

Phase-equilibrium constraints on titanite and rutile activities in mafic epidote amphibolites and geobarometry using titanite–rutile equilibria

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ABSTRACT Activities of titanite (Ttn, CaTiSiO₅) and/or rutile (Rt, TiO₂) phase components were calculated for 45 well-characterized natural titanite- or rutile-undersaturated epidote–amphibolites by using the equilibria: (i) 3 anorthite + 2 zoisite/clinozoisite + rutile + quartz = 3 anorthite + titanite + water (referred to as TZARS) and (ii) anorthite + 2 titanite = grossular + 2 rutile + quartz (referred to as GRATIS). In titanite-bearing and rutile-absent samples a_{Rt} is 0.75 ± 0.26 . In titanite-absent, rutile-bearing samples a_{Ttn} is 0.89 ± 0.16 . Mean values derived for a_{Rt}/a_{Ttn} are 0.92 ± 0.12 for rutile + titanite-bearing samples and 0.42 ± 0.27 for samples lacking both titanite and rutile. Use of these values with TZARS yields pressure estimates for epidote–amphibolites that differ on average by <0.5 kbar from those recorded by established mineral barometers, even where both titanite and rutile are lacking. Despite rather large uncertainties in the average values obtained for a_{Rt} , a_{Ttn} or a_{Rt}/a_{Ttn} , application of TZARS yields pressure estimates that agree with independent estimates to within ± 0.5 kbar for titanite- and/or rutile-saturated samples, and to within ± 0.8 kbar for samples that contain neither Ti-phase. The accuracy and precision of the TZARS barometer are comparable to that of many well-calibrated barometers. TZARS offers a much-needed barometer for mafic rocks metamorphosed at epidote-bearing amphibolite and blueschist facies conditions. In addition, the results provide a basis for application of other thermobarometers, such as Ti-in-zircon, where rutile activity is required as input.

Key words: activity; epidote amphibolites; geobarometry; rutile; titanite.

INTRODUCTION

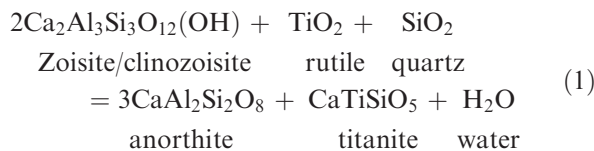
The epidote–amphibolite and epidote–blueschist facies comprise a large range of pressure (P) and temperature (T) that is encountered during metamorphism associated with convergent-margin processes (e.g. Evans, 1990; Spear, 1993). However, with the exception of some pelitic bulk compositions, reliable geobarometers are scarce at these conditions, especially when garnet, clinopyroxene and/or phengite are lacking from the lithology. Equilibria involving titanite and/or rutile offer an opportunity to overcome this problem and in addition provide P – T information to supplement studies in which these minerals are used for U–Pb geochronology (e.g. Frost *et al.*, 2000; Rubatto & Hermann, 2001) or as monitors of trace-element cycling (e.g. Zack *et al.*, 2002; Klemme *et al.*, 2005).

The potential utility of titanite–rutile equilibria can be appreciated by considering mafic bulk compositions. Equilibria involving the Ti-bearing phases have been explored for some assemblages (Ghent & Stout, 1984; Sorensen & Barton, 1987; Manning & Bohlen, 1991; Tropper *et al.*, 2002; Trop-

per & Manning, 2008), but not for metabasites containing amphibole + chlorite + epidote + plagioclase + quartz + Ti-bearing phase are common over a wide range of metamorphic conditions (Laird & Albee, 1981). This may reflect several uncertainties facing the petrologist. First, while this assemblage may contain coexisting rutile and titanite (e.g. Sorensen & Barton, 1987; Hansen, 1992), textural relations may suggest that the two minerals were stable at different points along a P – T path. Rutile is generally cited as being the stable phase at higher metamorphic pressure and lower temperature, whereas titanite is favoured at lower pressure and higher temperature (Laird & Albee, 1981; Spear, 1981; Ernst & Liu, 1998) and overgrowth or replacement textures are common. However, the fact that phases participating in the relevant net transfer reactions need not be pure – and titanite itself may contain Al and OH or F (e.g. Enami *et al.*, 1993) – highlights that there can be a finite P – T interval over which titanite and rutile may coexist. A second issue is that metabasites are commonly undersaturated with respect to one or both minerals. However, the absence of titanite and/or rutile need not prevent the use of

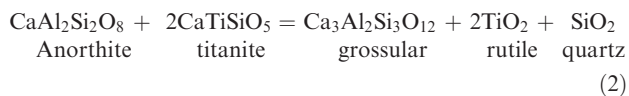
titanite–rutile equilibria if the extent of undersaturation is minimal or can be estimated. Ghent & Stout (1984) calculated that TiO_2 activities range from 0.43 to near rutile saturation in rutile-free mafic garnet–amphibolites. TiO_2 activities calculated for rutile-absent amphibolite facies metapelites (Ghent & Stout, 1984), eclogites (Manning & Bohlen, 1991) and granulites (Mukhopadhyay *et al.*, 1992) are even higher (~ 0.8 to near unity). On similar lines, Ti-in-zircon thermometry (Watson & Harrison, 2005; Watson *et al.*, 2006) can be successful even in rutile-undersaturated systems because of robust thermodynamic modelling (Ferry & Watson, 2007). Accordingly, titanite–rutile equilibria would appear to represent an unrealized opportunity for quantitative thermobarometry.

The net transfer reaction,



(referred to as TZARS) includes phases that are common in epidote-bearing metamorphic rocks. Forward progress of the TZARS reaction consumes epidote and is thus one of the reactions responsible for the prograde transition from epidote–amphibolite to amphibolite facies. The stoichiometric TZARS equilibrium lies roughly in the middle of the epidote–amphibolite stability field (Fig. 1). It exhibits a relatively shallow Clapeyron slope ($\sim 27 \text{ bar } ^\circ\text{C}^{-1}$ for pure phases) and a large $(\partial \ln K / \partial P)_T$ (Holland & Powell, 1998), where K is the equilibrium constant. Therefore, it has the potential to yield precise pressure estimates for epidote-bearing rocks, if temperatures and relevant phase activities can be determined. While the presence of a fluid phase may limit the utility of many reactions for quantitative thermobarometry or activity calculations, it will be shown that TZARS is weakly sensitive to the activity of water ($a_{\text{H}_2\text{O}}$) and that the TZARS assemblage in the absence of calcite is stable only if X_{CO_2} in the fluid phase is very low (implying $a_{\text{H}_2\text{O}}$ values > 0.9 if the fluid is a binary H_2O – CO_2 mixture).

In this study, TZARS is first used to estimate mean activities of rutile (a_{Rt}) and titanite (a_{Ttn}), or the mean activity ratio $a_{\text{Rt}}/a_{\text{Ttn}}$ in natural epidote–amphibolites that are variably undersaturated with respect to these phases, and which equilibrated under P – T conditions constrained in previous studies. For samples that contain garnet with the TZARS assemblage, the H_2O -absent equilibrium



provides additional constraints on a_{Rt} , a_{Ttn} or $a_{\text{Rt}}/a_{\text{Ttn}}$. This equilibrium is referred to by the acronym GRATiS,

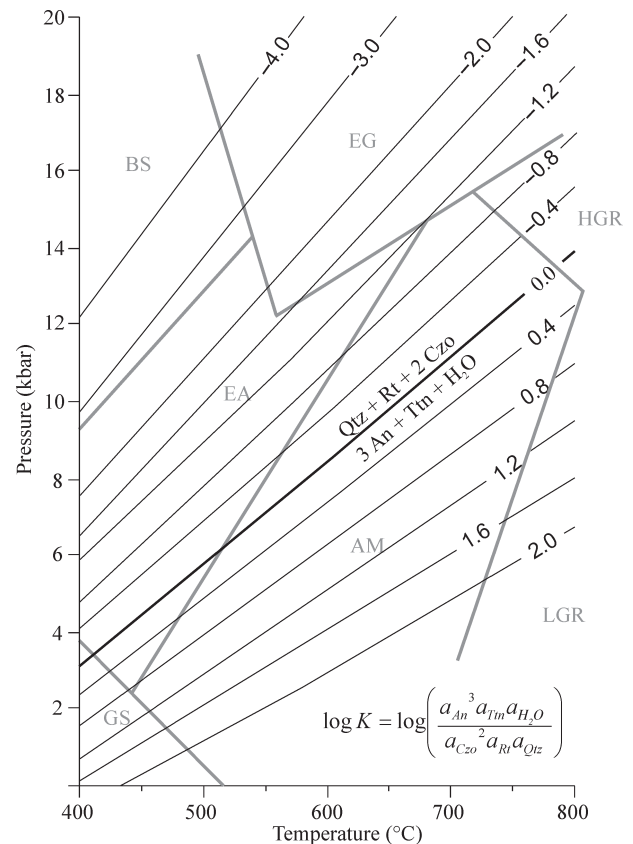


Fig. 1. Location of TZARS equilibrium (bold line) on P – T projection, contoured with isopleths of $\log K$. Locations of principal metamorphic facies boundaries are shown according to Oh & Liou (1998): BS, blueschist facies; GS, greenschist facies; EA, epidote–amphibolite facies; AM, amphibolite facies; EG, eclogite facies; LGR, low-pressure granulite facies; HGR, high-pressure granulite facies.

to highlight that when garnet is present, an additional thermobarometer is available. It is then shown that calculated mean activities of a_{Rt} , a_{Ttn} or $a_{\text{Rt}}/a_{\text{Ttn}}$ are sufficiently constrained that their use with TZARS provides accurate and precise pressure estimates for titanite- and/or rutile-absent epidote–amphibolites.

METHODOLOGY

Activity-composition and phase-equilibrium calculations

Mineral compositions were recalculated to atoms per formula unit using the program AX of Holland & Powell (2001, also see <http://rock.esc.cam.ac.uk/staff/holland/>), except for titanite. When multiple compositions were reported or obtained for a particular phase within a single sample, the average composition and corresponding standard deviation was used. This simplification is reasonable for most samples, where phases were found to be relatively homogeneous. Normalization schemes and activity

Table 1. Normalization schemes and a - X models used in the calculations.

Phase	Normalization scheme	Activity-composition models
Epidote	12.5 oxygen $Si + Al + Fe^{3+} = 6.0$	Holland & Powell (1998): extended version of Bird & Helgeson (1980) assuming non-ideal mixing Berman (1990)
Garnet	12 oxygen 8 cations	
Plagioclase	All Fe is Fe^{3+}	Fuhrman & Lindsley (1988) fully ordered model (1) of Holland & Powell (1992)
Titanite	1.0 Si per formula unit	$a_{Ttn} = \gamma X_{Ti}$, $X_{Ti} = Ti/(Ti + Al)$, $\gamma = 1$
Phengite	11 oxygen	
Chlorite	14 oxygen, 10 cations maximum $Fe^{3+}/Fe^{2+} = 0.3$	Holland & Powell (1998)
Amphibole	Holland & Blundy (1994)	$a_{tremolite} = \left(\frac{X_{Ca}^{Mg}}{mg}\right)^2 (mg)^5 \left(\frac{X_{Si}^{Fe}}{mg}\right)^8$; $mg = Mg/(Mg + Fe^{2+})$; $a_{glaucophane} = \left(\frac{X_{Na}^{M4}}{al}\right)^2 (mg)^2 (mg)^3$; $al = Al^{VI}/(Al^{VI} + Fe^{3+})$

models used are listed in Table 1. An ideal molecular activity model was used for titanite, as X_{Ti} of the titanite is very high (>0.9) and a recent evaluation of the influence of titanite activity model on phase-equilibrium calculations shows that in this compositional range, these activities are very similar to those obtained with an ionic activity model (the difference in activity is <0.03 , leading to negligible shifts in calculated intensive variables; Tropper *et al.*, 2002; Tribus & Tropper, 2008; Tropper & Manning, 2008).

All phase-equilibrium calculations in this study were conducted using the TWEEQU program of Berman (1991), which uses an internally consistent thermodynamic data set (Berman, 1988). Selected calculations were also performed using THERMOCALC (Holland & Powell, 1998), results were indistinguishable from those from TWEEQU at the metamorphic conditions considered in this study.

Data set

Compositional data were compiled for the mineral assemblage epidote + plagioclase \pm titanite \pm garnet from 59 natural epidote–amphibolites documented in the literature and for which P – T conditions of equilibration have been independently constrained. In several cases, compositions of epidote or plagioclase were assumed based on general descriptions of mineral chemistry (bold entries in Table 2; see below). Of the 59 samples, 11 contain both titanite and rutile (six metabasites and five pelites), 14 are rutile-bearing and titanite-absent (12 metabasites, one pelite and one calcsilicate), 13 are titanite-bearing and rutile-absent (eight metabasites, four pelites and one calcsilicate) and 21 contain neither titanite nor rutile (10 metabasites and 11 pelites). Existing experimental studies on amphibolites either lack appropriate compositional data or have demonstrated that plagioclase compositions in the run-products are strongly influenced by

those of the starting plagioclase compositions at temperatures of epidote stability (Apted & Liou, 1983). Consequently, our data set is restricted to natural samples. Caution should be used when using epidote–amphibolite samples that contain albitic plagioclase ($X_{An} < 0.15$). This is because plagioclase activity-composition models are known to greatly underestimate a_{An} at the low X_{An} side of the peristerite solvus (Ghent & Stout, 1981; Holland & Powell, 1992), thus making the utility of anorthite-bearing equilibria for samples with albitic plagioclase difficult (e.g. Todd, 1998).

Selection of values to use for the preferred P – T conditions of equilibration is subjective for epidote–amphibolite samples where different workers offered contrasting interpretations. We do not re-evaluate previous thermobarometric studies and simply note in Table 2 the literature source(s) from which the preferred P – T conditions were obtained. More than half of the epidote–amphibolite samples occur in compilations of previous workers that were used for the calibration of amphibole-involving thermobarometers (Graham & Powell, 1984; Kohn & Spear, 1990; Holland & Blundy, 1994). For these samples, uncertainties of ± 0.5 kbar and ± 40 °C are reasonable based on their calibration uncertainties. For the remainder of the samples, uncertainties in preferred P – T conditions cited in the original literature source (generally ± 1.0 kbar and ± 50 °C) are used when evaluating the precision of activity estimates using TZARS and GRATIS. Preferred P – T conditions lie within an accepted range for epidote–amphibolites, consistent with theoretical phase relations (Evans, 1990) and the location of the experimentally determined epidote-out reaction boundary (Apted & Liou, 1983) as shown in Fig. 2. They exhibit a wide range of P – T values ranging from 5.5 to 12 kbar and from 496 to 770 °C, which allows any systematic variation in calculated activities of undersaturated titanite and/or rutile as a function of temperature, pressure or activity values of other phases to be investigated. The mole fraction of anorthite in plagioclase (X_{An}) from the samples generally increases with increasing temperature and decreases with increasing pressure, a trend that is commonly observed for amphibolites (Spear, 1993).

Assumptions

The utility of phase equilibria for thermobarometry is limited by the ability to accurately determine activities for pure end-member phases from compositional data for minerals that are solid-solutions (Spear, 1993). However, equilibria may be more sensitive to certain phase activities more than others. This is illustrated for the TZARS equilibrium (Eq. 1) by examining its mass-action expression,

$$\log K_1 = \log \frac{a_{An}^3 a_{Ttn} a_{H_2O}}{a_{Czo}^2 a_{Rt} a_{Qtz}}$$

Table 2. Calculated activities for undersaturated rutile and/or titanite using TZARS and GRATIS and application of TZARS barometry.

Sample no. Chakravarti & Kuehner (1992) ^f Enami (1980) ^f OP-03 OP-06 OP-07 OP-10 OE-02 Konzett & Hoinkes (1996) ^{ef} SW601/1 SW614 Surour (1995) ^f Zabara Trzcinski (1988) ^f B17 Begin (1992) ^f B29 Enami (1980) ^f OP-04.05 Hansen (1992) ^a 296A.4 Henry & Dokka (1992) ^f HL89-20b (M1b) Konzett & Hoinkes (1996) ^{ef} SW169 SW173/1 SW610/2 SW613 Poli (1991) ^a Stage 1 Stage 2 Selverstone <i>et al.</i> (1984) ^{bf} Z3-M Z3-Mp FH-IM cores Titanite-bearing, rutile-absent (<i>n</i> = 13) Burton <i>et al.</i> (1989) ^f R60 R223 Hansen (1992) ^a 263.2 290.1 294.1 Henry & Dokka (1992) ^{ph, T^f} HL89-20b (M2)	<i>T</i>	Comp.	Activities for saturated phases						Activities for undersaturated phases calculated using preferred <i>P-T</i> estimates						TZARS barometry using average of preferred activities					
			TZARS						GRATIS						TZARS					
			<i>X</i> _{An}	<i>a</i> _{An}	<i>a</i> _{Czo/Zo}	<i>a</i> _{Tin}	<i>a</i> _{H2O}	<i>a</i> _{Gr}	log <i>K</i> ₁	¹ <i>a</i> _{Rt} / ¹ <i>a</i> _{Tin}	log <i>K</i> ₂	² <i>a</i> _{Rt} / ² <i>a</i> _{Tin}	avg <i>a</i> _{Rt} / ^{avg} <i>a</i> _{Tin}	log <i>K</i> ₁	1 σ	<i>P</i>	1 σ	ΔP		
6.0	0.385	0.667	<i>X</i> _{An}	<i>a</i> _{An}	<i>a</i> _{Czo/Zo}	<i>a</i> _{Tin}	<i>a</i> _{H2O}	<i>a</i> _{Gr}	log <i>K</i> ₁	¹ <i>a</i> _{Rt} / ¹ <i>a</i> _{Tin}	log <i>K</i> ₂	² <i>a</i> _{Rt} / ² <i>a</i> _{Tin}	avg <i>a</i> _{Rt} / ^{avg} <i>a</i> _{Tin}	log <i>K</i> ₁	1 σ	<i>P</i>	1 σ	ΔP		
10.1	0.230	0.413	0.96	0.95	0.024	0.95	0.95	0.024	-1.05	0.84	-0.94	1.40	1.12	-1.10	0.22	10.2	0.5	0.1		
9.4	0.270	0.432	0.96	0.95	0.031	0.95	0.95	0.031	-0.82	0.55	-1.05	1.11	0.83	-1.04	0.08	10.0	0.3	0.6		
10.2	0.190	0.293	0.97	0.95	0.026	0.95	0.95	0.026	-1.08	0.89	-0.92	1.38	1.13	-1.11	0.22	10.3	0.4	0.1		
10.8	0.190	0.293	0.95	0.95	0.027	0.95	0.95	0.027	-1.30	0.53	-0.84	1.25	0.89	-1.54	0.08	11.5	0.3	0.7		
10.9	0.180	0.278	0.95	0.95	0.032	0.95	0.95	0.032	-1.34	0.50	-0.82	1.15	0.82	-1.61	0.10	11.7	0.3	0.8		
9.0	0.286	0.477	0.58	0.99	0.011	0.95	0.95	0.011	-0.44	0.84	-1.04	1.97	0.84	-0.48	0.12	9.2	0.4	0.2		
9.0	0.207	0.332	0.54	0.90	0.019	0.95	0.95	0.019	-0.44	0.33	-1.04	1.26	0.79	-0.89	0.10	10.4	0.4	1.4		
7.7	0.206	0.372	0.65	0.95	0.018	0.95	0.95	0.018	-0.70	0.58	-1.08	1.33	0.95	-0.90	0.10	8.4	0.3	0.7		
10.0	1.000	1.000	1.00	0.93	0.057	0.95	0.95	0.057	0.05	0.85	-1.24	1.00	0.93	0.01	0.06	10.0	0.3	0.0		
8.0	0.269	0.502	0.56	0.93	0.057	0.95	0.95	0.057	-0.82	2.53	-1.02	0.92	0.92	-0.38	0.15	6.8	0.4	-1.2		
8.5	0.213	0.373	0.59	0.97	0.012	0.97	0.95	0.012	-0.75	1.22	-1.02	0.56	0.89	-0.89	0.11	9.0	0.6	0.5		
10.0	0.230	0.413	0.95	0.97	0.024	0.95	0.95	0.024	-1.11	1.02	-0.96	0.71	0.86	-1.17	0.23	10.5	0.3	0.5		
12.0	0.139	0.194	0.45	0.97	0.009	0.95	0.95	0.009	-0.45	10.01	-0.85	0.56	0.56	-1.50	0.39	15.6	1.3	3.6		
11.0	0.902	0.886	0.63	0.97	0.083	0.97	0.57	0.083	0.60	3.87	-1.17	1.14	1.14	-0.04	0.12	13.2	0.6	2.2		
9.0	0.233	0.384	0.58	0.97	0.05	0.95	0.95	0.05	-0.44	2.21	-	-	-	-0.83	0.11	10.1	0.4	1.1		
9.0	0.290	0.481	0.54	0.97	0.011	0.95	0.95	0.011	-0.44	0.97	-1.04	0.49	0.97	-0.48	0.14	9.2	0.5	0.2		
9.0	0.301	0.501	0.65	0.97	0.019	0.95	0.95	0.019	-0.44	1.24	-1.04	0.63	1.24	-0.59	0.13	9.5	0.5	0.5		
9.0	0.255	0.421	0.77	0.97	0.006	0.95	0.95	0.006	-0.44	2.94	-	-	-	-0.96	0.11	10.5	0.5	1.5		
11.0	0.146	0.227	0.44	0.97	0.036	0.95	0.95	0.036	-1.20	1.07	-0.61	0.78	0.93	-1.28	0.17	11.1	0.5	0.1		
11.0	0.146	0.189	0.57	0.97	0.033	0.95	0.95	0.033	0.30	98.04	-1.08	1.41	-	-1.74	0.23	18.2	0.7	7.2		
7.0	0.324	0.559	0.39	0.97	0.05	0.95	0.95	0.05	0.05	1.00	-	-	1.00	0.00	0.17	7.1	0.4	0.1		
7.0	0.325	0.560	0.38	0.97	0.05	0.95	0.95	0.05	0.05	0.94	-	-	0.94	0.03	0.17	7.0	0.3	0.0		
7.0	0.338	0.582	0.34	0.97	0.002	0.95	0.95	0.002	-1.30	0.67	-1.30	0.28	0.67	0.17	0.18	6.7	0.4	-0.3		
10.0	0.147	0.215	0.40	0.97	0.006	0.95	0.95	0.006	-1.24	0.95	-0.77	0.40	0.95	-1.27	0.19	10.1	0.4	0.1		
7.5	0.340	0.593	0.57	0.95	0.007	0.95	0.95	0.007	-0.23	0.98	-1.21	2.17	0.98	-0.11	0.19	7.2	0.5	-0.3		
7.8	0.313	0.549	0.66	0.95	0.004	0.95	0.95	0.004	-0.30	0.68	-1.17	2.89	0.68	-0.34	0.18	8.1	0.7	0.3		
8.5	0.295	0.454	0.45	0.95	0.012	0.95	0.95	0.012	0.18	0.28	-1.23	1.40	0.84	-0.26	0.33	9.6	0.9	1.1		
11.0	0.317	0.494	0.45	0.95	0.086	0.95	0.95	0.086	-0.36	1.23	-0.93	0.78	1.01	-0.14	0.30	10.2	0.7	-0.8		
10.0	0.099	0.139	0.45	0.95	0.031	0.95	0.95	0.031	-0.30	0.02	-1.02	0.62	0.62	-1.80	0.44	14.9	1.4	4.9		
6.0	0.699	0.776	0.98	0.95	0.083	0.95	0.93	0.083	0.70	0.09	-1.65	0.43	0.43	-0.24	0.16	8.8	0.7	2.8		

Table 2. (Continued)

		Activities for saturated phases				Activities for undersaturated phases calculated using preferred <i>P-T</i> estimates				TZARS barometry using average of preferred activities							
		TZARS				GRATIS				TZARS							
Sample no.	<i>P</i> (kbar)	<i>T</i>	<i>X</i> _{An}	<i>a</i> _{CaO,ZrO}	<i>a</i> _{Ttn}	<i>a</i> _{H₂O}	<i>a</i> _{Gr}	log <i>K</i> ₁	¹ <i>a</i> _{Rt} / <i>a</i> _{Ttn}	log <i>K</i> ₂	² <i>a</i> _{Rt} / <i>a</i> _{Ttn}	avg <i>a</i> _{Rt} / <i>a</i> _{Ttn}	log <i>K</i> ₁	<i>P</i>	1 σ	ΔP	
Mengel & Rivers (1991) ^f as opposed to 5.0, 600 ^a	5.5	555	m	0.567	0.769	0.49	0.95	0.95	0.70	0.34	–	0.34	0.36	0.20	6.4	0.5	0.9
F84-70	5.5	555	m	0.567	0.769	0.49	0.95	0.95	0.70	0.34	–	0.34	0.36	0.20	6.4	0.5	0.9
Miyake (1984) ^f	6.5	610	m	0.340	0.604	0.43	0.95	0.050	0.03	1.00	–1.35	0.85	0.16	0.27	8.1	0.4	1.6
#I-9	6.5	610	m	0.340	0.604	0.43	0.95	0.050	0.03	1.00	–1.35	0.85	0.16	0.27	8.1	0.4	1.6
O'Beirne-Ryan <i>et al.</i> (1990) ^f	6.5	650	m, cal	0.420	0.623	0.47	0.95	0.023	1.11	0.07	–1.57	0.81	0.10	0.18	9.4	0.6	2.9
–	6.5	650	m, cal	0.420	0.623	0.47	0.95	0.023	1.11	0.07	–1.57	0.81	0.10	0.18	9.4	0.6	2.9
Sivaprakash (1982) ^f	8.7	520	m	0.260	0.475	0.82	0.95	0.009	–0.85	1.02	–0.96	1.02	–0.70	0.17	8.2	0.7	–0.5
124	8.7	520	m	0.260	0.475	0.82	0.95	0.009	–0.85	1.02	–0.96	1.02	–0.70	0.17	8.2	0.7	–0.5
Spear (1982) ^f , <i>T</i> ^c	5.5	570	m, cal	0.395	0.648	0.36	0.95	–	0.81	0.29	–	0.29	0.40	0.21	6.5	0.7	1.0
73-19a	5.5	570	m, cal	0.395	0.648	0.36	0.95	–	0.81	0.29	–	0.29	0.40	0.21	6.5	0.7	1.0
White <i>et al.</i> (2001) ^f	9.1	580	p, cal	0.226	0.367	0.33	0.95	0.007	–0.40	0.84	–1.04	0.84	–0.35	0.20	8.9	0.6	–0.2
CW88-115A	9.1	580	p, cal	0.226	0.367	0.33	0.95	0.007	–0.40	0.84	–1.04	0.84	–0.35	0.20	8.9	0.6	–0.2
NB87-4107	7.7	580	p, cal	0.322	0.532	0.32	0.95	0.016	0.10	0.72	–1.26	1.00	0.08	0.22	7.6	0.7	–0.1
Rutile- and titanite-absent (<i>n</i> = 21)																	
Sample no.	<i>P</i> (kbar)	<i>T</i>	<i>X</i> _{An}	<i>a</i> _{CaO,ZrO}	<i>a</i> _{Ttn}	<i>a</i> _{H₂O}	<i>a</i> _{Gr}	log <i>K</i> ₁	¹ <i>a</i> _{Rt} / <i>a</i> _{Ttn}	log <i>K</i> ₂	² <i>a</i> _{Rt} / <i>a</i> _{Ttn}	avg <i>a</i> _{Rt} / <i>a</i> _{Ttn}	log <i>K</i> ₁	<i>P</i>	1 σ	ΔP	
Burton <i>et al.</i> (1989) ^{est}			comp.														
260B	5.6	496	p	0.437	0.745	1.00	0.95	0.004	0.05	0.35	–1.43	2.63	–0.03	0.30	4.8	0.5	–0.8
GD22B	7.2	580	m, cal	0.386	0.637	0.45	0.90	0.022	0.27	0.62	–1.27	1.25	0.44	0.30	6.7	0.7	–0.5
GD49B	7.2	580	m	0.392	0.641	0.51	0.95	0.037	0.27	0.52	–1.27	0.96	0.36	0.30	7.0	0.8	–0.2
GD480	7.2	580	m	0.464	0.718	0.55	0.95	0.010	0.27	0.63	–1.27	1.93	0.44	0.29	6.7	0.7	–0.5
Graham & Powell (1984) ^d and Jacobson (1995)																	
Pelona OA	10.0	610	m	0.142	0.197	0.33	0.95	0.065	–0.40	0.17	–0.98	0.56	–0.80	0.31	11.1	0.8	1.1
Laird (1980) ^a																	
V113B	5.7	550	m	0.215	0.374	0.28	0.95	0.009	0.55	0.18	–1.42	1.26	0.18	0.32	6.7	0.8	1.0
Poli (1991) ^a																	
Stage 3	8.0	625	m	0.402	0.617	0.57	0.95	n/a	0.40	0.27	–	0.27	0.21	0.29	8.5	0.8	0.5
Richardson & Powell (1976) ^a																	
B	7.2	540	p	0.180	0.307	0.61	0.95	0.014	–0.10	0.09	–1.24	1.12	–0.75	0.29	8.8	0.9	1.6
C	7.2	540	p	0.154	0.255	0.78	0.95	0.003	–0.10	0.03	–1.24	2.33	–	0.30	10.2	0.8	3.0
D	7.2	540	p	0.246	0.432	0.56	0.95	0.001	–0.10	0.31	–1.24	6.79	0.31	0.30	7.3	0.8	0.1
E	7.2	540	p	0.177	0.298	0.41	0.95	0.004	–0.10	0.19	–1.24	2.21	–0.23	0.30	8.1	0.8	0.9
F	7.2	540	p	0.160	0.266	0.33	0.95	0.001	–0.10	0.21	–1.24	3.31	–0.41	0.32	8.0	0.8	0.8
G	7.2	540	p, cal	0.216	0.378	0.72	0.90	n/a	–0.10	0.12	–	0.12	–0.65	0.29	8.6	0.8	1.4
H	7.2	540	p, cal	0.220	0.382	0.75	0.90	n/a	–0.10	0.11	–	0.11	–0.67	0.29	8.7	0.8	1.5
Spear (1982) ^c																	
73-18b	5.5	570	m, cal	0.440	0.698	0.41	0.90	–	0.81	0.28	–	0.28	0.64	0.31	5.9	0.9	0.4
73-25a	5.5	570	m, cal	0.400	0.656	0.42	0.90	0.008	0.81	0.22	–1.58	1.48	0.54	0.31	6.1	0.8	0.6
73-28e	5.5	570	m, cal	0.390	0.645	0.50	0.90	n/a	0.81	0.15	–	0.15	0.36	0.30	6.5	0.7	1.0
73-20a	5.5	570	m	0.410	0.672	0.38	0.95	0.002	0.81	0.31	–1.58	3.05	0.68	0.31	5.8	0.8	0.3

Inferred activity values are shown in bold. n/a, not analysed; –, not present; comp., bulk composition; m, metabasite; p, pelite; es, calcisilicate; cal, calcite-present. avg, calculated average activity ratio between *a*_{Rt}/*a*_{Ttn} calculated using TZARS and *a*_{Rt}/*a*_{Ttn} calculated using GRATIS using preferred *P* and *T*; ΔP , pressure calculated using TZARS equilibrium at preferred *T* minus preferred *P*.

¹Calculations using TZARS.
²Calculations using GRATIS.
^aHolland & Blundy (1994).
^bKohn & Spear (1990).
^cIntermediate between Holland & Blundy (1994) and Kohn & Spear (1990).
^dGraham & Powell (1984).
^eDale *et al.* (2000).
^fOriginal source.

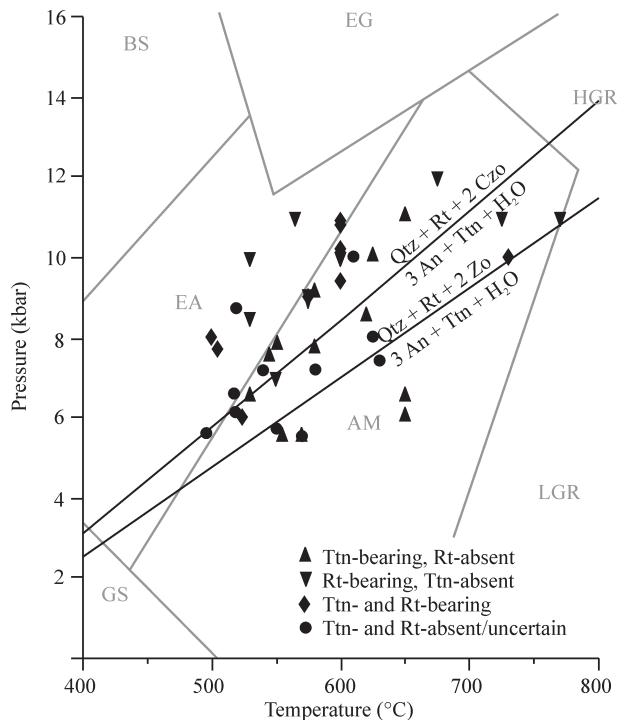


Fig. 2. Preferred P - T conditions of equilibration for epidote-amphibolite samples used to calculate values of undersaturated titanite and/or rutile. Location of TZARS equilibrium is shown for pure end-member phases. The facies boundaries are also according are the same as in Fig. 1.

where a_i represents the activity of the subscripted phase component. The value of $\log K_1$ and its corresponding position in P - T space (Fig. 1) are weakly dependent on a_{Ttn} , $a_{\text{H}_2\text{O}}$, a_{Rt} and a_{Qtz} , at least over the ranges of activities commonly calculated for these phase components in epidote-amphibolites. For example, changing $a_{\text{H}_2\text{O}}$ or a_{Ttn} from unity to 0.2 shifts the TZARS equilibrium to higher pressure by < 2 kbar (Fig. 3a). Similarly, decreasing a_{Rt} to moderate values only slightly depresses the position of the TZARS equilibrium. In contrast, major shifts in the position of the TZARS equilibrium occur due to small changes in a_{An} and, to a lesser but still significant degree, a_{Czo} , chiefly due to reaction coefficients is > 1 .

As small uncertainties in activity-composition relations of plagioclase may result in large errors for calculated pressures or activities of other phases when using TZARS, a_{An} was calculated using two different models: that of (Fuhrman & Lindsley, 1988) and the fully ordered model (model 1) of Holland & Powell (1992) (Table 1). For plagioclase compositions evaluated in this study with $X_{\text{An}} > 0.2$ [where $X_{\text{An}} = \text{Ca}/(\text{Ca} + \text{Na} + \text{K})$ on a molar basis], the Fuhrman & Lindsley (1988) model yields activities that are slightly higher (generally $< 6\%$) than those provided by the model of Holland & Powell (1992). In contrast, at $0.1 < X_{\text{An}} < 0.2$, the Holland & Powell (1992) model tends to yield slightly higher values for a_{An} . For our calculations, the average of the two a_{An} values provided by these models is used, and the

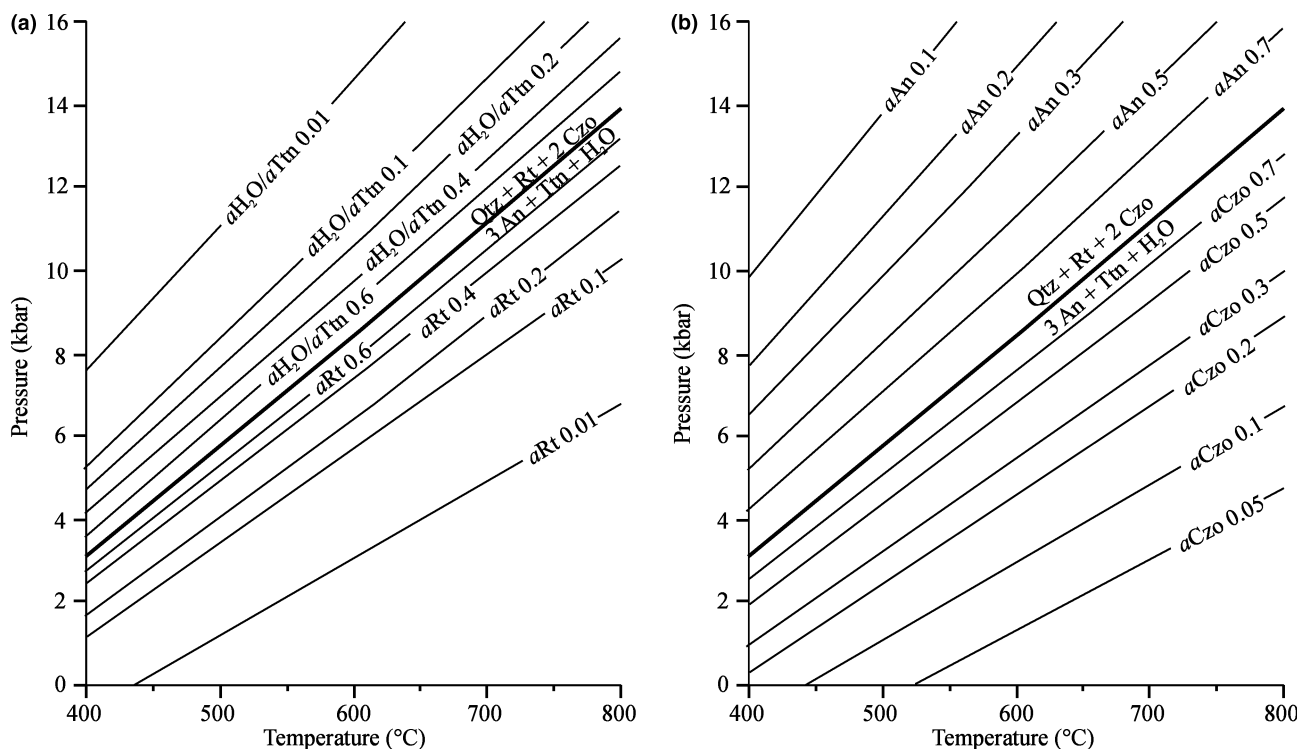


Fig. 3. Changes in the P - T position of the stiochiometric TZARS equilibrium due to changes in activities of (a) water ($a_{\text{H}_2\text{O}}$), rutile (a_{Rt}) and titanite (a_{Ttn}), (b) anorthite (a_{An}) and clinozoisite (a_{Czo}).

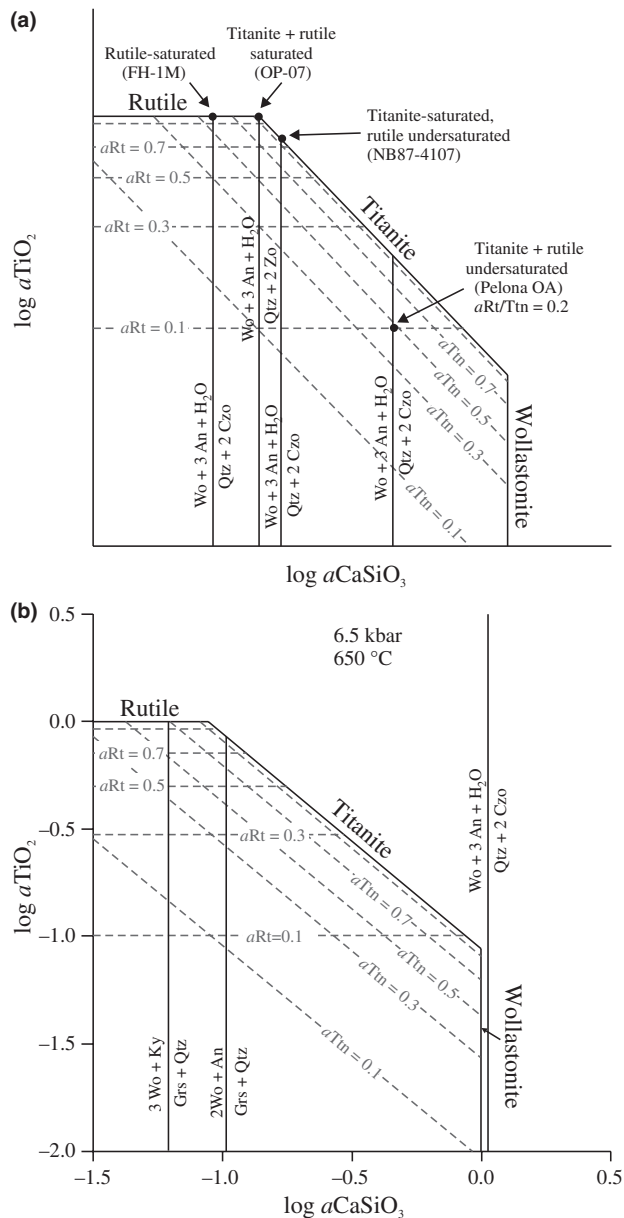
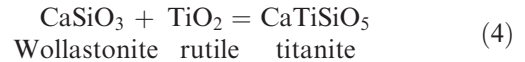


Fig. 6. Activity diagrams illustrating constraints from phase relations on activities of rutile and titanite in epidote-amphibolites. (a) Schematic a - a diagram where the vertical lines show values of $\log a_{\text{CaSiO}_3}$ necessary for samples analysed in this study, that are variably saturated with respect to titanite and rutile, to be in equilibrium. For samples that contain either titanite or rutile, phase relations place tight constraints on the activity of the undersaturated Ti-bearing phase. (b) Calculated equilibria at 650 °C and 6.5 kbar for a titanite-bearing and rutile-absent epidote-amphibolite (O'Beirne-Ryan *et al.*, 1990). Phase relations show that wollastonite should be saturated with respect to clinozoisite, suggesting that analysed plagioclase and epidote may not have been in equilibrium.

Constraints on the activities of the Ti-phases involved in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2\text{-H}_2\text{O}$ system can be examined using a logarithmic activity-activity diagram at fixed P - T as shown schematically in

Fig. 6a, with a_{TiO_2} and a_{CaSiO_3} as independent variables. Surfaces of rutile, titanite and wollastonite saturation ($a_i = 1.0$) can be calculated at a specified pressure and temperature by solving the relevant mass-action equations for $\log a_{\text{TiO}_2}$ or $\log a_{\text{CaSiO}_3}$. As an example, consider the equilibrium



for which mass-action equation can be written

$$\log a_{\text{TiO}_2} = \log a_{\text{Ttn}} - \log a_{\text{CaSiO}_3} - \log K_4 \quad (5)$$

At titanite saturation, Eq. (5) describes a straight line in Fig. 6a, with unit negative slope and an intercept of $-\log K_4$. Contours of reduced activities can also be calculated, as shown for titanite and rutile in Fig. 6a. This analysis places constraints on the a_{CaSiO_3} that is needed in order for stoichiometric rutile and/or titanite to be saturated. Assemblages undersaturated with respect to wollastonite, and in equilibrium, should not plot at values of $\log a_{\text{CaSiO}_3}$ greater than zero.

The mass-action equations for selected reactions among stoichiometric wollastonite, anorthite, clinozoisite/zoisite, grossular, quartz and H_2O can be solved for the a_{CaSiO_3} values required by equilibrium, using phase-component activities at P - T conditions determined for a specific sample. The equilibria should intersect lines of rutile and/or titanite saturation depending on which of these phases coexist with the assemblage. Figure 6a shows the schematic position of equilibria involving anorthite + epidote + quartz + water for four epidote-amphibolite samples that are variably saturated with respect to rutile and titanite. They are *feasible* equilibrium assemblages, in that they intersect lines of rutile and/or titanite saturation that are appropriate to the assemblage present. For samples that contain either titanite or rutile, the intersection points provide a maximum estimate for a_{Ttn} in rutile-bearing and titanite-absent samples and a minimum estimate for a_{Rt} in titanite-bearing and rutile-absent samples. For rutile-bearing assemblages, there are limits to how low $\log a_{\text{CaSiO}_3}$ values (and hence a_{Ttn} values) may be before kyanite should be saturated (Fig. 6b).

Some of the samples in the data set include mineral assemblages that plot at values of $\log a_{\text{CaSiO}_3}$ greater than that corresponding to wollastonite saturation or lower than that corresponding to kyanite saturation. This may be due to uncertainties in the P - T estimates, mineral activities and thermodynamic data, or it may indicate that the analysed phases in these assemblages were not in equilibrium. This is illustrated for a titanite-bearing sample in Fig. 6b. For this sample, the equilibrium involving anorthite + water + quartz + clinozoisite plots at a value for $\log a_{\text{CaSiO}_3}$ greater than that corresponding to wollastonite saturation. For this case, use of TZARS for estimation of a_{Rt} would yield erroneously low values. However,

for the same sample, the equilibrium involving garnet + quartz + anorthite plots at a reasonable value of $\log a_{\text{CaSiO}_3}$, which intersects the line of titanite saturation. Therefore, application of GRATiS should provide a reasonable estimate of a_{Rt} for this sample.

Calculation of activities for undersaturated titanite and rutile

Table 2 lists calculated $\log K$ -values for TZARS ($\log K_1$) and GRATiS ($\log K_2$) using the preferred P - T conditions of the samples and calculated/assumed activities for saturated phases. With these values, it is possible to solve for a_{Rt} or a_{Ttn} in titanite-absent and rutile-absent samples, respectively, and the ratio $a_{\text{Rt}}/a_{\text{Ttn}}$ for samples that contain neither titanite nor rutile. The ratio $a_{\text{Rt}}/a_{\text{Ttn}}$ was also calculated for samples that contain both titanite and rutile, to evaluate the extent to which these phases are in equilibrium. For TZARS,

$$\frac{a_{\text{Rt}}}{a_{\text{Ttn}}} = \frac{a_{\text{An}}^3 a_{\text{H}_2\text{O}}}{K_1 a_{\text{Czo}}^2 a_{\text{Qtz}}}$$

and for GRATiS,

$$\frac{a_{\text{Rt}}}{a_{\text{Ttn}}} = \left(\frac{K_2 a_{\text{An}}}{a_{\text{Gr}} a_{\text{Qtz}}} \right)^{\frac{1}{2}}$$

Activities calculated using assemblages that do not plot at reasonable values of $\log a_{\text{CaSiO}_3}$ are considered suspect and excluded from consideration.

Precision

The TZARS isopleths are relatively insensitive to $a_{\text{Rt}}/a_{\text{Ttn}}$. Thus, commonly cited uncertainties of ± 50 °C and ± 0.5 kbar in preferred P - T conditions would result in large uncertainties of $>50\%$ for activities estimated using TZARS. If preferred P - T conditions are taken to be perfectly known, the uncertainties may be reduced to $\sim 25\%$ for most samples, with uncertainties in plagioclase compositions and plagioclase activity-composition models becoming the main factor limiting precision. For GRATiS, precision in calculated titanite-rutile activities is limited not by errors in preferred P - T conditions, as its $\log K$ -values are more sensitive to variations in $a_{\text{Rt}}/a_{\text{Ttn}}$ than TZARS, but by uncertainties in a_{Gr} . In general, the latter result in a precision of $<20\%$ for activity calculations. However, for samples where garnet exhibits significant variability in composition, uncertainties could be larger.

RESULTS

Titanite- and rutile-bearing samples

Values of a_{Rt} and a_{Ttn} should be near saturation and $a_{\text{Rt}}/a_{\text{Ttn}} \approx 1$, in equilibrium assemblages that

include titanite and rutile. Therefore, comparison of calculated activity values for these samples (Table 2) with those expected is useful for evaluating the accuracy of TZARS and GRATiS. GRATiS generally overestimates a_{Rt} relative to a_{Ttn} ($a_{\text{Rt}}/a_{\text{Ttn}}$ values range from 0.92 to 1.40 with an average of 1.20). In contrast, TZARS underestimates a_{Rt} relative to a_{Ttn} , yielding values that are in most cases significantly less than unity (0.33–0.84, with an average of 0.65). The significant and systematic differences in activity estimates provided by the two equilibria suggest that inaccuracies are larger than uncertainties in individual activity estimates. Consequently, we ignore uncertainties in individual activity estimates and focus instead on the systematic differences provided by the two equilibria in evaluating their utility to estimate $a_{\text{Rt}}/a_{\text{Ttn}}$ in epidote-amphibolites. When both equilibria are applied to the same sample, the calculated activities appear to bracket the permissible values and the midpoints tend to be less than but reasonably close to unity. The midpoint values are therefore taken as the preferred estimates for $a_{\text{Rt}}/a_{\text{Ttn}}$ in these samples. The average of preferred $a_{\text{Rt}}/a_{\text{Ttn}}$ estimates for all the rutile- and titanite-bearing samples is 0.92 ± 0.12 (Fig. 7). This approach is extended to samples that are undersaturated with respect to titanite and/or rutile, because as will be shown in the next section, they also yield similar systematic differences in estimated activities.

Rutile-bearing, titanite-absent samples

For rutile-bearing and titanite-absent samples, TZARS yields a_{Ttn} values that range from 0.67 to 1.24, with an average of unity. GRATiS tends to provide lower estimates for a_{Ttn} , ranging from 0.56 to 1.14, with an average of 0.73. The average of preferred a_{Ttn} values calculated for all the samples is 0.89 ± 0.16 (Fig. 7). This result suggests that titanite is nearly saturated in many rutile-bearing and titanite-absent epidote-amphibolites.

Titanite-bearing, rutile-absent samples

For titanite-bearing and rutile-absent samples, TZARS yields slightly lower values of a_{Rt} (0.28–1.23 with an average of 0.74) than GRATiS (0.43–1.28 with an average of 0.86). The average of preferred a_{Rt} values is 0.75 ± 0.26 (Fig. 7). The limited database of this study and large uncertainties involved with TZARS make it difficult to evaluate whether or not the spread in calculated a_{Rt} is reflective of true variability in epidote-amphibolites. However, estimates of a_{Rt} calculated by Ghent & Stout (1984) for rutile-absent amphibolite facies metabasites exhibit a similar range (0.43–1.16) and average (0.71 ± 0.28). This similarity in the results calculated from different equilibria supports the potential for significant

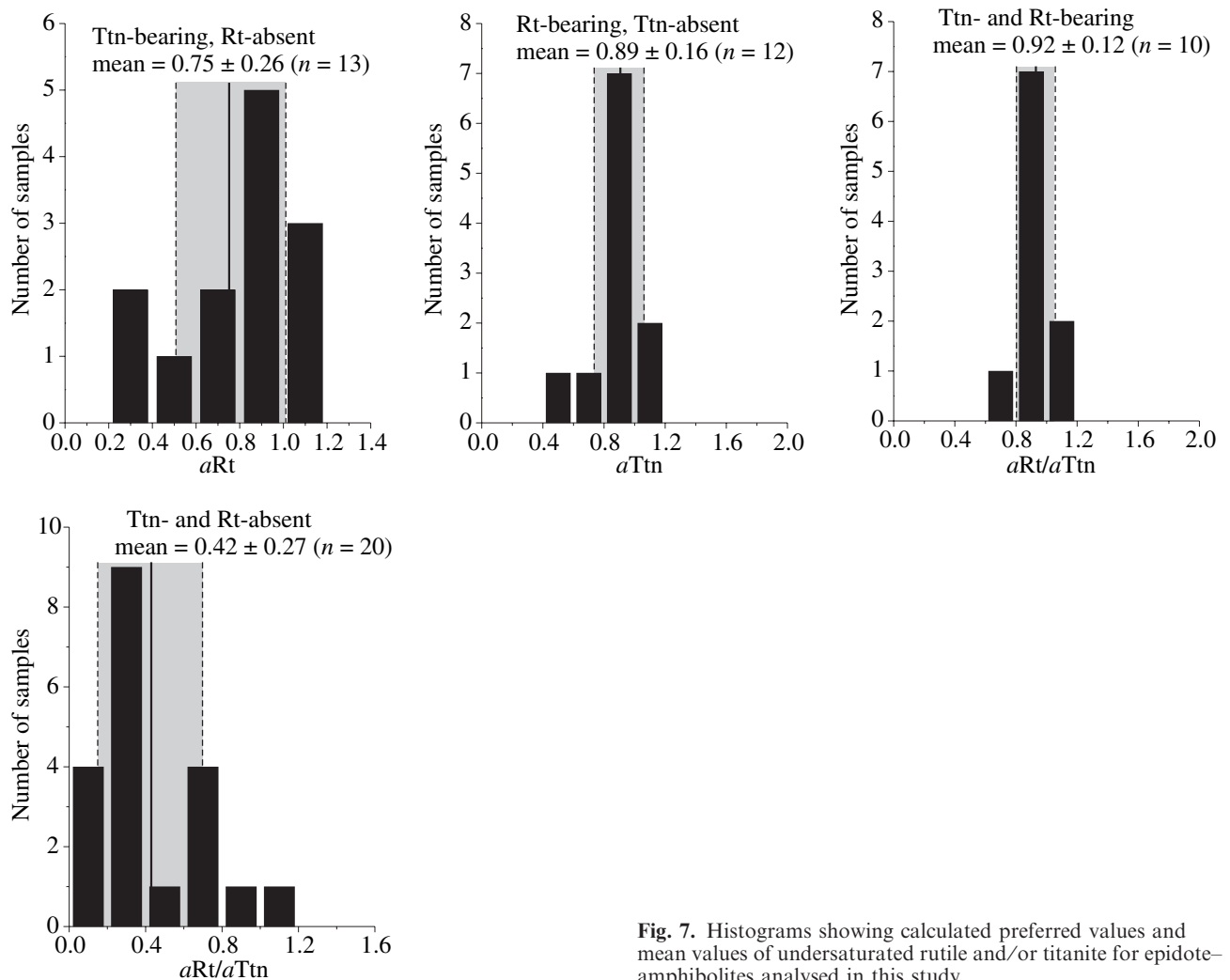


Fig. 7. Histograms showing calculated preferred values and mean values of undersaturated rutile and/or titanite for epidote-amphibolites analysed in this study.

variability of a_{Rt} , but also places confidence that the average calculated value for a_{Rt} is representative for titanite-bearing and rutile-absent amphibolites.

Samples lacking titanite and rutile

For samples that contain neither titanite nor rutile, calculated values of a_{Rt}/a_{Ttn} by TZARS (average = 0.33 ± 0.24) are significantly lower than those calculated using GRATiS (1.03 ± 0.29). The average of the preferred a_{Rt}/a_{Ttn} values is 0.42 ± 0.27 (Fig. 7). Despite significant variability in calculated values of a_{Rt}/a_{Ttn} , our results suggest that rutile tends to be more undersaturated than titanite in titanite- and rutile-absent epidote-amphibolites. If titanite and rutile are in slight disequilibrium in the samples that contain both of these phases, this conclusion may explain why the calculated average a_{Rt}/a_{Ttn} for the titanite- and rutile-bearing samples is less than unity (0.92).

Variations in calculated activities as a function of lithology and phase composition

In their analysis of garnet-bearing amphibolites, Ghent & Stout (1984) found that calculated values of a_{Rt} tended to be higher (near unity) in pelites than in metabasites (~ 0.71). In contrast, there are no obvious differences in the calculated titanite and/or rutile activities between the metabasite, pelite and calc-silicate samples analysed in this study (Table 2), although our database is smaller. In addition, there are no obvious correlations between activity estimates and preferred P - T conditions of equilibration for the samples, the plagioclase activity-composition model used or with magnitudes of $a_{Czo/Zo}$ or a_{An} values (Table 2).

Systematic differences in activity estimations

Systematic differences in activity estimates calculated using TZARS and GRATiS cannot be attributed to an

incorrect assumption of high $a_{\text{H}_2\text{O}}$ for TZARS, as decreasing $a_{\text{H}_2\text{O}}$ would increase the differences between the activity estimates. Inaccuracies in activity-composition models for phases that are common to both equilibria are unlikely to be large enough to explain the differences, either. It is interesting to note that the two garnet–rutile equilibria used by Ghent & Stout (1984) tend, like GRATiS, to yield $a_{\text{Rt}} > 1$. It is possible that such systematic differences may be explained by inaccuracies in the thermodynamic properties of the end-member equilibria. For instance, taking into account the small positive deviation of 0.01 ± 0.01 from $\log K = 0$ for the experimentally determined TARK reaction (titanite + kyanite = anorthite + rutile) (Manning & Bohlen, 1991) could explain some fraction of the observed discrepancies in activity calculations. Our ability to constrain the value of this fraction is limited by the precision of the activity estimates and the potential for disequilibrium among analysed phases, as earlier emphasized.

TZARS barometry of epidote–amphibolites: an outlook

We have characterized to a first-order the extent to which rutile and titanite are undersaturated in epidote–amphibolites that lack one or both of these Ti-bearing phases. Additional studies may help better address potential variability in the activities of undersaturated titanite and/or rutile or require some modification to our preferred estimates and corresponding uncertainties for a_{Rt} , a_{Ttn} or $a_{\text{Rt}}/a_{\text{Ttn}}$ in epidote–amphibolites that are

variably saturated with respect to titanite and rutile. However, the average calculated activities are sufficiently constrained that their use with TZARS yields accurate and precise pressure estimates for epidote–amphibolites. This is illustrated for the samples analysed in this study, excluding those that show signs of disequilibrium between epidote and plagioclase and where $a_{\text{An}} < 0.2$ as shown in Fig. 8. TZARS yields pressures that differ by < 2 kbar from those cited and on average by < 0.5 kbar, even for samples that are undersaturated with respect to both titanite and rutile (Table 2; Fig. 8). Despite rather large uncertainties in the average values obtained for a_{Rt} , a_{Ttn} or $a_{\text{Rt}}/a_{\text{Ttn}}$, TZARS yield pressure estimates with a precision of about ± 0.5 kbar for samples that are saturated in titanite and/or rutile and about ± 0.8 kbar for samples that contain neither titanite nor rutile. This accuracy and precision of the TZARS barometer is comparable to that of many well-calibrated barometers. TZARS exhibits a tendency to slightly overestimate pressures for all the assemblages. This tendency, if real, can be explained if GRATiS overestimates a_{Rt} relative to a_{Ttn} slightly more than TZARS underestimates a_{Rt} relative to a_{Ttn} , recalling that we simply used the averages of the activity estimates provided by TZARS and GRATiS as preferred values.

CONCLUSIONS

The extent to which rutile and/or titanite are undersaturated in epidote–amphibolites is constrained by

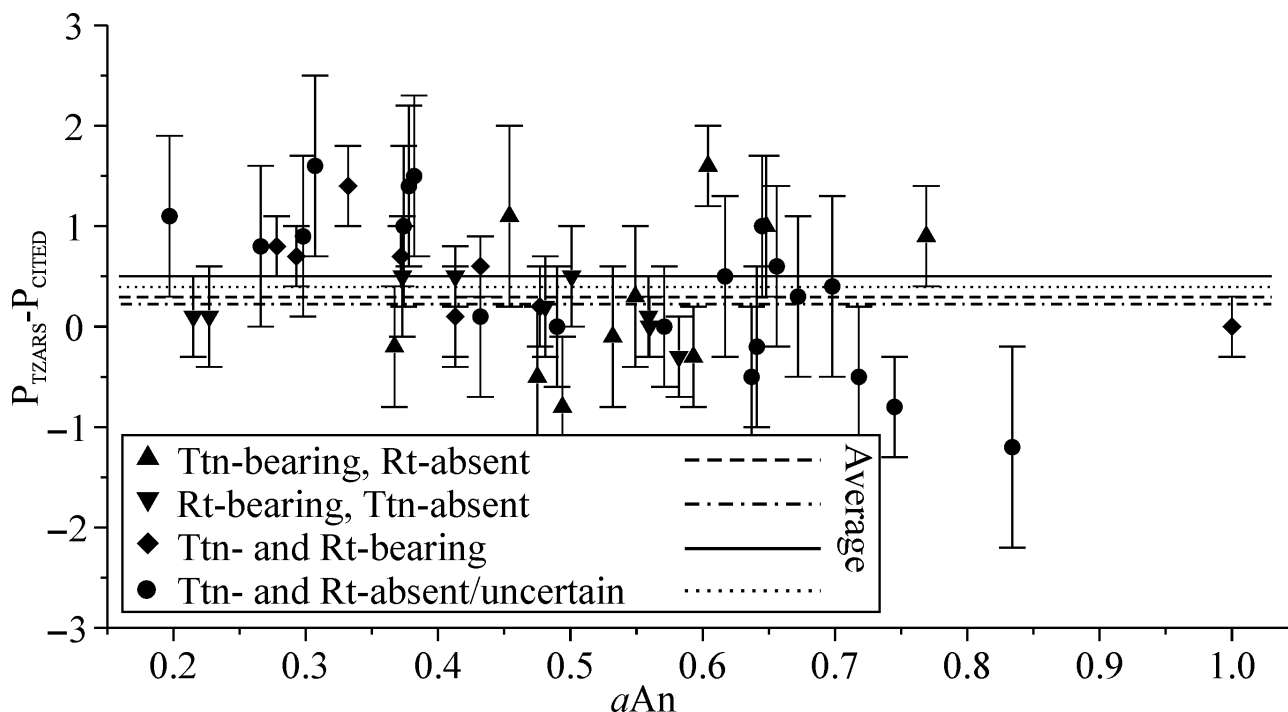


Fig. 8. Deviation in pressures determined for epidote–amphibolites using TZARS from preferred values as a function of the activity of the anorthite component in plagioclase (a_{An}) and mineral assemblage.

phase relations and can be estimated accurately for samples that equilibrated under well-constrained P – T conditions by using a combination of titanite–rutile equilibria (TZARS, GRATIS). Average activity values for undersaturated rutile and/or titanite are sufficiently well-constrained for epidote–amphibolites, that they can be used with TZARS to provide accurate and precise pressure estimates, even for those samples that contain neither titanite nor rutile.

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