ORIGINAL PAPER

Modeling prograde TiO$_2$ activity and its significance for Ti-in-quartz thermobarometry of pelitic metamorphic rocks

Kyle T. Ashley · Richard D. Law

Abstract Since its calibration, the Ti-in-quartz thermobarometer has been applied to a wide variety of geologic scenarios. The abundance of quartz in the continental crust and the involvement of silica in metamorphic reactions, deformation, and fluid flux processes make it a particularly powerful tool for constraining the pressure and temperature evolution of rocks, which is essential for developing tectonic models. Being able to quantitatively determine the solubility of Ti in quartz, however, is dependent upon being able to determine the activity of TiO$_2$ in the rock during quartz growth or re-equilibration. Here we calculate TiO$_2$ chemical potentials of the system relative to that of rutile (as a standard state), projected in P–T space for an average sub-aluminous pelite composition. Titania activities are calculated from these dependent potentials, with resultant activities used to correct for Ti isopleth projection in the Thomas et al. (2010) solubility equation. The modeling results are in good agreement with previous studies that suggest ilmenite-bearing assemblages buffer high TiO$_2$ activities and titanite-bearing assemblages have much lower activities (≥ 0.5). At elevated temperatures, however, significant deviation from an assumed average pelite activity of 1.0 occurs, where the projected Ti concentration in quartz is up to 400 % different when assuming a dynamic system activity. This is due, in part, to the sequestering of Ti in biotite during heating and the destabilization of Ti-oxides at higher temperatures. With quartz-producing reactions, deformation-driven solution-transfer processes and other Si-mobilization events occur during the prograde and retrograde history of metapelites, and assuming TiO$_2$ activities associated with the peak metamorphic paragenesis may be misleading and result in significant errors in P–T calculations.

Introduction

The solubility of TiO$_2$ in quartz is strongly temperature and (to a lesser extent) pressure dependent, thereby providing a potentially powerful thermobarometer. This thermobarometer is increasingly informative due to the ubiquity of quartz in continental crust and the involvement of silica in metamorphic reactions, solution-transfer processes, and Si-charged fluid flux. Quantifying the amount of Ti likely to be incorporated into the quartz lattice is dependent upon several variables, including thermodynamic controls (enthalpy, entropy, and volume), temperature (T), pressure (P), and the activity of TiO$_2$ (a_{TiO_2}). Growth experiments at elevated P and T constrain the thermodynamics of the exchange of Ti for Si in the tetrahedral site in quartz (Wark and Watson 2006; Thomas et al. 2010; Huang and Audétat 2012). The lesser dependence of pressure on the system allows for adequate temperature estimation even if pressure can only be approximately constrained. Solubility of Ti in quartz is dependent on a_{TiO_2}, which is typically assumed to be fixed when quartz is grown or recrystallized in the presence of Ti-bearing phases. Titania activity may be calculated in systems where TiO$_2$ is not an essential stoichiometric component. It is important to accurately constrain

K. T. Ashley (✉) · R. D. Law
Department of Geosciences, Virginia Tech, 4044 Derring Hall (0420), Blacksburg, VA 24061, USA
e-mail: ktashley@vt.edu

this activity, because errors in calculated temperatures may arise if deviation from the true activity is large.

Ghent and Stout (1984) defined potential equilibria assemblages where titania activity could be reasonably constrained, with results suggesting activities of ~1 and ≥ 0.8 for metapelites and amphibolite facies felsic gneisses, respectively. In rutile-absent samples, the Gibbs free energy of the reaction $2FeTiO_3 = TiO_2 + Fe_2TiO_4$ has been used to calculate the effective (bulk) a_{TiO_2} (Wark et al. 2007; Ashley et al. 2013), where $FeTiO_3$ is ilmenite and Fe_2TiO_4 is ulvöspinel (TiO_2 is dissolved in phases). The Gibbs energy of formation $\left(\Delta G_{fmn}^{\circ} \right)$ from the Holland and Powell (1998) database can be used to calculate the Gibbs energy for the above reaction. A Van't Hoff (or Vukancic–Vukovic equation) chemical thermodynamic reaction isotherm can be used in conjunction with the equilibrium constant that relates ΔG_{rxn} to the chemical equilibrium constant (K_{eq}), where $\Delta G_{rxn} = -RT \ln (K_{eq})$. Incorporating the end-member activities of the products and reactants gives

$$\Delta G_{rxn} = -RT \ln \left[\frac{a_{TiO_2} a_{Fe_2TiO_4}}{\left(a_{FeTiO_3} \right)^2} \right].$$

Assuming ideality, where component activity is equivalent to the mole fraction of the Ti end-members, the equation can be re-arranged to calculate titania activity:

$$a_{TiO_2} = \frac{\exp \left(\frac{-\Delta G_{rxn}}{RT} \right) \cdot Y^2}{X}$$

where X and Y are the activities of ulvöspinel and ilmenite, respectively. Despite the utility of implementing these reactions for activity calculation in the absence of rutile, several problems may prevent the successful application of this potential thermometer. For example, ilmenite may form hematite lamellae and re-equilibrate (Harlov 2000; McEnroe et al. 2002). Also, there is very little ulvöspinel component in most metamorphic magnetites, and small analytical errors are likely to extrapolate to large errors in a_{TiO_2}, restricting this application to magmatic rocks (F. Spear, personal communications).

In this paper, we implement pseudosection modeling to calculate system a_{TiO_2} across the modeled P–T space. This approach bypasses the need for considering various Ti-reactions and allows for the calculation of titania activity in the absence of rutile, ilmenite, and titanite. With the output activity maps, corrected Ti isopleth projections into P–T space can be computed. The benefit to this approach is that quartz-producing metamorphic reactions can be better interpreted with respect to modeled a_{TiO_2}, giving pressure or temperature estimates with less uncertainty than would be expected if it is assumed that TiO_2 activity is constant throughout the prograde evolution.

Modeling approach and considerations

Thermodynamic modeling was conducted for the system MnO–Na_2O–CaO–K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O–TiO_2 (MnNCKFMASHT) through gridded minimization calculations using the program Perple_X (Connolly 2009) with the 2004 update of the Holland and Powell (1998) thermochemical database. Perple_X predicts the most stable configuration of phases through a Gibbs free energy minimization approach (Connolly and Kerrick 1987). Results from these calculations should be identical to results acquired in other programs (e.g., THERMOCALC; Powell et al. 1998) as long as the thermodynamic data and solution models are the same. Solution models used are as follows: (1) staurolite, garnet, chlorite, chloritoid, and hydrous cordierite formulation after Holland and Powell (1998), extended for Mn solid solution after Mahar et al. (1997). (2) ideal mixing for ilmenite–geikielite–pyrophanite; ternary feldspar from Fuhrman and Lindsley (1988); white mica (Coggon and Holland 2002; Auzanneau et al. 2010), not allowing for tschermaks or Ti substitutions in the Ca- and Na-subsystems; Ti–Fe^{3+}-biotite (Tajčmanová et al. 2009), extended to Mn solution after Tinkham et al. (2001). (3) Amphibole model after Dale et al. (2005); (4) compound formation for orthopyroxene after Powell and Holland (1999), with Holland and Powell (2011) modified site populations. (5) Clinopyroxene based on the Holland and Powell (1996) non-ideal quasi-ordered omphacite, modified for non-ideal Ca-tschermaks after Zeh et al. (2005). (6) Silicate melt modeling after White et al. (2001), with the White et al. (2007) modification of the faL (fayalite in melt) and foL (forsterite in melt) olivine melt end-members (an enthalpy adjustment to more closely reflect total Fe + Mg in silicate melt). It is safe to assume that the ilmenite–geikielite–pyrophanite solid solution is an ideal solution for two reasons. First, the majority of metamorphic ilmenites are restricted close to the ideal $FeTiO_3$ composition, with very high (>0.9) ilmenite activities in sub-aluminous metapelites (e.g., Ashley et al. 2013) and metabasites (e.g., Ghent and Stout 1984). In addition, only small deviations from ideality are detectable in such ilmenite–pyrophanite solution (O'Neill et al. 1989), and the exchange would not alter the stoichiometry with respect to TiO_2. Quartz, rutile, and titanite were considered as pure phases. Fluid was considered in excess and treated as pure H_2O.

Mineral abbreviations follow Whitney and Evans (2010) with the exception of "wm" for white mica. Calculations were based on the Mahar et al. (1997) modified average sub-aluminous pelite composition of Shaw (1956), including MnO with a reduced CaO content (Table 1). Additionally, modeling of an average greywacke composition (after Brownlow 1996, and references therein) was conducted to observe the effects of

Table 1 Bulk rock chemical data for average rock-type compositions (in mol%)

Rock-type	SiO_2	TiO_2	Al_2O_3	FeO_{tot}	MnO	MgO	CaO	Na_2O	K_2O	Ref.
Pelite	71.13	0.67	11.61	5.78	0.10	4.65	1.39	1.99	2.68	1, 2
Greywacke[a]	75.71	0.21	9.42	2.79	0.05	3.18	2.63	4.14	1.88	3

References: 1—Shaw (1956); 2—Mahar et al. (1997); 3—Brownlow (1996, and references therein)

[a] A minor MnO component was added because no data were reported for this component

Fig. 1 Modeled mineral stability for an average pelitic rock in the system Mn–Na₂O–CaO–K₂O–FeO–MgO–Al₂O₃–SiO₂–H₂O. *Bold lines* denote stability limits of the Ti-oxide phases. The position of the isobaric profile shown in Fig. 2 is indicated by the *dotted line*. Quartz and water is considered in excess. *Darker shaded* fields denote higher variance. Mineral abbreviations from Whitney and Evans (2010)
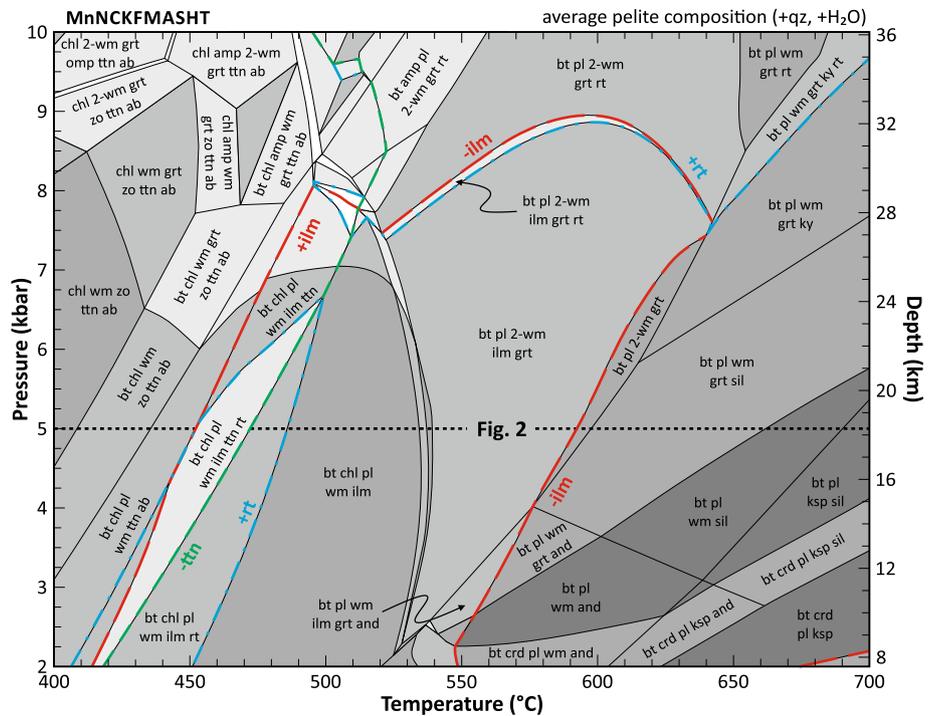
a lower clay component in the protolith rock (for metapsammitic and semi-pelitic rocks). The composition used did not include a MnO component; therefore, a minor amount (0.05 mol%) was included to better reflect concentrations observed in nature.

For the modeled P–T window, chemical potentials of the TiO_2 component (μ_{TiO_2}) were calculated with Perple_X (being the result of the computed molar Gibbs free energy). Modeling was performed on the complex (and realistic) MnNCKFMASHT system to take into account the effects of solid solution. Initial calculations were isobaric along a heating profile (Figs. 1, 2). Titania activity may be calculated when evaluating μ_{TiO_2} against an idealized standard state chemical potential ($\mu^\circ_{TiO_2}$). These standard state values were calculated for the P–T conditions of interest by saturating the modeled system in TiO_2 (thus stabilizing rutile in every mineral assemblage stability field), and calculating the dependent potential of rutile at each P and T. This is completed using the modeled entropy (S) and enthalpy (H) of rutile to determine the molar Gibbs free energy of pure TiO_2 at the T and P of interest—which is equal to

the chemical potential of rutile at these conditions (Spear 1993). This is expressed by

$$\mu^\circ_{TiO_2} = \bar{G}^\circ_{TiO_2} = U + PV - TS = H - TS \quad (1)$$

where U is the internal energy and V is volume. Component activity can then be calculated by the expression

$$a_{TiO_2} = \exp\left[\frac{\mu_{TiO_2} - \mu^\circ_{TiO_2}}{RT}\right] \quad (2)$$

where R is the gas constant (8.31446 J K⁻¹ mol⁻¹) and T is temperature (in K). If pure rutile is present as a phase in the bulk rock, then $\mu^\circ_{TiO_2} = \mu_{TiO_2}$ and $a_{TiO_2} = 1.0$.

Corrections to the fixed a_{TiO_2} projection of Ti isopleths (e.g., Fig. 3a; Thomas et al. 2010) can be completed through any of the Ti-in-quartz solubility equations. Here, we use the equation by Thomas et al. (2010) and calculate expected Ti concentrations ([Ti]) in quartz with the expression

$$RT \ln X^{quartz}_{TiO_2} = -60952 + 1.520 \cdot T(K)$$
$$- 1741 \cdot P(kbar) + RT \ln a_{TiO_2}. \quad (3)$$
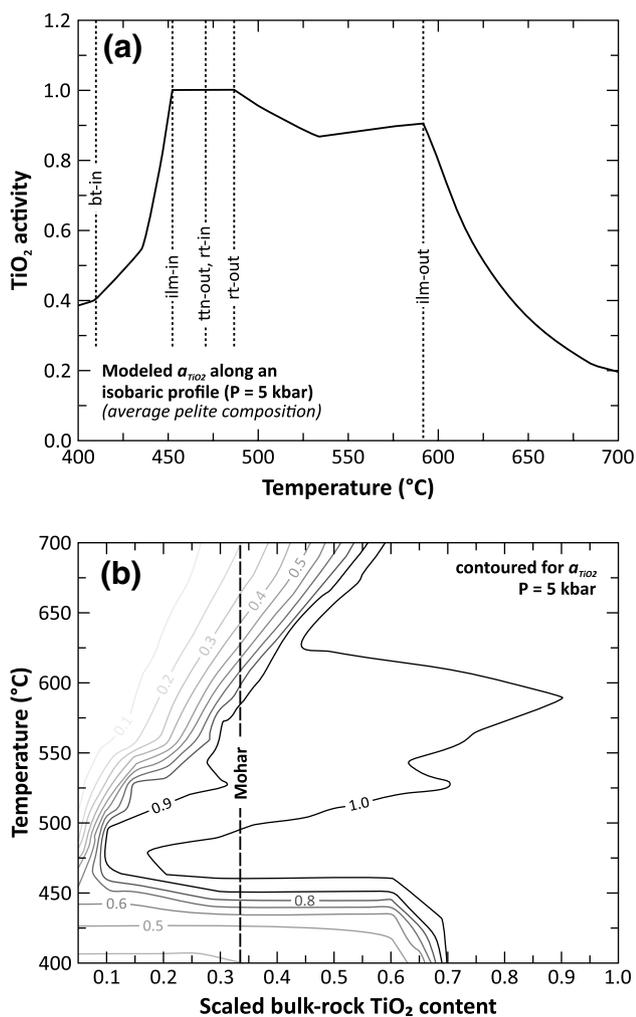
Fig. 2 **a** Calculated TiO_2 activity for an isobaric (5 kbar) profile of increasing temperature for an average pelite composition. This modeling suggests that TiO_2 activity is quite dynamic and rapidly decreases outside the ilmenite stability field. **b** The effects of varying bulk rock TiO_2 on corresponding component activity. The *x*-axis represents TiO_2 variation (in molecular proportions) between 0.1 (at $x = 0.05$) and 2.0 % (at $x = 1.0$). The *bold line* indicates the average pelite composition shown in (*a*)

Results

Pseudosection modeling of the average pelite composition shows the stabilization of ilmenite and rutile at the expense of titanite at ~450 °C, with rutile being largely restricted to high-*P* space (>8 kbar) and ilmenite stable at pressures below this (Fig. 1). Ilmenite breakdown occurs starting at 550 °C, extending to higher temperatures for higher pressures. This is consistent with what is observed in rocks from eastern Vermont (Ashley et al. 2013) and northern Scotland (Thigpen et al. 2013), where garnet porphyroblasts contain an abundance of ilmenite inclusions that the matrix is largely devoid of. With garnet growth initiated at

<550 °C in both these studies, heating to peak temperatures would result in ilmenite breakdown and explain the ilmenite distribution observed in these rocks. Outside the ilmenite window, mica (particularly biotite) is the major reservoir for Ti budgeting, with biotite sequestering more Ti at higher temperatures (e.g., Henry et al. 2005; Chambers and Kohn 2012).

Chemical potential of TiO_2 was modeled at 5 kbar between 400 and 700 °C (Fig. 2a). Calculated a_{TiO_2} across this profile shows that high activities are coincident with the presence of ilmenite (>0.85) and rutile (1.0). When buffered by the presence of titanite, the modeled activity is found to be variable, between 0.4 and 1.0 within a 50 °C window. At temperatures above the stability field of ilmenite (>480 °C), a_{TiO_2} rapidly decreases down to 0.2 at 700 °C. In Fig. 2b, the effect of varying bulk rock TiO_2 in the modeled activity profiles is considered, from 0.1 to 2.0 mol% (*x*-axis = 0.05–1.0). Results of this variation modeling suggest rocks that are depleted in TiO_2 relative to the average pelite considered here (labeled "Mahar" in Fig. 2b) produce a significant reduction in a_{TiO_2} in the modeled *P–T* space; minor increases in TiO_2 saturate the rock with this component and increase the activity across the temperature profile.

Pressure has a significant effect on resultant a_{TiO_2}, due to the stabilization of rutile at higher *P* (Fig. 3b), and results in larger temperature windows where titania activity is ~1.0. For example, at 9 kbar titania activities are <0.9 between 490 and 690 °C; at 4 kbar this temperature range is limited to 435–510 °C, with activities down to 0.2 at 700 °C. The implications of this variable activity become evident when Ti isopleths are projected in *P–T* space (Fig. 3c) and compared to isopleths calculated assuming a constant activity of 1.0 for pelites (Fig. 3a). At temperatures above 600 °C, Ti concentrations in quartz decrease with increasing temperature, which is counterintuitive to the substitution. When considering [Ti] of 35–40 ppm with a constant a_{TiO_2} of 1.0, the calculated temperature is 575 °C (at 6 kbar). When using the variable activity-corrected isopleths, two solutions are possible for this concentration and pressure: at 580 and 650–675 °C. At lower pressures, this offset would be even greater. The relative discrepancy between assuming a fixed versus variable titania activities can be considered by taking the percent difference between projected isopleth concentration in *P–T* space (Fig. 3d). In the titanite stability field, differences up to 100 % are observed. Even greater offsets occur at high temperatures and moderate pressures (up to 400 %). If bulk rock compositions are semi-pelitic or psammitic, Ti solubility in quartz is buffered with very low titania activities (Fig. 4), and only a very small window (425–475 °C, below 3 kbar) results in activities above 0.9.
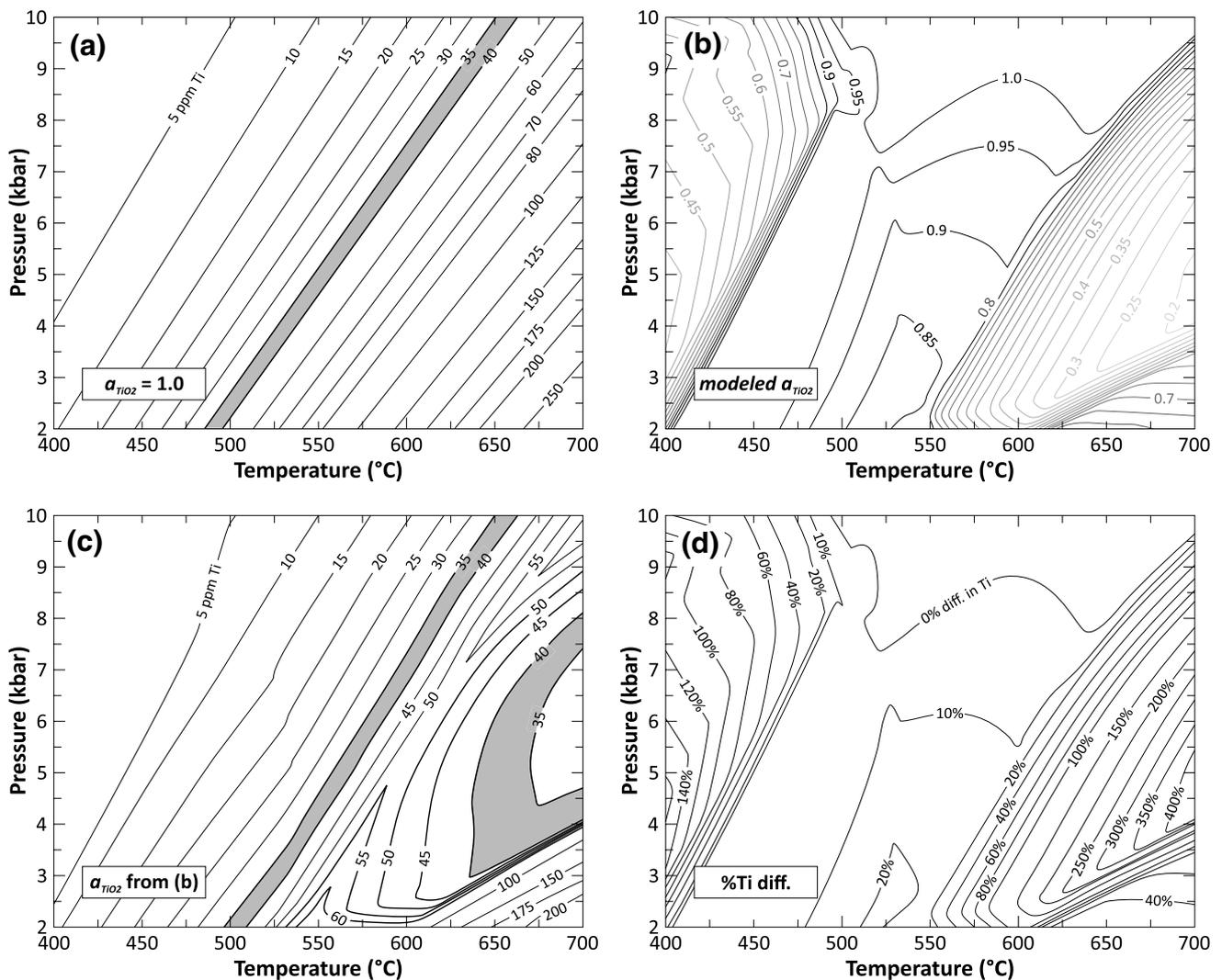
Fig. 3 **a** P–T projected Ti isopleths assuming a fixed titania activity of 1.0 (from Thomas et al. 2010). **b** Modeled a_{TiO_2} for average pelitic bulk composition from Mahar et al. (1997). **c** Corrected Ti isopleth projection, based on the activity map calculated in (*b*). **d** Percent dif- ference between [Ti] in quartz assuming a fixed activity of 1.0 and the modeled a_{TiO_2} shown in (*b*). Temperature >600 °C and <450 °C have significant variance in [Ti], up to 400 % at 700 °C (4 kbar)

Discussion

The modeling presented here suggests that a_{TiO_2} has a dynamic variability in P–T space for average pelite compositions. If quartz is produced within the ilmenite and rutile stability fields, it would equilibrate with high a_{TiO_2}. If growth occurs in the presence of titanite, the activity is typically 0.5 or above. These results are consistent with previous studies that calculate component activities based on appropriate reactions (Ghent and Stout 1984; Wark et al. 2007; Chambers and Kohn 2012). Chambers and Kohn (2012) calculated titania activities using Ti in biotite, muscovite, and amphibole; however these calculations result in considerable scatter and sometimes produce values above 1.0, which suggests supersaturation and is

thermodynamically impermissible. Their study does recognize that garnet–rutile–ilmenite–plagioclase–quartz equilibrium (GRIPS)-based estimation of TiO$_2$ activity in ilmenite-bearing rocks is consistently nearly rutile saturated; results are replicated here. It is important to note that thermodynamic calculations are sensitive to the solution models and thermodynamic datasets chosen and may vary if other models are implemented.

In this study, the Ti-in-quartz solubility equation by Thomas et al. (2010) was preferred for several reasons. First, Ti analyses by Ashley et al. (2013) in eastern Vermont indicate temperatures consistent with temperatures of quartz-producing metamorphic reactions when this calibration is considered. Use of the Huang and Audétat (2012) calibration results in temperatures >100 °C higher than
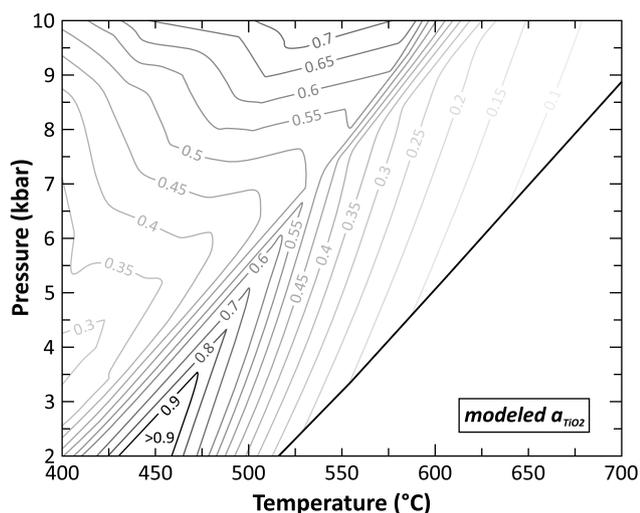
Fig. 4 Calculated titania activities in *P–T* space for a metamorphosed greywacke. The field to the *right of the bold line* only has biotite, feldspar, and quartz stable, and no activities could be calculated

expected for these rocks, based on the peak metamorphic paragenesis and exchange thermobarometry results. In addition, the Huang and Audétat (2012) experiments produced quartz with highly variable Ti concentrations. A recent study (Thomas et al. 2015) conducted static recrystallization reversal experiments that confirm the ability of quartz to re-equilibrate at various pressures and temperatures, despite its original starting composition, that is identical to concentrations predicted by the Thomas et al. (2010) solubility equation. A more critical evaluation of the various solubility equations is made by Thomas et al. (2015).

The susceptibility of quartz to participate in metamorphic reactions and the mobility of silica in deformation processes during the prograde evolution of a rock may result in zoned quartz (such as reported by Ashley et al. 2013) that has radically different observed a_{TiO_2} during different re-equilibration events. Owing to the slow diffusivity of TiO_2, post-growth modifications through volume diffusion due to perturbations in pressure and temperature are minimal unless temperatures are high (e.g., >700 °C) and/or metamorphic heating occurring over sufficiently long timescales (Spear et al. 2012; Ashley et al. 2013). Therefore this evolutionary record is expected to be preserved, unless re-equilibrated through dynamic recrystallization (see Discussion by Ashley et al. 2014 on the effects of dynamic recrystallization on Ti resetting). The modeled Ti isopleth projections presented here show the effects of such variability on Ti solubility in quartz. Therefore, assuming fixed activities of ~1.0 for pelites could result in large temperature errors, unless re-equilibration occurred in the presence of ilmenite or rutile. Rocks metamorphosed via contact metamorphism are expected to be most impacted

by these solubility consequences. The approach we present here provides a simple method for observing the evolution of this component activity and allows for better constraints when interpreting prograde quartz growth.

References

Ashley KT, Webb LE, Spear FS, Thomas JB (2013) *P–T–D* histories from quartz: a case study of the application of the TitaniQ thermobarometer to progressive fabric development in metapelites. Geochem Geophys Geosyst 14(9):3821–3843

Ashley KT, Carlson WD, Law RD, Tracy RJ (2014) Ti resetting in quartz during dynamic recrystallization: mechanisms and significance. Am Mineral 99:2025–2030

Auzanneau E, Schmidt MW, Vielzeuf D, Connolly JAD (2010) Titanium in phengite: a geobarometer for high temperature eclogites. Contrib Miner Petrol 159:1–24

Brownlow AH (1996) Geochemistry. Prentice Hall, Upper Saddle River

Chambers JA, Kohn MJ (2012) Titanium in muscovite, biotite, and hornblende: modeling, thermometry, and rutile activities of metapelites and amphibolites. Am Mineral 97:543–555

Coggon R, Holland T (2002) Mixing properties of phengitic micas and revised garnet-phengite thermobarometers. J Metamorph Geol 20(7):683–696

Connolly JAD (2009) The geodynamic equation of state: what and how. Geochem Geophys Geosyst 10(10):1–19

Connolly JAD, Kerrick DM (1987) An algorithm and computer program for calculating composition phase diagrams. Calphad 11(1):1–55

Dale J, Powell R, White RW, Elmer FL, Holland TJB (2005) A thermodynamic model for Ca–Na clinoamphiboles in Na_2O–CaO–FeO–MgO–Al_2O_3–SiO_2–H_2O–O. J Metamorph Geol 23:771–791

Fuhrman ML, Lindsley DH (1988) Ternary-feldspar modeling and thermometry. Am Mineral 73:201–215

Ghent ED, Stout MZ (1984) TiO_2 activity in metamorphosed pelitic and basic rocks: principles and applications to metamorphism in southeastern Canadian Cordillera. Contrib Miner Petrol 86:248–255

Harlov DE (2000) Titaniferous magnetite-ilmenite thermometry and titaniferous magnetite-ilmenite-orthopyroxene-quartz oxygen barometry in granulite facies gneisses, Bamble Sector, SE Norway: implications for the role of high-grade CO_2-rich fluids during granulite genesis. Contrib Miner Petrol 139(2):180–197

Henry DJ, Guidotti CV, Thomson JA (2005) The Ti-saturation surface for low-to-medium pressure metapelitic biotites: implications for geothermometry and Ti-substitution mechanisms. Am Mineral 90:316–328

Holland TJB, Powell R (1996) Thermodynamics of order-disorder in minerals: II. Symmetric formalism applied to solid solutions. Am Mineral 81:1425–1437

Holland TJB, Powell R (1998) An internally consistent thermodynamic data set for phases of petrological interest. J Metamorph Geol 16:309–343

Holland T, Powell R (2011) An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids. J Metamorph Geol 29:333–383

Huang R, Audétat A (2012) The titanium-in-quartz (TitaniQ) thermobarometer: a critical examination and re-calibration. Geochim Cosmochim Acta. doi:10.1016/j.gca.2012.01.009:31

Mahar E, Powell R, Holland TJB, Howell N (1997) The effect of Mn on mineral stability in metapelites. J Metamorph Geol 15(2):223–238

McEnroe SA, Harrison RJ, Robinson P, Langenhorst F (2002) Nanoscale haematite-ilmenite lamellae in massive ilmenite rock: an example of 'lamellar magnetism' with implications for planetary magnetic anomalies. Geophys J Int 151(3):890–912

O'Neill HSC, Pownceby MI, Wall VJ (1989) Activity-composition relations in $FeTiO_3$–$MnTiO_3$ ilmenite solid solutions from EMF measurements at 1050–1300 K. Contrib Miner Petrol 103:216–222

Powell R, Holland TJB (1999) Relating formulations of the thermodynamics of mineral solid solutions: activity modeling of pyroxenes, amphiboles, and micas. Am Mineral 84:1–14

Powell R, Holland TJB, Worley B (1998) Calculating phase diagrams involving solid solutions via non-linear equations, with examples using THERMOCALC. J Metamorph Geol 16:577–588

Shaw DM (1956) Geochemistry of pelitic rocks. Part III: major elements and general chemistry. Geol Soc Am Bull 67:919–934

Spear FS (1993) Metamorphic phase equilibria and pressure-temperature-time paths. Mineralogical Society of America, Washington D.C

Spear FS, Ashley KT, Webb LE, Thomas JB (2012) Ti diffusion in quartz inclusions: implications for metamorphic time scales. Contrib Miner Petrol 164:977–986

Tajčmanová L, Connolly JAD, Cesare B (2009) A thermodynamic model for titanium and ferric iron solution in biotite. J Metamorph Geol 27:153–165

Thigpen JR, Law RD, Loehn CL, Strachan RA, Tracy RJ, Lloyd GE, Roth BL, Brown SJ (2013) Thermal structure and tectonic evolution of the Scandian orogenic wedge, Scottish Caledonides: integrating geothermometry, deformation temperatures, and kinematic-thermal modeling. J Metamorph Geol 31:813–842

Thomas JB, Watson EB, Spear FS, Shemella PT, Nayak SK, Lanzirotti A (2010) TitaniQ under pressure: the effect of pressure and temperature on the solubility of Ti in quartz. Contrib Miner Petrol 160(5):743–759

Tinkham DK, Zuluaga CA, Stowell HH (2001) Metapelite phase equilibria modeling in MnNCKFMASH: the effect of variable Al_2O_3 and MgO/(MgO + FeO) on mineral stability. Mineral Soc Am Geol Mater Res 3(1):1–43

Wark DA, Watson EB (2006) TitaniQ: a titanium-in-quartz geothermometer. Contrib Miner Petrol 152:743–754

Wark DA, Hildreth W, Spear FS, Cherniak DJ, Watson EB (2007) Pre-eruption recharge of the Bishop magma system. Geology 35(3):235–238

White RW, Powell R, Holland TJB (2001) Calculation of partial melting equilibria in the system Na_2O–CaO–K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O (NCKFMASH). J Metamorph Geol 19:139–153

White RW, Powell R, Holland TJB (2007) Progress relating to calculation of partial melting equilibria for metapelites. J Metamorph Geol 25:511–527

Whitney DL, Evans BW (2010) Abbreviations for names of rock-forming minerals. Am Mineral 95:185–187

Thomas JB, Watson EB, Spear FS, Wark DA (2015) TitaniQ recrystallized: experimental confirmation of a Ti-in-quartz calibration. Contri Mineral Petrol. doi:10.1007/s00410-015-1120-0

Zeh A, Klemd R, Barton JM (2005) Petrological evolution in the roof of the high-grade metamorphic Central Zone of the Limpopo Belt, South Africa. Geol Mag 142(2):229–240