-quartz (GRIPS) equilibrium and our new calibrations in rutile-absent, ilmenite-bearing rocks whose peak $P$-$T$ conditions are otherwise known. Metapelites have average $a(rt)$ of 0.9 (GRIPS) and 0.8 (R1), whereas amphibolites have $a(rt)$ of 0.95 (GRIPS and R3). A value for $a(rt)$ of 0.80 ± 0.20 (metapelites) and 0.95 ±0.05–0.25 (amphibolites) is recommended for trace-element thermobarometers in ilmenite-bearing, rutile-absent rocks. The dependence of Ti contents of minerals on $a(rt)$ and the reequilibration of Ti during metamorphic reactions both deserve further exploration, and may affect application of trace-element thermobarometers.

Keywords: Titanium, rutile, muscovite, biotite, hornblende

INTRODUCTION

Trace-element thermobarometry holds promise of superior accuracy and precision in metamorphic rocks. For example, combined calibration and analytical errors for Ti-in-zircon, Ti-in-ilmenite, and Zr-in-rutile thermometers are as low as ±5–10 °C (Watson et al. 2006; Wark and Watson 2006; Tomkins et al. 2007) and ±20 °C for Zr-in-titanite (Hayden et al. 2008), similar to the measured reproducibility of these thermometers in natural rocks (e.g., Zack et al. 2004; Spear et al. 2006). Recently, the Ti content of muscovite/phengite was proposed as a barometer based on the exchange $^{VI}$Ti$^{IV}$Al$^{IV}$Al$^{IV}$Si in mica in equilibrium with rutile + quartz/coesite, and was calibrated using an experimental database (Auzanneau et al. 2010). Here we further explore the $P$- and $T$-dependencies of this exchange in muscovite/phengite, biotite, and hornblende, augmenting experimental data with a rich database of natural samples.Considering a broad interest in determining the activity of TiO$_2$ in rutile [$a(rt)$] in metamorphic rocks, we further explore implications of these equilibria for estimating this quantity in typical metapelites and amphibolites, with a large database of ilmenite-bearing, rutile-absent rocks.

Note that we use the term “$a(rt)$” to refer to the activity of pure TiO$_2$ in rutile rather than “$a(TiO_2)$,” because TiO$_2$ can form numerous structural states—rutile, anatase, brookite, etc.—each with its own reference thermodynamic properties. This notation follows the convention of referring to activities of end-member mineral species with abbreviations in lowercase, e.g., $a(an)$ = activity of pure anorthite in feldspar, $a(fo)$ = activity of pure forsterite in olivine, etc. We do, however, capitalize element abbreviations, e.g., $a(Tibt)$ = activity of the pure titanium biotite end-member.