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$^{IV}$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

\[ K(Al_2)(AlSi_3)O_{10}(OH)_2 + TiO_2 = K(AlTi)(AlSi_3)O_{10}(OH)_2 + SiO_2 \]  

(R1)

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

(R2)

\[ Ca_2Mg_5Al_2Si_6O_{22}(OH)_2 + 2TiO_2 = Ca_2Mg_5Ti_2Al_2Si_6O_{22}(OH)_2 + 2SiO_2 \]  

(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 $<1 \text{ °C/kbar}$, implying that the equilibria are poor barometers. Model reproducibility of the ideal portion of the equilibrium constant ($K_0$) is excellent (ca. $\pm 0.1$ to 0.3, $2\sigma$), but the absolute value of the combined term $\Delta S^{id} + K_0$ is quite small (absolute values from 0 to 4), so calibration residuals propagate to temperature errors $>\pm 50–100 \text{ °C}$. 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 $P$ well. 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 $\pm$ 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 $\pm 5–10 \text{ °C}$ (Watson et al. 2006; Wark and Watson 2006; Tomkins et al. 2007) and $\pm 20 \text{ °C}$ 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$^{IV}$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 “$a(\text{TiO}_2)$,” 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.
EXPERIMENTAL METHODS

Data were obtained from the literature (Appendix 1 and online resources), focusing on studies that documented pressure, temperature, and a well-equilibrated mineral assemblage for each sample. Most data (ca. 85%) are from natural samples. Each natural or synthetic rock contained rutile and either quartz or coesite, and we assumed these minerals were chemically pure. To avoid regression bias, we sought to pair each P-T condition with a single mica or hornblende composition. A few studies present a single average P-T condition, but tabulate mica compositions from multiple rocks. In these cases, we rationalized that each mica composition might reflect a different P-T condition (either higher or lower than the average), and calculated an average mica composition. That is, if authors chose to present a single representative (average) P-T estimate, then we averaged all their mica compositions into a single representative composition. We recognize that this may obscure important compositional dependencies between Ti and other mica components, and return to this issue in our discussion. Ultimately, we calibrated equilibria based on 367 muscovite analyses, 104 hornblende analyses, and 191 biotite analyses. Two compositions of wonesite (Spear 1982) were included with biotite to better constrain mixing properties of Na in biotite. Besides rutile, quartz/coesite and muscovite, biotite or hornblende, nearly all natural samples also contained garnet and most contained plagioclase, without which temperature and pressure are difficult to calculate.

Pressures and temperatures span a wide range (Fig. 1) and were taken directly from each study without recalculation, except for three studies (Sevigny and Ghent 1989; Lang 1991; Sarour 1995), which we knew a priori had inconsistent P-T estimates compared with modern thermobarometric calibrations. For these instances, P-T conditions were calculated using a set of internally consistent thermobarometers: garnet-biotite temperatures were recalculated using the Ferry and Spear (1978) end-member calibration with the Berman (1990) garnet solution model, garnet-hornblende temperatures were calculated based on Graham and Powell (1984), and garnet-plagioclase-hornblende-quartz pressures were calculated based on Kohn and Spear (1990). Average temperature and pressure for data from Spear (1982) were based on Graham and Powell (1984) and Spear and Rumble (1986) [see also Kohn and Spear (1990)]. For samples that contained coesite, not quartz, we used THERIAK (De Capitani and Brown 1987) to calculate the activity of quartz, using the Holland and Powell database (1998), which considers key experiments on the quartz-coesite transition (Bose and Ganguly 1995; Zhang et al. 1996). We acknowledge that use of published P-T conditions that were determined with different methods may increase data scatter and degrade precision slightly. We chose not to recalculate all thermobarometric estimates to a single thermodynamic database, however, for several reasons. First, with the exception of three studies, the different methods used are already quite thermobarometrically consistent—typically within 20–30 °C and <1 kbar. Second, databases may be internally consistent, but inaccurate; by using a range of thermobarometric methods, we potentially improve accuracy. Last, and most importantly, the wide range in P-T conditions (Fig. 1) implies that even relatively large inconsistencies in P-T conditions in some data would not significantly affect our results.

Mica and hornblende compositions were calculated for minimum Fe3+ consistent with stoichiometry (Spear and Kimball 1984). Fe3+/Fe2+ = 0.0 for each biotite and muscovite analysis and nearly all hornblende analyses. A similar approach is assumed for many equilibria, including most Fe-Mg thermometers. Corrections for Fe3+ in hornblende do not significantly affect our results. For example, a model that uses average Fe3+ (calculated using Spear and Kimball 1984) results in R2 values of 0.990 vs. 0.995 for minimum Fe3+ for biotite and hornblende, compositions were projected into an idealized set of end-member components (Appendix 2), which are needed for regressing interaction parameters. For hornblende and biotite, Fe2+ was grouped with Al, and Fe3+ and Mn were grouped with Mg, noting that distinguishing between separate Fe- and Mg-components in biotite and hornblende did not resolve statistically different mixing parameters. This result has important implications for compositional trends and mixing behavior in biotite, which we discuss with respect to Mg-Ti “exclusion.” Titanium-end-members were chosen to conform to Al-Mg (Holland and Powell 1990). For biotite, the end-members were phillogopite [phl; K(MgAl)Si3O10(OH)2]; celadonite [cel; K4Al8Si8O24(OH)4]; and Na-biotite [Na4Al10Si8O26(OH)8]. For hornblende, the end-members were tremolite [tr; Ca2Mg3Si2O7(OH)4], cummingtonite [cmt; Mg3Si2O7(OH)], edenite [edn; NaCaMg2Si3O10(OH)2], glauconep; [Na2Mg2Al3Si3O10(OH)4], Ti-celadonite [Tiam; CaMg2Al3Si3O10(OH)4], and Ti-celadonite [tsc; CaMg2Al3Si3O10(OH)4]. For muscovite, projecting compositions resulted in poorer regression results than simply following standard procedures of assigning mica mole fractions based on cation sums and differences for assumed end-member components (Coggan and Holland 2002; Auzanneau et al. 2010). These standard end-members were muscovite [ms; KAl3Si3O10(OH)2], Ti-muscovite [Tims; KTiAl3Si3O10(OH)2], paragonite [par; NaAlSi3O10(OH)4], pyrophyllite [prl; Al2Si4O10(OH)8], celadonite [cel; K4Al8Si8O24(OH)4], and phlogopite [phl; K2Mg3Si3O10(OH)4]. Note that we modeled Ti-muscovite, rather than Ti-phlogopite (Auzanneau et al. 2010), and the end-member proportion of Ti-muscovite (xms) equals Ti atoms per formula unit (apfu). As with hornblende and biotite, we again grouped Fe-Mg-Mn. As demonstrated in Appendix 3, the choice of Ti-end-members makes no difference for modeling because they are derivable by adding other valid exchanges. Although certain compositions may appear to favor different exchanges (Henry and Guidotti 2002; Henry et al. 2005), we presume no ideal-interaction terms account for this effect.

The modeled reactions for muscovite, biotite, and hornblende are, respectively:

\[ K(Al)(AlSi3O10(OH)2) + TiO2 = K(Al2Ti)(AlSi3O10(OH)2) + SiO2 \] (R1)

\[ K[2MgAl]Si3O10(OH)2 + TiO2 = K2[2MgTi]AlSi3O10(OH)2 + SiO2 \] (R2)

\[ CaMg2Al3Si3O10(OH)4 + 2TiO2 = Ca2Mg2TiAl3Si3O10(OH)4 + SiO2 \] (R3)

Recent studies have focused on inferring mica mixing properties within the context of existing thermodynamic databases and thermochemical models (White et al. 2000; Coggan and Holland 2002; Tajcamová et al. 2009; Auzanneau et al. 2010). Although this approach confers modeling advantages, any database or modeling errors propagate to additional scatter in regressions and degrade reliability of a calibrated equilibrium. Consequently, we chose to regress all interaction parameters in addition to end-member properties. This independence from a thermodynamic database also allows more freedom to explore mixing models.

Various solution models were tested. For ideal ionic mixing in muscovite, our best-fit model corresponds to the site partitioning scheme of Coggan and Holland (2002). Their model distinguishes two octahedral sites (M2A and M2B) and uses Al-avoidance, i.e., random mixing of Al and Si on a single tetrahedral (T1) site that has a site multiplicity of two

\[ K_d[R1] = [\sigma(qz)(X_{Al},X_{O})(X_{Al},X_{O})][\sigma(qz)(X_{Al},X_{O})][\sigma(qz)(X_{Al},X_{O})][\sigma(qz)(X_{Al},X_{O})] \] (1)

Thus, octahedral Ti and Al are assumed to occupy the same octahedral sub-site (M2B) with a multiplicity of 1 (Coggan and Holland 2002; Auzanneau et al. 2010).

For biotite and hornblende, octahedral-only vs. octahedral-tetrahedral models produce nearly indistinguishable regression statistics, and for simplicity we use octahedral-only models

\[ K_d[R2] = [\sigma(qz)(X_{Al},X_{O})][\sigma(qz)(X_{Al},X_{O})][\sigma(qz)(X_{Al},X_{O})][\sigma(qz)(X_{Al},X_{O})] \] (2)

\[ K_d[R3] = [\sigma(qz)(X_{Al},X_{O})][\sigma(qz)(X_{Al},X_{O})][\sigma(qz)(X_{Al},X_{O})][\sigma(qz)(X_{Al},X_{O})] \] (3)

where octahedral Ti and Al are assumed to occupy the same site in biotite and the M2 site in hornblende. The assumed number of octahedral sites occupied by Ti and Al in biotite (i.e., 1, 2, or 3) affects the numerical value of \( K_d [\text{biotite}] \) by a constant factor, but has no influence on goodness of fit.

For non-ideal terms, van Laar (Holland and Powell 2003) and Margules models were considered, and the van Laar model produced superior regression diagnostics. For example, maximum Margules vs. van Laar R2 values were ca. 0.85 vs. 0.99, respectively. The van Laar model accommodates non-ideality both through interaction energies (W values) and pseudo-volume terms (V values). These terms cannot all be solved for simultaneously using linear regression, so we iterated on pseudo-volume values, seeking to maximize the quality of regression diagnostics (R2 and F) for the end-member properties [changes in volume (AV), entropy (ΔS),

1 Deposit item AM-12-022, Appendices 1–4 and data tables. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.
We maintained pseudo-volume values between 0.25 and 1.0, thus also limiting asymmetry but extending the range slightly. Outliers at the ±2σ level were successively eliminated, ultimately rejecting 71 muscovite analyses (19% of data), 18 hornblende analyses (17%), and 35 biotite analyses (18%). Quality of fit was evaluated by using stepwise linear regressions (probability of removal > 0.05) and through R² and F-statistics.

For comparing results of the new calibrations to rutile-absent rocks, data were taken from the literature focusing on the assemblage garnet + plagioclase + ilmenite + quartz coexisting with either muscovite + biotite or with hornblende (Appendix 1). The α(t) in these rocks was calculated following Ghent and Stout (1984). We first calculated the peak metamorphic P-T condition using established thermobarometers, and then solved for α(t) at that P-T condition using the garnet + rutile + ilmenite + quartz (GRAIL) equilibrium (thermochemical data from Thermocalc; Holland and Powell 1990, 1998; Appendix 4). Ilmenite compositions are rarely reported, so a composition of ilm_{hem}, was assumed, except for granulites, where a more appropriate composition of ilm_{hem} was assumed (e.g., Coolen 1980). We preferred not to use the garnet + rutile + aluminosilicate + ilmenite + quartz (GRAIL) barometer (Bohlen et al. 1983) for calculating α(t) in metapelitic rocks because the slope is substantially flatter than other barometric equilibria. Consequently, any errors in temperature lead to increased uncertainty in α(t). Typical pressure uncertainties of ±500–1000 bars for the different barometers yield uncertainties in calculated α(t) of ±0.1—0.2.

We also compared predicted and measured Ti concentrations for biotite compositions tabulated by Henry et al. (2005). Rather than calculating and plotting results for all data (in excess of 500 analyses), we followed Henry et al. (2005) in splitting data into 11 distinct metamorphic groups, then subdivided each group according to biotite Fe/(Fe+Mg) ratio, and averaged. The Fe/(Fe+Mg) subgroups were based on data density (greatest between 0.4 and 0.65) with Fe/(Fe+Mg) ratios of 0.2, 0.0—0.3, 0.3—0.4, 0.4—0.5, 0.4—0.5, 0.5—0.55, 0.55—0.8, 0.8—1.0, and >0.65. This approach resulted in 55 subgroups, most with 5–20 analyses, but one with 98, and several with only 1. The average biotite composition for each subgroup was projected into the same components used for calibration, and K_{cal} was calculated at the average P-T condition. The biotite Ti content was then predicted (T_{pred}) assuming α(qtz) = α(t) = 1.0 and compared with measured Ti (T_{meas}). All the rocks contain quartz, but >90% are rutile undersaturated, and most have insufficient data to allow us to calculate α(t). For rutile undersaturated rocks, we expect T_{pred} ≥ T_{meas} because, for a fixed value of K_{cal}, as defined by Equation 4, calculated Ti content increases with increasing α(t).

**RESULTS**

Regressions consistently produced high values for R² (0.976 for muscovite, 0.989 for biotite, and 0.995 for hornblende) and F (Table 1; Fig. 2). Overall, all equilibria are highly insensitive to pressure with slopes of –1 °C/kbar (muscovite), 0 °C/kbar (biotite), and 1 °C/kbar (hornblende; Fig. 1). The ±2σ scatter of data about the best-fit lines (±0.29, ±0.13, and ±0.19 in lnK_{cal}}
for muscovite, biotite, and hornblende reactions, respectively), is small in comparison to the spacing of $\ln K$ isopleths (Fig. 1). This does not necessitate, however, good temperature sensitivity. With large contributions from non-ideal interaction parameters and comparable magnitudes of entropy ($\Delta S$) and $\ln K_{id}$, calculated temperatures may be quite sensitive to composition. We return to this point in our discussion of Ti-thermometry.

**DISCUSSION**

**Ti-in-mica and Ti-in-hornblende thermobarometry**

Auzanneau et al. (2010) proposed that the $^{3+}\text{Ti}^{4+}\text{Al}^{3+}\text{Al}^{4+}\text{Si}$ exchange in muscovite and phengite in equilibrium with rutile and quartz or coesite could be used as a barometer, but based their calibration only on experimental data collected at extreme $P$-$T$ conditions (15–80 kbar and 800–1050 °C). In contrast, our regressed value for $\Delta V$ including more typical $P$-$T$ conditions is approximately 10 times smaller, and isopleths of $\ln K_{id}$ are nearly vertical in $P$-$T$ plots. Thus, we infer a pressure dependence too small to be useful for geobarometry. Although Ti content in muscovite can decrease with increasing pressure at a particular temperature, we ascribe this to non-ideal interaction with increasing celadonite and Fe-celadonite components. The disparity between the Auzanneau et al. (2010) calibration and ours cannot be definitively identified, but we note that their calibration is for limited bulk compositions at the extreme $P$-$T$ conditions amenable to experiments. Correlations between parameters occur in all regressions, and a different $\Delta V$ for their data would be balanced by different values for end-member thermodynamic properties and interaction parameters. Although the different assumed Ti end-members do not allow direct comparison between these two studies, our model generally includes much larger interaction terms among octahedral Mg-Al-Ti than does theirs, and a negative, rather than positive $\Delta S$; these terms may be balanced by a lower $\Delta V$.

The steep slopes and close spacing of $\ln K$ isopleths (Fig. 1) at first suggest the equilibria might be useful as thermometers. Thermometric accuracy and precision, however, also depend on mixing energetics, specifically $\Delta H + (P - 1)\Delta V + RT\ln K_{id}$, and $\Delta S - \ln K_{id}$

$$T = \frac{H + (P - 1)V + RT\ln K_{id}}{S - R\ln K_{id}}$$  (9)

In some rocks, $|\Delta S - \ln K_{id}|$ is so small that calculated temperatures are uncertain by over 1000 °C, although $\ln K$ is fit closely. For example, plots of calculated vs. calibrant temperature (Fig. 3) consistently show large scatter, in excess of ±100 °C, even when restricting consideration to compositions that correspond with the maximum values of $|\Delta S - \ln K_{id}|$, and for which temperatures should be most accurate. We have checked these results against our own samples that contain rutile + quartz + muscovite + biotite + hornblende, but have recovered accurate temperatures in only a few cases. Therefore, we have little confidence that equilibria R1–R3 can be useful as thermometers. We also tested numerous solution model permutations, and all appear to share these large errors. Thus, we presume that thermometric imprecision is an inherent property of Ti contents of micas and hornblende, at least within the context of the simple reactions that we modeled.

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**Table 1.** Regressed parameters for Ti equilibria

<table>
<thead>
<tr>
<th>Muscovite</th>
<th>Biotite</th>
<th>Hornblende</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H/RT\Delta T$</td>
<td>$-8302 \pm 207$</td>
<td>$-3010 \pm 124$</td>
</tr>
<tr>
<td>$\Delta V/RT\Delta T$</td>
<td>$-5.13 \pm 0.11$</td>
<td>$-1.733 \pm 0.083$</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.976</td>
<td>0.989</td>
</tr>
</tbody>
</table>

*Note: Pseudo-volume values (θ) for biotite and hornblende are 1.0 (celbt, Tibt, Mgts, phil, Tiam, edn), 0.63 (cel, ms, phl), 0.5 (prl), and 0.37 (pa); R is the ideal gas constant; R* is the multiple correlation coefficient.*
Titanium systematics in biotite and Mg-Ti exclusion

A negative correlation between Mg/(Fe+Mg) and Ti has long been recognized in biotite (e.g., Guidotti 1984). Mg-Ti exclusion could reflect greater non-ideality of mixing for Mg-Ti than for Fe-Ti, but could also simply reflect correlation between Fe/(Fe+Mg) and other components that mix non-ideally with titanium. These possibilities are explored here within the context of two models: Henry et al. (2005), which has an explicit dependence of Ti on Fe/(Fe+Mg), and our model, which has identical Mg-Ti and Fe-Ti interactions. The Ti content of biotite coexisting with either rutile or ilmenite in metapelitic rocks clearly correlates with temperature and composition (Henry and Guidotti 2002; Henry et al. 2005), and the Henry et al. (2005) model accurately represents such biotite Ti contents (Fig. 4). In comparison, our

**Figure 3.** Modeled vs. calibrated temperature, showing large scatter, even when restricting consideration to samples with relatively large $\Delta S - R\ln K_{id}$. (a) Muscovite. (b) Biotite. (c) Hornblende.

**Figure 4.** Predicted vs. measured Ti in biotite. (a) Model of Henry et al. (2005), which accounts for temperature and Fe/(Fe+Mg), showing generally good predictive accuracy for all compositions. (b) This study, showing predicted values greater than or equal to measured values, as expected in rocks at or below rutile saturation. Deviations for highest Ti biotite are for high-temperature, ilmenite-bearing rocks. (c–e) Biotite from restricted ranges of metamorphic grade (temperature) and Fe/(Fe+Mg) (=FM). Our model shows generally good correlation with observed Ti contents, whereas the model of Henry et al. (2005) shows nearly invariant predicted values. These data suggest that Mg-Ti interaction alone does not explain the correlation between Fe/(Fe+Mg) and Ti content (Mg-Ti exclusion).
model as applied to the same data set, predicts Ti contents that equal or exceed measured Ti, as expected for rocks at or below rutile saturation. The largest deviations from a 1:1 line occur at the highest Ti values for biotite with Mg/(Fe + Mg) > 0.5 that coexists with ilmenite at the highest temperatures. We ascribe this misfit to lower \(a(rt)\) in these rocks. Thus, both models can be reconciled with the data, and do not directly discriminate the cause of negative Mg/(Fe+Mg)–Ti correlation.

Because \(a(rt)\) cannot yet be quantified in the most of the data tabulated by Henry et al. (2005), we also consider compositional trends within individual subgroups, i.e., at nearly fixed \(P\) and \(T\). In principle, if Ti contents reflect Mg-Ti exclusion, then there should be little Ti variation within a subgroup. If instead non-ideal mixing between Ti and other biotite components is important, then our model should match variations in Ti content better. For these subsets, the predicted Ti content (\(T_{\text{pred}}\)) with the Henry et al. (2005) model is nearly constant, with the largest differences reflecting different assumed temperatures. In fact, if temperatures are assumed to be the same in all rocks from the same subgroup, then \(T_{\text{pred}}\) is the same to within ±0.005 atoms per formula unit. Some subgroups show little variation in Ti or other measures of biotite chemistry (Fig. 4c), but others show measured Ti (\(T_{\text{meas}}\)) up to 5–10 times larger than the variation predicted by Henry et al. (2005) (Figs. 4d–4e). In contrast, our model predicts variable Ti contents related to other compositional components, e.g., extent of other exchanges such as Tschermak’s, diotahedral, talc, etc. Our model generally matches \(T_{\text{meas}}\) much more closely than does Henry et al.’s (2005), especially at higher temperatures where compositional variability is greater. Thus non-ideal mixing with other biotite components, not just Fe/(Fe+Mg), must be important for understanding Ti contents.

We further explored Mg-Ti exclusion by regressing our compilation of biotite compositions in rutile-bearing rocks for separate phlogopite vs. annite interactions, reasoning that true Mg-Ti exclusion would imply statistically different interaction terms. Yet the two interaction terms are identical in error: \(W_{\text{phl}}/R = 2400 ± 250\) vs. \(W_{\text{ann}}/R = 2120 ± 220\), or \(W_{\text{ann-phl}}/R = 280 ± 330\). In principle this could reflect compensation among Mg-Ti, Mg-Al, Fe-Ti, and Fe-Al interactions because \(W_{\text{phl}}/Ti = W_{\text{phl-celt}}\) and \(W_{\text{ann}}/Ti = W_{\text{ann-celt}}\). Although some studies have argued for different interactions for Fe-Al vs. Mg-Al (e.g., Tajcmanová et al. 2009), most show or assume indistinguishable values (e.g., Hoisch 1990; Auzanneau et al. 2010), implying that Mg-Ti interaction is similar to Fe-Ti.

So, does Mg-Ti exclusion occur in biotite? Certainly biotite with higher Mg/(Fe+Mg) tends toward lower Ti in many rocks, but also toward lower Al and higher silicon. Given these considerations as well as trends in rocks from restricted \(P\)-\(T\) conditions (Figs. 4c–4e) and regression results, negative correlation between Mg/(Fe+Mg) and Ti content in biotite probably reflects interactions between Ti and other components that may be correlated with Mg/(Fe+Mg), rather than predominant Mg-Ti interaction alone.

**\(a(rt)\) in typical metamorphic rocks**

Pioneering work by Ghent and Stout (1984) for rocks that contained assemblages that lacked rutile but buffered \(a(rt)\) implied \(a(rt) = 1.0\) in metapelites and low-temperature amphibolites, but \(a(rt) = 0.5\) in higher-temperature, clinopyroxene-bearing amphibolites. The calculated \(a(rt)\) values depended critically on pressures derived from the GRIPS or GAIL barometers (Bohlen et al. 1983; Ghent and Stout 1984; Bohlen and Liotta 1986) and the assumed pressure of equilibration. In the case of the higher-\(T\) amphibolites, subsequent advances in metabasite barometry revealed much higher peak pressures (Kohn and Spear 1990), implying higher calculated \(a(rt)\). In addition, the intervening years have generated a far larger database for these rocks. Thus, a reevaluation of typical \(a(rt)\) values based on GRIPS is warranted. The new calibrations offer additional measures of \(a(rt)\), independent of garnet equilibria.

Unfortunately, GRIPS-based estimates of \(a(rt)\) are quite scattered, with many values that exceed 1.0, even approaching 1.5 (Figs. 5–6). Such values, which are thermodynamically impermissible, imply large pressure errors (ca. 2 kbar) in either GRIPS or assumed \(P\)-\(T\) conditions. Both GRIPS and \(P\)-\(T\) estimates are based on garnet-plagioclase equilibria, strongly correlating these calculations, and making such a large uncertainty unlikely. Nonetheless, with values of 0.9 ± 0.25 in metapelites and 0.95 ± 0.25 in amphibolites, GRIPS does imply that most ilmenite-bearing rocks are nearly rutile saturated. This result is consistent with Henry et al. (2005), who noted that the Ti content of biotite did not depend on whether rutile or ilmenite was the saturating Ti oxide.

Our new calibrations can also be solved for \(a(rt)\) in these rocks, and similarly imply high-average \(a(rt)\) of 0.8 ± 0.2 for metapelites (muscovite) and 0.95 ± 0.25 for amphibolites (hornblende). Biotite compositions imply \(a(rt) = 0.95 ± 0.2\). Although these results are scattered, with the exception of hornblende in granulites, few \(a(rt)\) values exceed 1.0 by more than the 2σ calibration error (corresponding to 5 biotite analyses or <2% of the total data set). The large range of \(a(rt)\) based on hornblende in granulites probably reflects differential reequilibration of minerals during cooling (e.g., Pattison et al. 2003).

Comparison of \(a(rt)\) estimates using our new equilibria vs. GRIPS is disappointingly inconsistent (Fig. 6), perhaps reflecting large uncertainties in GRIPS-based estimates. Regardless, the new equilibria and GRIPS on average consistently imply near-saturation of most ilmenite-bearing rocks with rutile. Considering all equilibria, we recommend conservative values for \(a(rt)\) in rocks that lack rutile but contain ilmenite of 0.80 ± 0.20 in metapelites and 0.95 ± 0.05/−0.25 in amphibolites. This range covers nearly all the lower values but does not exceed saturation. A higher average value and more restricted range for \(a(rt)\) in amphibolites is generally consistent with rutile saturation in more Mg-rich bulk compositions (Guidotti 1984; Spear 1993). As applied to trace-element thermometers, the preferred \(a(rt)\) values shift calculated temperatures by less than 20 °C at a specified pressure, while the uncertainty limits of ±0.15 to ±0.2 introduce temperature uncertainties of ca. ±10–20 °C (Watson et al. 2006; Wark and Watson 2006; Tomkins et al. 2007; Hayden et al. 2008).

We also tested the muscovite model of Auzanneau et al. (2010) against experimental and natural data for rutile-bearing rocks, and for rutile-absent, ilmenite-bearing rocks (Fig. 6d). Their model predicts \(a(rt) \sim 1.0\) for experiments (the basis of their calibration), as expected, but drastically underestimates \(a(rt)\) for natural rocks: the average estimated \(a(rt)\) for rutile-
bearing rocks is ~0.17 (vs. 1.0), and for ilmenite-bearing rocks is ~0.07 (vs. ~0.9; Fig. 6d). The reason for the underprediction may lie simply in Auzanneau et al.’s (2010) regressed value of $\Delta V$, which is considerably larger than calibration on an expanded data set indicates. Because $a_{\text{rt}}$, in the denominator of $\ln K_{\text{id}}$ (Eqs. 1–3), decreases with decreasing $P\Delta V$, a larger $\Delta V$ causes a larger decrease to $a_{\text{rt}}$. This appears not only in the spuriously low values for natural rutile-bearing rocks, but also when comparing rutile-absent (ilmenite-bearing) and rutile-bearing assemblages (Fig. 6d).
Titanium contents of major minerals

One surprising result of our study is that the Ti contents of micas and hornblende approximate expected compositions in equilibrium with rutile, even when rutile is not present. We have tried numerous different regression approaches, and this result appears independent of solution model choice, and not simply an artifact of our chosen regressions. This could indicate that most rocks are nearly rutile-saturated. Yet, one might alternatively question whether Ti fully equilibrates in metamorphic rocks—does a high-valence ion, hosted exclusively in accessory phases or as a minor or trace constituent of major phases, maintain equilibrium on a scale of millimeters to centimeters in rocks?

If Ti concentrations in major phases generally increase during heating, then Ti-bearing accessory minerals must progressively dissolve. Thus, if equilibration is limited through intergranular transport, Ti concentrations near micas and amphiboles should be lower than near accessory minerals, the local $a$ of micas and amphiboles—“see” will be lower than anticipated, and major mineral $a$ contents will be too low. While this hypothesis deserves additional attention, we do note its inconsistency with the systematic behavior of Ti in micas and amphiboles—how could so many rocks with such a range of bulk compositions, assemblages, and reaction histories produce such remarkably consistent calibrations? This hypothesis also cannot explain the high-Ti contents of mica and amphibole in rutile-undersaturated rocks. Continuing questions regarding Ti systematics during metamorphism, and its importance to trace-element thermometry, recommend further exploration that particularly focuses on rutile-absent rocks with low a and on low-temperature rocks where transport is likely to be slowest.

**Concluding Remarks**

The cation exchange $\text{V}^2\text{Ti}^4\text{Al}^3\text{Si}$ in micas, amphiboles, and potentially other mineral groups is the basis for equilibria in rocks containing rutile and either quartz or coesite. Calibration of this reaction in muscovite, biotite, and hornblende shows nearly vertical isopleths of $K_{\text{eq}}$ on $P$-$T$ diagrams and ineffective barometers, in strong contrast to the systematic pressure-dependence and large $A\delta$ of reaction inferred by Auzanneau et al. (2010). The equilibria do not appear successful as thermometers, however, because $A\delta$ ~ $\text{Rln}K_{\text{eq}}$. A decrease in Ti content with increasing Mg/Fe+Mg does not appear to reflect non-ideal Mg-Ti interaction alone, but rather correlated changes in Fe/Fe+Mg with other components that also mix non-ideally. Average $a$ in typical ilmenite-bearing metapelites and amphibolites appears $\geq 0.8$.

**Acknowledgments**

M. Williams and D. Henry provided detailed and incisive reviews to earlier versions of this manuscript that wholly changed our outlook on Ti contents of micas and hornblende, and significantly improved the scientific content. Subsequent reviews from D. Henry, J. Ferry, and D. Pattison helped focus our thoughts and discussion further. These reviews, taken together, form the most comprehensive, insightful, and useful commentary on a manuscript that we have ever received. Funded by NSF EAR0809428 and EAR010242 to M.J.K.

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