

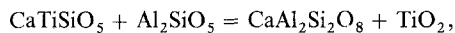
The Reaction Titanite + Kyanite = Anorthite + Rutile and Titanite-Rutile Barometry in Eclogites

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Abstract. Titanite and rutile are a common mineral pair in eclogites, and many equilibria involving these phases are potentially useful in estimating pressures of metamorphism. We have reversed one such reaction,

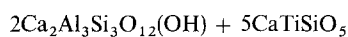


Titanite Kyanite Anorthite Rutile

using a piston-cylinder apparatus. Titanite + kyanite is the high-pressure assemblage and our results locate the equilibrium between 15.5–15.9, 17.7–17.9, 18.8–19.0, and 20.0–20.2 kb at 900, 1000, 1050, and 1100°C, respectively. The experiments require a positive dP/dT of between 20.5 and 23.5 bars/°C for the reaction. We use the reversed equilibrium and two other reactions,

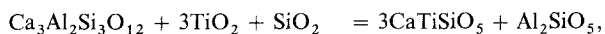


Grossular Rutile Quartz



Zoisite Titanite

and



Grossular Rutile Coesite Titanite Kyanite

to calculate metamorphic conditions for three eclogite localities. Using these reactions in conjunction with garnet-clinopyroxene Fe^{2+} -Mg exchange equilibria, conditions of metamorphism were 16 kb and 750°C for kyanite-eclogites from Glenelg, Scotland, 21 kb and 625°C for eclogite-facies mica schists from the Tauern Window, Austria, and 46 kb and 850°C for eclogite-facies biotite gneisses from the Kokchetav Massif, USSR. For the Scottish and Austrian eclogites, the pressures derived from the titanite-rutile reactions provide additional constraints on pressures for these localities, leading to precise estimates of metamorphic conditions. In the case of the Soviet Union eclogites, the results show that the silicate-oxide assemblage is consistent with the remarkable occur-

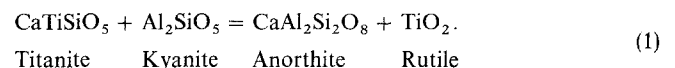
rence of diamond inclusions in the garnets. The results of this study suggest that titanite and rutile stably coexist in many eclogites and that titanite solid solutions are ideal or nearly so.

Introduction

The high pressures of eclogite metamorphism have long attracted the attention of geologists, but precise determination of these pressures is often difficult (e.g., Newton, 1986). However, recognition of diverse crustal lithologies that have been subjected to eclogite-facies metamorphic conditions (e.g., Schreyer 1985; Koons and Thompson 1985; Mottana et al. 1990) has increased the number of mineral assemblages with which to constrain temperature and pressure associated with the development of these rocks.

Titanite and rutile are an important mineral association in eclogites (Blake and Morgan 1975). These two phases form the basis for a set of equilibria useful in the determination of pressure in high-pressure rocks. Coleman and Lee (1963) recognized the importance of titanite-rutile parageneses and used equilibria involving these phases to distinguish between lower temperature blueschists and higher temperature eclogites. Recent studies indicate that eclogite-facies titanite may contain substantial concentrations of Al, Fe^{3+} , F, and OH (Smith 1977, 1980; Smith and Lappin 1982; Franz and Spear 1985; Oberti et al. 1985) via the coupled substitution $[(\text{Al}, \text{Fe}^{3+})(\text{F}, \text{OH})]^{2+} = [\text{Ti}, \text{O}]^{2+}$. Smith (1981) suggested that the extent of this substitution is dependent on pressure and temperature.

In this paper, we present experimental reversals of the reaction:



This reaction defines equilibrium among the four phase assemblage which we will refer to as TARK, an acronym

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formed from the first letter of each phase. The TARK assemblage is uncommon, but, where it has been described in detail (e.g., Sanders 1988; Krogh et al. 1990), it appears to be associated with the late-stage formation of plagioclase during eclogite decompression from peak metamorphic pressures. Despite only rare occurrence, however, equilibrium (1) is essential to any investigation of titanite-rutile equilibria because the absence of H₂O allows study of anhydrous, Al-free titanite. Using the results of these experiments, we have calculated pressures for eclogites using (1) and additional equilibria in the system CaO-Al₂O₃-TiO₂-SiO₂-H₂O. These calculations provide pressure estimates that agree closely with those calculated independently.

Experimental methods

Starting materials

Natural kyanite and synthetic rutile, titanite, and anorthite were used as starting materials. The kyanite (from Faido, Switzerland) was purified by hand picking and contains 0.15 wt% Fe₂O₃ as the major impurity. Synthetic rutile was made from Fisher reagent-grade TiO₂ by firing at 1000°C and 1 atm for 5 days. Anorthite was prepared from synthetic corundum, natural Brazilian quartz, and Fisher reagent-grade CaCO₃. The stoichiometric mixture was ground under alcohol for 20 min and decarbonated at 950°C for ~12 h. After melting at 1600°C for 20 min, temperature was lowered to 1300°C in 50°C increments over a period of 3 days, resulting in 100% crystalline anorthite.

Titanite was synthesized from Fisher reagent-grade CaCO₃, synthetic rutile (see above), and natural Brazilian quartz. After grinding under alcohol for 30 min in an agate mortar and decarbonating at 850°C for 3 h, the material was melted at 1400°C in a Pt crucible for 30 min, held at 1300°C overnight, and then quenched rapidly. This procedure produced coarse-grained titanite with trace amounts of wollastonite and rutile.

Electron microprobe analyses (Table 1) reveal that the synthetic titanite has a Si deficiency and a Ti excess of 5 ± 1 mol%. Titanite

unit-cell parameters were determined from X-ray powder patterns collected at scanning rates of 1/4° 2θ per minute with Si metal as an internal standard. Least-squares refinement gave $a = 7.065(3)$ Å, $b = 8.719(4)$ Å, $c = 6.562(3)$ Å, $\beta = 113.84(2)^\circ$, and a unit-cell volume of 369.7(5) Å³, with peaks indexed following Speer and Gibbs (1976). These unit-cell dimensions are larger than those of synthetic titanite reported by Takenouchi (1971) and Hollabaugh and Rosenberg (1983), but similar to those of Robbins (1968) and Speer and Gibbs (1976). Hollabaugh and Rosenberg (1983) suggest that substitution of Ti for Si leads to a linear increase in unit-cell dimensions, and our measured parameters match closely those predicted for 5 mol% Si deficiency by their least-squares analysis of published data.

Apparatus and experimental procedure

A mixture of titanite, kyanite, rutile, and anorthite was weighed to within 0.1 mg of the stoichiometry of Eq. (1) and ground for ~3 min under alcohol in an alumina mortar. For each experiment, ~10 mg of this mixture was characterized by X-ray diffraction and then loaded into a 1.6 mm O.D. Ag₈₀Pd₂₀ capsule. The capsule opening was carefully cleaned, crimped, and sealed by arc welding. All experiments were performed dry, but no special measures were taken to eliminate moisture.

An end-loaded piston cylinder apparatus was used for all experiments. We employed 2.54 cm-diameter pistons and used furnace assemblies made of NaCl and graphite (Bohlen 1984). Pressures were calibrated against CsCl melting (Bohlen, 1984) and albite-jadeite-quartz equilibrium at 600°C (Hays and Bell 1973). Temperatures were not corrected for the effect of pressure on emf. In each experiment, pressure was advanced to ~80% of the desired value before temperature was increased to the final value. While temperature was raised, pressure increased as a result of thermal expansion of the NaCl furnace, but never was allowed to exceed the desired pressure. After the final temperature was attained, pressure was advanced to the desired value. Pressure was maintained to ± 100 bar during the experiment using digital Heise 710A gauges and temperature was monitored with a Pt-Pt₉₀Rh₁₀ thermocouple resting on the capsule. Capsules were oriented horizontally in the furnace assembly to minimize the temperature gradient in the charge ($\leq 5^\circ$ C, Bohlen, 1984).

Table 1. Representative electron microprobe analyses of synthetic phases

Experiment:	Titanite				Kyanite		Rutile		Anorthite	
	Starting material	32	30	47	32	30	27	46	27	49
SiO ₂	29.00	28.24	29.35	29.16	37.27	38.15	0.13	0.08	43.01	43.22
TiO ₂	42.29	43.00	42.42	42.89	0.28	0.36	98.33	98.45	0.35	0.02
Al ₂ O ₃	—	0.31	0.20	0.18	62.30	61.83	1.53	1.35	36.18	36.47
CaO	28.38	28.30	28.26	28.34	0.07	0.15	0.85	0.61	19.51	19.71
Total	99.67	99.85	100.23	100.57	99.92	100.49	100.84	100.49	99.05	99.42
	Atoms/5oxygens				Atoms/2oxygens		Atoms/8oxygens			
Si	0.95	0.93	0.96	0.95	1.01	1.02	0.00	0.00	2.01	2.01
Ti	1.05	1.06	1.04	1.05	0.01	0.01	0.97	0.97	0.01	0.00
Al	—	0.01	0.01	0.01	1.98	1.96	0.02	0.02	1.99	2.00
Ca	1.00	1.00	0.99	0.99	0.00	0.00	0.01	0.01	0.98	0.98
Total	3.00	3.00	3.00	3.00	3.00	2.99	1.00	1.00	4.99	4.99
T(°C)		900	1000	1100	900	1000	1000	1100	1000	900
P(kbar)		15.9	18.9	20.2	15.9	20.2	16.9	19.8	16.9	15.5

Operating conditions: 15 kV accelerating potential, 20 nA beam current (on Faraday cup), wavelength dispersive spectrometers, and 30 s counting times. Standards: kyanite, titanite, rutile, and anorthite

Experimental products

Each experiment was quenched rapidly by cutting power to the apparatus. The run products were gently disaggregated and examined optically and by X-ray diffraction. Changes in the intensities of diffraction peaks of $\geq 20\%$ were used to determine reaction direction in each experiment. Because extensive reaction was usually observed, reaction direction was also easily discerned by optical inspection.

Results

The experimental results are summarized in Table 2 and Fig. 1. Tight reversals at 900, 1000, 1050, and 1100°C show that titanite + kyanite is the high-pressure assemblage and anorthite + rutile is the low-pressure assemblage. Trace amounts of zoisite are present in the products of experiments conducted at 900°C, probably caused by minor amounts of moisture in the starting materials or capsules. Electron microprobe analyses of products (Table 1) show that, like the starting titanite, final titanite compositions have an average of 5 mol% Si deficiency. In addition, the presence of only minor Al in titanite (Table 1) reflects the absence of OH or F in the experimental charges. Kyanite and anorthite are nearly ideal in composition, and rutile contains minor Al and Ca.

The effect of these deviations from ideal compositions in the experimental products can be examined using the mass-action expression for equilibrium (1),

$$\log K_1 = \log \frac{a_{\text{an}} a_{\text{rt}}}{a_{\text{tn}} a_{\text{ky}}}, \quad (2)$$

where K_1 is the equilibrium constant for (1) and a is the activity of the relevant component in the subscripted phase. Adopting a standard state of unit activity of stoichiometric phases at the temperature and pressure of interest and approximating activities with ideal ionic mixing equations (e.g., Kerrick and Darken 1975; Helgeson and Aagaard 1985), $\log K_1$ for individual experiments is 0.01 ± 0.01 and shows no systematic variation with pressure or temperature. This deviation from $\log K_1 = 0$, which is required if the experiments are to represent equilibrium among the pure minerals, corresponds to a deviation from the calculated position of the stoichiometric reaction of -100 ± 100 bar at constant temper-

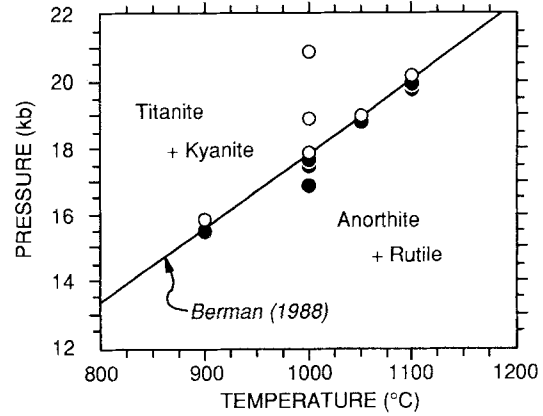
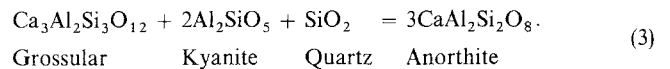


Fig. 1. Pressure-temperature diagram showing experimental reversals of reaction (1). Open circles signify growth of titanite + kyanite and filled circles signify growth of anorthite and rutile. The equilibrium boundary was calculated for pure minerals from the data of Berman (1988)

ature. Because this uncertainty in pressure is the same as the pressure variation during each experiment (see earlier), and because no systematic variation in composition was noted, no corrections for compositional variation were applied to the reversals.

The experiments indicate that dP/dT for the equilibrium is between 20.5 and 23.5 bar/°C. As shown in Fig. 1, the thermodynamic data of Berman (1988) predict precisely the experimentally determined position of the equilibrium. This gives great confidence in using this data set for calculating the pressures and temperatures of equilibration of natural assemblages containing titanite and rutile.

Figure 2A shows reaction (1) with selected equilibria in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{SiO}_2$. Equilibria were calculated using the Ge0-Calc software package (Brown et al. 1988) and the thermodynamic data of Berman (1988). It can be seen that the slope of reaction (1) is similar to that of:



At any temperature, the TARK equilibrium lies about

Table 2. Summary of experimental results

Experiment	Temperature (°C)	Pressure (kb)	Duration (h)	Result
32	900	15.9	189.0	Tn + Ky grew
49	900	15.5	188.0	An + Rt grew
26	1000	20.9	90.0	Strong Tn + Ky growth
27	1000	16.9	115.5	An + Rt grew
30	1000	18.9	91.0	Tn + Ky grew
33	1000	17.9	143.5	Tn + Ky grew
38	1000	17.5	146.5	An + Rt grew
39	1000	17.7	161.0	An + Rt grew
44	1050	19.0	20.5	Tn + Ky grew
45	1050	18.8	65.0	An + Rt grew
46	1100	19.8	36.0	An + Rt grew
47	1100	20.2	22.5	Tn + Ky grew
48	1100	20.0	45.0	An + Rt grew

Abbreviations: Tn, titanite; Ky, kyanite; An, anorthite; Rt, rutile

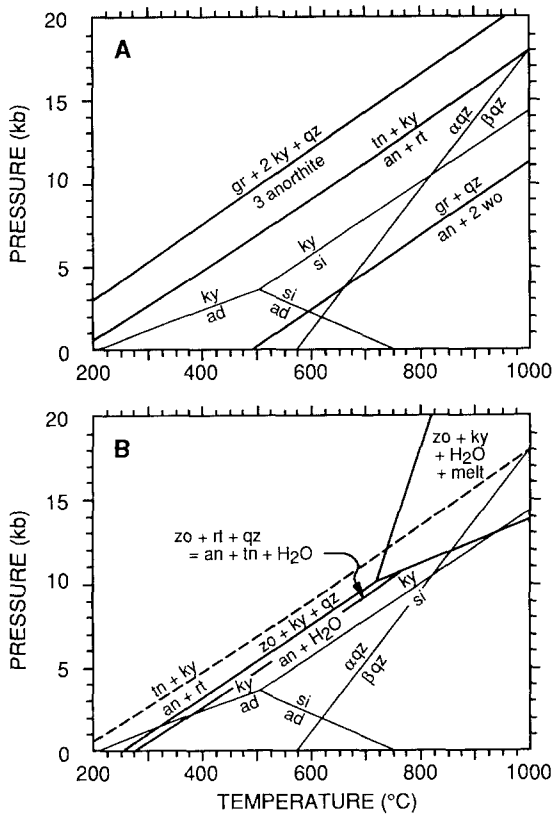
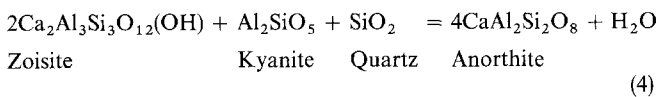


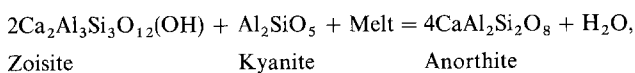
Fig. 2A-B. Pressure-temperature projections showing phase relations in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{SiO}_2 \pm \text{H}_2\text{O}$. **A** Selected equilibria in the H_2O -absent system. **B** Selected equilibria with excess H_2O . Reaction (1) is metastable and is shown with a dashed line. Mineral abbreviations: *ad*, andalusite; *an*, anorthite; *gr*, grossular; *ky*, kyanite; *qz*, quartz; *rt*, rutile; *tn*, titanite; *wo*, wollastonite; *zo*, zoisite

3 kb below reaction (3) and about 4 kb above the reaction kyanite = sillimanite. Figure 2B shows selected equilibria for the same system with H_2O as an additional system component. For these calculations, we used the data of Haar et al. (1984) for H_2O and a standard state of unit activity of pure H_2O at any pressure and temperature. In the presence of H_2O , the TARK equilibrium is metastable because of the instability of anorthite at lower pressures via the reactions



(4)

below 725°C , and:



(5)

above 725°C (Goldsmith, 1981).

Equilibria in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{SiO}_2-\text{CO}_2$, including calcite and meionite and excess CO_2 , are complex, with 4 invariant points at 14.6–14.8 kb and $855-865^\circ\text{C}$. The TARK assemblage is calculated to be

stable only from 856°C to 860°C and at ~ 14.7 kb. In the presence of an $\text{H}_2\text{O}-\text{CO}_2$ fluid the stoichiometric assemblage titanite, kyanite, anorthite and rutile is stable only at CO_2 mole fractions near 1.0. Because kyanite and rutile are nearly stoichiometric in natural samples, titanite activity must be reduced relative to anorthite activity to increase the range of fluid compositions with which the TARK assemblage can coexist stably.

Titanite-rutile barometry in eclogites

The close agreement between the experimentally determined and calculated positions of reaction (1) suggests that calculated equilibria involving titanite and rutile in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{SiO}_2-\text{H}_2\text{O}$ can be used confidently to determine pressures of eclogite equilibration. Below we present examples using the TARK equilibrium and two other titanite-rutile reactions. These calculations are based on the displacement of equilibria involving pure substances using the same standard-state conventions and sources of data as above, appropriate solid solution models, and the relation:

$$-\frac{\Delta G_r^0}{2.303 RT} = \log K_r = \log \prod_i a_i^{v_i}, \quad (6)$$

where ΔG_r^0 is the apparent standard-state Gibbs free energy of reaction r , R is the gas constant, K_r is the equilibrium constant of r , a_i is the activity of the i th phase component and v_i is the stoichiometric reaction coefficient of i in reaction r (negative for reactants, positive for products).

Titanite + kyanite = anorthite + rutile

Figure 3A shows isopleths of $\log K_1$ as a function of pressure and temperature. The utility of equilibrium (1) for determining pressures can be illustrated using the mineral assemblage documented by Sanders (1988). Sanders reported the assemblage titanite, kyanite, plagioclase, and rutile in one of two kyanite-eclogites (sample S341) from Glenelg, Scotland, and he inferred that plagioclase formed during isothermal decompression of these rocks. The pressure recorded by this assemblage can be determined using the reported titanite and plagioclase compositions, appropriate solid-solution models, and temperatures derived from coexisting garnet-clinopyroxene pairs. Ideal ionic mixing was assumed for titanite, such that $a_{\text{tn}} = X_{\text{Ca}}X_{\text{Ti}}X_{\text{Si}}X_{\text{O}}^5$, where X is the atom fraction of the subscripted element. The number of O atoms in titanite was calculated by assuming F and OH substitution for O were charge balanced by Al and Fe^{3+} substitution for Ti; X_{O} is thus $(5 - X_{\text{Al}} - X_{\text{Fe}^{3+}})/5$. Sanders (1988) reported a titanite composition of $\text{CaTi}_{0.89}\text{Al}_{0.11}\text{Si}(\text{O},\text{OH})_5$ which corresponds to $a_{\text{tn}} = 0.796$. The mole fraction of anorthite in plagioclase from this assemblage is 0.22 to 0.25, with a midpoint of 0.235. At 700°C and 2 kb the activity coefficient for anorthite in the midpoint plagioclase composition is 1.6 (Schliestedt and Johannes 1990). Extrapolating this activity coefficient to the conditions of eclogite metamorphism at Glenelg yields $a_{\text{an}} = 0.376$. Assuming stoi-

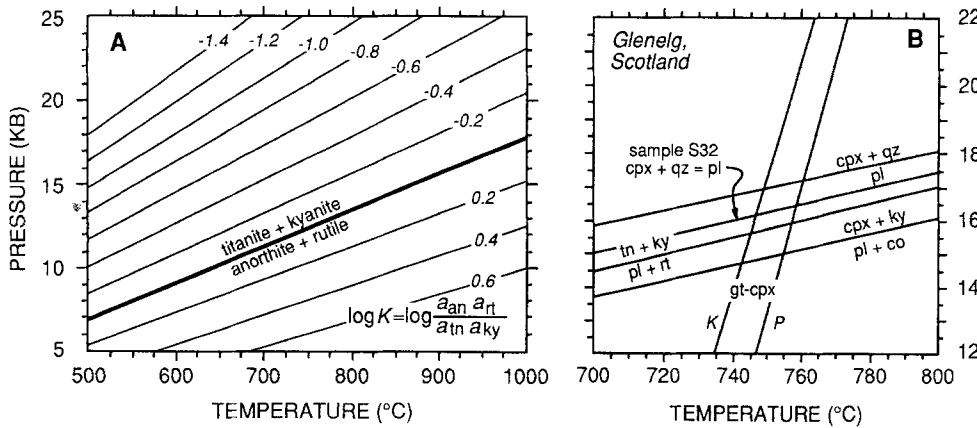
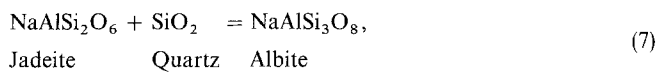


Fig. 3. A Pressure-temperature diagram showing the position of equilibrium (1) for pure phases (bold line) with isopleths of $\log K$ (light lines labeled with values of $\log K$). Calculated from Eq. (6) and the data of Berman (1988). B Conditions of equilibration of eclogites from Glenelg, Scotland. All equilibria are for sample S341 of Sanders (1988) except for the cpx + qz = pl equilibrium, which is for sample

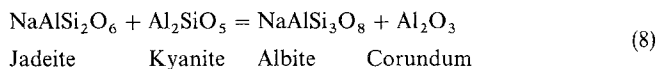
S32 (see text). The curves labeled "K" and "P" correspond to garnet-clinopyroxene (gt-cpx) equilibrium using Krogh (1988) and Powell (1985), respectively. Mineral abbreviations given in Fig. 2, except: cpx, clinopyroxene solid solution; pl, plagioclase solid solution; co, corundum

chiometric rutile and kyanite, $\log K_1$ is thus -0.326 . The intersection of this isopleth of $\log K$ with the curve defining Fe^{2+} -Mg exchange equilibrium between garnet and clinopyroxene gives a pressure of 16.0 kb and a temperature of 758°C (Fig. 3B) using Powell's regression of experimental data (Råheim and Green 1974; Mori and Green 1978; Ellis and Green 1979). The Krogh (1988) expression gives slightly lower values of 15.7 kb and 745°C.

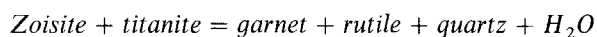
Sanders (1988) gave clinopyroxene compositions coexisting with the TARK assemblage, but noted that quartz is absent from sample S341. Pressure calculated using reaction (1) must therefore lie within the stability field of clinopyroxene + plagioclase + kyanite as defined by the equilibria.



and



(Fig. 3B). These reactions define the range in a_{SiO_2} below quartz saturation that is permissible for stable coexistence of clinopyroxene, plagioclase, and kyanite. Figure 3B shows that, using the solid-solution model of Holland (1983) for clinopyroxene, conditions calculated for sample S341 are consistent with those required by the absence of both corundum and quartz in the assemblage. In addition, the other eclogite from Glenelg discussed by Sanders (sample S32) contains quartz as well as clinopyroxene and plagioclase, and conditions calculated for this sample using (7) agree well with those for sample S341 (Fig. 3B).



Orthorhombic and monoclinic members of the epidote group coexist with garnet, titanite, rutile, and quartz in many eclogites. This assemblage corresponds to the

equilibrium:

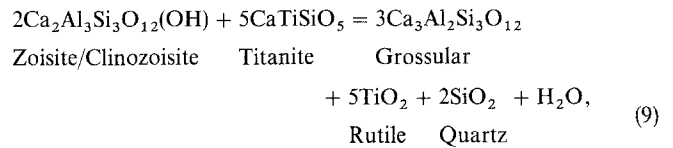


Figure 4A shows isopleths of $\log K_9$ as a function of temperature and pressure. Although the stoichiometric reaction lies at very high pressures and temperatures, the reaction coefficient of grossular in (9) is 3. As a consequence, even with the relatively high mole fractions of grossular common in eclogite-facies garnets, the numerator to the mass-action expression for (9) is usually small, resulting in values of $\log K_9$ in eclogites of -2 to -3 .

The assemblage defined by (9) is found in rocks of the eclogite zone of the Tauern Window, Austria, where mineral compositions are well documented. Franz and Spear (1985) and Spear and Franz (1986) described this assemblage in their sample 82-41, a kyanite-bearing mica-schist. Compositions of titanite and garnet were given by Franz and Spear (1985) for this sample, but compositions of coexisting zoisite were not reported. Because compositions of zoisite vary little in the eclogite-zone lithologies (J. Selverstone personal communication 1991), we used compositions of zoisite from nearby siliceous dolomites (Franz and Spear 1983, Table 1). Assuming Fe^{3+} and Al mix ideally in octahedral M(3) sites in zoisite (Bird and Helgeson 1980), the activity of $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$ in zoisite solid solutions can be represented as $X_{\text{Ca}}^2(1 - \text{Fe}^{3+})X_{\text{Si}}^3$, giving a_{ZO} of 0.833 to 0.994. The positions of equilibrium (9) can be calculated from these values, the activity of titanite (0.688), and the activity of grossular in garnet (Berman 1990), with the activities of H_2O , rutile, and quartz assumed to be 1 (Fig. 4B). The curve lying at higher pressures in Fig. 4B is for $a_{\text{ZO}} = 0.833$, whereas that at lower pressures is for $a_{\text{ZO}} = 0.994$.

Garnet-clinopyroxene pairs in basaltic eclogites of the Tauern Window have K_d values of 9 to 14, where $K_d = [(X_{\text{Fe}^{2+}}/X_{\text{Mg}})_{\text{gt}}/(X_{\text{Fe}^{2+}}/X_{\text{Mg}})_{\text{cpx}}]$, and an average mole

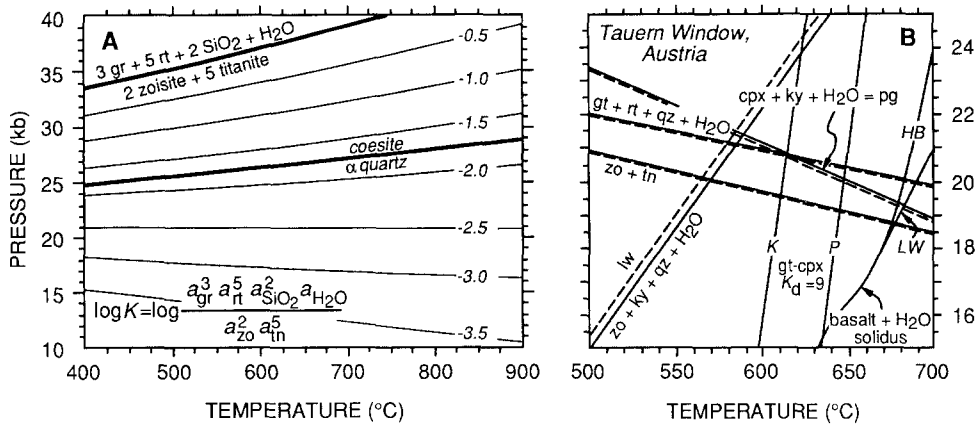


Fig. 4. **A** Pressure-temperature diagram showing the position of equilibrium (9) for pure phases (*bold line*) with isopleths of $\log K$ (*light lines* labeled with values of $\log K$). Calculated from Eq. (6) and the data of Berman (1988). Coesite = α -quartz equilibrium is from Bohlen and Boettcher (1982). The stable SiO_2 polymorph was used in all calculations of $\log K$. **B** Conditions of equilibration of eclogites from the Tauern Window, Austria. The *two curves* representing (9) are for $a_{\text{ZnO}} = 0.833$ (higher pressures) and $a_{\text{ZnO}} = 0.994$ (lower pres-

ures). Lines labeled “HB” and “LW” are H_2O -saturated basalt solidi of Hill and Boettcher (1970) and Lambert and Wyllie (1972). *Solid lines* denote equilibria for which $X_{\text{H}_2\text{O}} = 1$ and *dashed lines* equilibria for which $X_{\text{H}_2\text{O}} = 0.96$ (see text). The curves labeled “K” and “P” correspond to garnet-clinopyroxene (*gt-cpx*) equilibrium using Krogh (1988) and Powell (1985), respectively. Mineral abbreviations given in Figs. 2 and 3, except: *lw*, lawsonite; *pg*, paragonite

fraction of Ca in garnet of ~ 0.2 (Holland 1979a). Temperatures derived from these data at 21 Kb are 554–650°C and 519–615°C (Fig. 4B) based on the equations of Powell (1985) and Krogh (1988), respectively. As noted by Spear and Franz (1986), an additional temperature constraint can be derived from the stable coexistence of zoisite, kyanite, and quartz in the absence of lawsonite in these rocks. In the presence of H_2O , equilibrium among these phases requires temperatures greater than those of the reaction:

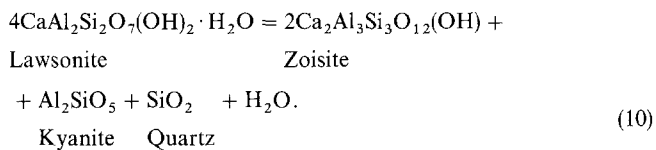


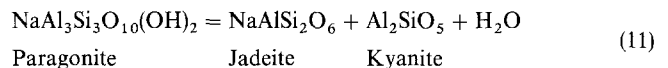
Figure 4B shows the position of (10) calculated using the minimum a_{ZnO} of 0.833. The minimum temperatures calculated for this equilibrium are greater than those required by the maximum K_d values of Holland (1979a). Combination of (9), (10), and garnet-clinopyroxene Fe^{2+} -Mg exchange data thus suggest that the eclogite-zone lithologies of the Tauern Window equilibrated at 570–650°C and 19.2–21.2 kb. Possible pseudomorphs of lawsonite in the mica schists (Spear and Franz 1986) indicate that the garnet-clinopyroxene pairs yielding higher K_d values may preserve earlier Fe^{2+} -Mg exchange equilibrium.

Holland (1979a) and Franz and Spear (1983) used phase equilibria in basaltic kyanite eclogites and siliceous dolomites to show that the high-pressure rocks of the Tauern Window coexisted with an H_2O - CO_2 fluid with a maximum X_{CO_2} of 0.04 during eclogite-facies metamorphism. As can be seen in Fig. 4B, reduction of H_2O activity to that corresponding to $X_{\text{H}_2\text{O}} = 0.96$ (dashed lines) decreases the pressure of equilibrium (9) by only 150 bar at any given temperature. This reduction of $X_{\text{H}_2\text{O}}$ also has a minor effect on the position of equilibrium (10),

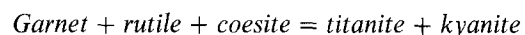
decreasing the temperature at any pressure by $\sim 6^\circ\text{C}$.

The inferred metamorphic conditions are consistent with the absence of melting in the basaltic kyanite-eclogites (Holland 1979a; Spear and Franz 1986). Because these rocks coexisted with nearly pure H_2O at peak metamorphic conditions (Holland 1979a), temperatures in excess of $\sim 680^\circ\text{C}$ at ~ 20 kb would have caused partial melting (Fig. 4B), based on the solidi of Hill and Boettcher (1970) and Lambert and Wyllie (1972).

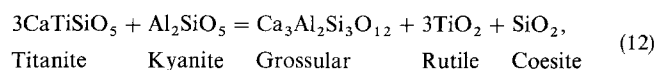
The accuracy of the pressure range calculated from (9) can be assessed using the reaction:



(Holland 1979b). The assemblage kyanite, omphacite, quartz, and paragonite occurs in basaltic kyanite eclogites of the Tauern Window (Holland 1979a). Combining the compositions reported by Holland (1979a), an ideal ionic activity model for paragonite, and Holland’s (1983) activity model for omphacite, (11) requires pressures of 20.2–21.4 kb at temperatures of 590–650°C, virtually identical to the conditions predicted from (9) (Fig. 4B). As shown with the dashed line in Fig. 4B, reduction of $X_{\text{H}_2\text{O}}$ to 0.96 also has little effect on pressures calculated from (11). The close agreement between pressures calculated from equilibria (9) and (11) suggests that (9) allows accurate determination of pressures of eclogite metamorphism.



The reaction:



defines the high-pressure stability of titanite + kyanite. As can be seen in Fig. 5A, the reaction involving stoichio-

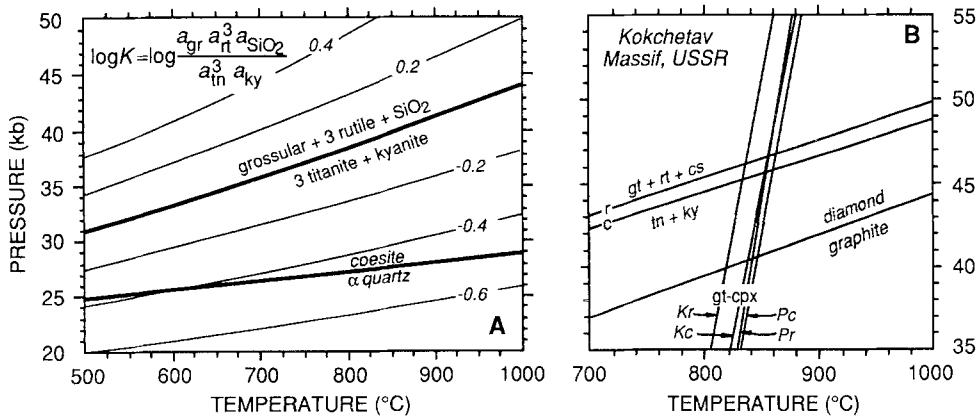


Fig. 5. **A** Pressure-temperature diagram showing the position of equilibrium (12) for pure phases (bold line) with isopleths of $\log K$ (light lines labeled with values of $\log K$). Calculated from Eq. (6) and the data of Berman (1988). Coesite = α -quartz equilibrium is from Bohlen and Boettcher (1982). The stable SiO_2 polymorph was used in all calculations of $\log K$. **B** Conditions of equilibration of eclogites

from the Kokchetav Massif, USSR. Curves were calculated for Sobolev and Shatsky's (1990) reported garnet core compositions (labeled "c") and rim compositions (labeled "r"). The curves labeled "K" and "P" correspond to garnet-clinopyroxene (gt-cpx) equilibrium using Krogh (1988) and Powell (1985), respectively. Mineral abbreviations given in Figs. 2 and 3

metric phases lies at extremely high pressures. For rocks inferred to have experienced unusually high pressures based on the occurrence of coesite or diamond, (12) allows independent calculation of pressures of metamorphism.

The utility of (12) can be illustrated with the data of Sobolev and Shatsky (1990) for diamond-bearing crustal eclogites from the Kokchetav Massif, USSR. Sobolev and Shatsky reported diamond inclusions in garnets and zircons from garnet-pyroxene rocks, biotite-schists, and biotite-gneisses. Other inclusion phases in the biotite-gneisses are titanite, rutile, quartz, and kyanite, and the garnets coexist with clinopyroxene. Pressures can thus be derived using (12) combined with garnet-clinopyroxene equilibria. Garnets in the biotite-gneisses are Ca-rich, ranging in X_{Ca} from 0.302 to 0.398. The values of K_d for Mg-Fe²⁺ exchange between garnet and clinopyroxene in biotite-gneiss sample 53 are 8.1 for the garnet core composition, and 9.5 for the rim composition (Sobolev and Shatsky 1990, Table 1). Figure 5B shows that, using the Powell (1985) thermometer, these compositions correspond to temperatures of $\sim 830^\circ C$ at 35 kb and $\sim 880^\circ C$ at 55 kb. A garnet-clinopyroxene pair in sample 81/5, described as a garnet-pyroxene rock, gives higher temperatures of 1000 to 1060 $^\circ C$ over the same pressure range. If Krogh's (1988) equation is employed, temperatures are $< 20^\circ C$ lower at any given pressure, consistent with Krogh's observation that the difference between his thermometer and Powell's (1985) is small at high pressures and high grossular content in garnet.

Sobolev and Shatsky (1990) reported a composition of titanite in biotite-gneiss sample 258 that, assuming all Fe is Fe³⁺ and normalizing to 3 cations, has a formula of $(Ca_{0.977}Mn_{0.014}Mg_{0.002})(Ti_{0.532}Fe_{0.023}Al_{0.441})Si_{1.023}F_{0.210}(O,OH)_{4.790}$. This titanite composition yields an activity of $CaTiSiO_5$ of 0.323. Using $a_{ky} = 1$, $a_{rt} = 0.993$ calculated from the composition reported by Sobolev and Shatsky for biotite-gneiss sample 83/3, and assuming that the stable SiO_2 polymorph was coesite, we calculate pressures of between 45 and 46.5 kb and temperatures of

830 to 860 $^\circ C$ by solving the mass-action expression in Fig. 5B and the Powell (1985) and Krogh (1988) equations for garnet-clinopyroxene Fe²⁺-Mg exchange. As is shown in Fig. 5B, the calculated pressures are ~ 4 to 5 kb above the diamond-graphite phase boundary of Kennedy and Kennedy (1976). Thus the remarkably great depths of metamorphism indicated by the occurrence of diamond in these rocks are independently required by the silicate-oxide assemblage. The pressures we derive for the biotite gneisses of the Kokchetav massif support the argument that these crustal lithologies were transported to depths of > 140 km before returning to the Earth's surface.

It is important to note that the calculated metamorphic conditions are an extreme extrapolation of the thermodynamic data for the phases involved. In particular, Berman (1988) noted that his expansivity and compressibility coefficients are unconstrained at pressures above ~ 15 kb. Thus, while our calculated pressures are accurate in that they are consistent with the presence of diamond inclusions, they may be imprecise.

Discussion

Estimates of pressures of metamorphism using three equilibria involving titanite and rutile, based on the experimental results on reaction (1), are in all cases consistent with pressures calculated independently. The success of these calculations leads to two observations. First, textural relations commonly suggest that rutile occurs as inclusions in titanite or vice versa. The consistent pressures calculated from independent equilibria suggest that mineral compositions changed little following reactions involving titanite and rutile in these rocks.

In addition, we assumed ideal ionic activity models for all phases except garnet and plagioclase. Because zoisite, rutile, and kyanite were all near end-member compositions, there should be little error introduced by this approximation. However, calculated $CaTiSiO_5$ activities

in titanite solid solutions range from ~ 0.3 to ~ 0.8 in the examples studied. Since inferred pressures using both titanite-rutile and independent equilibria agree closely, we suggest that, if titanite solid solutions are nonideal, the magnitude of this nonideality is unimportant in calculations of pressure and temperature.

The coexistence of titanite and rutile provides the basis for the derivation of intensive thermodynamic variables using a large number of equilibria. Numerous other reactions involving these two phases can be written in the system $\text{CaO-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2\text{-H}_2\text{O-CO}_2$ alone. The agreement between our reversals of reaction (1) and predictions based on Berman's (1988) data should give confidence in calculating metamorphic conditions using equilibria involving titanite and rutile that have not yet been experimentally investigated.

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