

Experimental investigations and geological applications of equilibria in the system $\text{FeO-TiO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$

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Abstract

A new mineralogic geobarometer for peraluminous rocks based on assemblages of ilmenite- Al_2SiO_5 -quartz-garnet-rutile has been calibrated from the equilibrium relation: 3 ilmenite + sillimanite + 2 quartz $\rightleftharpoons$ almandine + 3 rutile. The reaction boundary was located (± 0.2 kbar) using piston-cylinder apparatus at 11.5, 12.0, 12.5, 13.1, 14.6, 15.3 and 15.9 kbar at 750, 800, 850, 900, 1000, 1050, and 1100°C, respectively. The geobarometer is widely applicable as the univariant assemblage occurs in numerous terranes spanning middle amphibolite to garnet-granulite facies metamorphites. Pressures calculated for several terranes are consistent with the appropriate Al_2SiO_5 polymorph(s) and are generally in agreement with other well-calibrated geobarometers subject to choice of mixing properties for Fe-Ca-Mg-Mn garnets.

Introduction

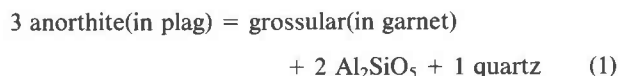
Field and laboratory studies of peraluminous metasedimentary rocks have played a prominent role in shaping current theories concerning the deformational and thermal processes in the crust. Consequently, geobarometry and geothermometry in pelitic rocks have been of considerable interest to metamorphic petrologists. As a result of an abundance of relatively pressure insensitive dehydration reactions in pelitic rocks, temperatures can be reasonably well established in amphibolite and transitional amphibolite-granulite facies rocks. At higher grades, Fe-Ti-oxide (Buddington and Lindsley, 1964; Spencer and Lindsley, 1981) and two-feldspar (Stormer, 1975) thermometry have been successfully applied. However, pressures have been more difficult to determine in pelitic

rocks, especially those of medium metamorphic grade. Historically, relative pressures have been inferred using Al_2SiO_5 index minerals. In rocks where two Al_2SiO_5 minerals coexist, quantitative assessment of pressure is possible if metamorphic temperatures are accurately known. However, there may be substantial uncertainty in such pressure estimates as a result of metastable growth or persistence of a given Al_2SiO_5 polymorph (Grambling, 1981) or uncertainty regarding textural relations, particularly for fibrolitic sillimanite (Vernon and Flood, 1977). Alternatively, pressure and temperature have been simultaneously inferred from assemblages containing two Al_2SiO_5 minerals and the products and reactants of a calibrated dehydration reaction (Carmichael, 1978). Such an approach is locally useful, but the necessary low variance assemblages are uncommon.

Another uncertainty inherent in geothermometry and geobarometry based on dehydration reactions results

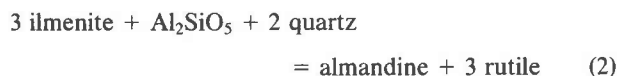
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from variable H_2O activity. Geobarometers based on anhydrous equilibria do not suffer from this disadvantage. One such barometer is based on the assemblage plagioclase-garnet- Al_2SiO_5 -quartz wherein the grossular component of the garnet is buffered by the equilibrium relation:



(Hays, 1967; Hariya and Kennedy, 1968; Goldsmith, 1980). In rocks the assemblage is multivariant as the result of solid solution in plagioclase and garnet. The four phase assemblage is stable over a wide range of pressure and temperature and can be used to infer pressures if equilibration temperatures are known (Ghent, 1976; Newton and Haselton, 1981). The primary difficulty in application of the barometer is that the garnet compositions in pelites containing the four-phase assemblage are typically less than 5 mole% grossular component. Relatively large errors accompany analysis of minor components in addition to errors resulting from uncertainty in the activity of grossular component in garnet at extreme dilution. Another potentially useful barometer is based on equilibria between cordierite and garnet-sillimanite-quartz. Unfortunately, experimental (Hensen and Green, 1971; Currie, 1971) and theoretical and/or semiempirical (Thompson, 1976; Newton and Wood, 1979; Perchuk *et al.*, 1981; Martignole and Sisi, 1981) calibrations are in conflict; pressures inferred from this widespread assemblage have large uncertainties. Given the problems and uncertainties associated with barometry in pelitic rocks, it is clear that additional, well-calibrated barometers are needed.

Assemblages containing ilmenite + Al_2SiO_5 + quartz and/or garnet + rutile are common in medium to high-grade peraluminous metamorphic rocks. The significance of the equilibrium:



has not been recognized previously. This equilibrium relation forms the basis of a useful geobarometer. Natural assemblages containing garnet-rutile- Al_2SiO_5 -ilmenite-quartz (hereafter referred to as GRAIL) are multivariant as the result of solid-solution in garnet and to a lesser extent, in ilmenite. Thus, to a first approximation the pressures inferred from the GRAIL assemblage (at fixed temperature) are a function of garnet composition. Therefore, application of equilibrium (2) in terranes for which metamorphic pressures are well determined by other barometers will allow the activities of almandine to be deduced empirically. This in turn will allow a critical evaluation of garnet solution models. In addition equilibrium (2) will allow inference of accurate thermochemical data for almandine. This is important as there are numerous, significant almandine-bearing reaction equilibria that are

difficult to investigate experimentally, but whose position in P - T - f_{O_2} - f_{S_2} space can be accurately calculated if thermochemical data for almandine are known. Therefore, in light of the overall significance of reaction (2), experiments have been undertaken to determine the relative stabilities of ilmenite- Al_2SiO_5 -quartz and almandine-rutile as a function of pressure and temperature.

Experimental methods

Starting materials

A combination of synthetic and natural minerals were used in the experimental investigation. Natural quartz from Brazil and a low Fe sillimanite from Brandywine, Delaware (Genth collection #399.15, The Pennsylvania State University) together with synthetic rutile, ilmenite, and almandine were used for starting materials. The quartz was prepared by grinding to approximately -200 mesh, followed by leaching in HNO_3 , and then firing at $\sim 800^\circ\text{C}$ for 24 hours. The sillimanite was ground to -200 mesh. Several grains of sillimanite were analyzed by electron microprobe to evaluate homogeneity and to obtain quantitative chemical analyses (Table 1). The sillimanite was homogeneous on the scale of the microprobe beam and contained no elements above background besides Al, Si, and very minor amounts of Fe. Rutile was prepared from Baker Reagent Grade TiO_2 (anatase) by heating at 1000°C for 6 days. X-ray analysis of the product indicated complete conversion to rutile. Ilmenite was synthesized by reacting at 1000°C in evacuated silica tubes appropriate molar quantities of Fe-metal, hematite, and TiO_2 (anatase) that previously had been ground together and pellet pressed. Optical, X-ray, and electron microprobe analyses indicate that the ilmenite is homogeneous and stoichiometric FeTiO_3 . Almandine was prepared using two different starting materials, a glass of almandine composition, and a mixture of appropriate molar quantities of fayalite, sillimanite, and quartz. The glass was prepared by reacting Fe_2O_3 , Al_2O_3 , and SiO_2 in a graphite crucible with a tight-fitting graphite lid at 1375°C for 45 minutes. The result was a black-green homogeneous glass. Optical examination of the material showed no unreacted starting material, and X-ray analysis showed no diffraction pattern. Finely ground glass was then loaded into a 2.5 mm diameter $\text{Ag}_{70}\text{Pd}_{30}$ capsule with approximately 1-2 wt.% H_2O and the capsule sealed. This

Table 1. Electron microprobe analyses of sillimanite

Run #	571	581	601	584	588	574	575	Sillimanite (Genth)
SiO_2	36.2	37.0	36.8	35.9	36.4	35.8	36.7	36.6
TiO_2	0.5	0.7	0.4	0.6	0.6	0.5	0.5	0.0
Al_2O_3	62.8	61.0	62.4	63.0	62.7	62.3	62.0	62.7
FeO	1.0	0.8	0.9	0.9	0.9	0.8	0.8	0.5
Total	100.5	99.5	100.5	100.4	100.6	99.4	100.0	99.8
Si	0.975	1.008	0.990	0.967	0.980	0.974	0.994	0.999
Al	1.993	1.959	1.980	2.001	1.989	1.998	1.978	1.991
Ti	0.010	0.014	0.009	0.011	0.011	0.009	0.010	0.000
Fe	0.022	0.018	0.021	0.020	0.020	0.018	0.018	0.010
T ($^\circ\text{C}$)	750	750	900	1000	1050	1100	1100	-
# points	7	8	7	7	8	9	8	15

capsule was then placed in a 5 mm diameter Pt capsule, along with ~300 mg of Fe-metal powder and sufficient water to react 75% of the Fe to Fe_{1-x}O and the outer capsule was sealed. Garnet was synthesized at 900°C and 15 kbar for 12–14 hours in piston-cylinder apparatus. Optical examination of the product revealed that the glass had reacted completely to garnet with traces ($\leq 0.1\%$) of a low index crystalline phase, probably quartz. X-ray analysis gives the diffraction pattern of garnet ($a = 11.521 \pm 0.001 \text{ \AA}$, determined from powder diffraction patterns, $1/4^\circ$ per minute scanning speed, with quartz as an internal standard) with no indications of other phases. Electron microprobe analyses indicate that the garnet is homogeneous, stoichiometric almandine. Almandine was also prepared from finely ground mixtures of fayalite, sillimanite, and quartz using the procedures outlined above. The fayalite used was stoichiometric Fe_2SiO_4 , and its preparation has been described (Bohlen *et al.*, 1980). The sillimanite and quartz were those described above. Synthesis products were almandine ($a = 11.520 \pm 0.001 \text{ \AA}$) with traces of quartz. Almandine prepared from crystalline starting materials has all of the same physical and chemical properties as that prepared from glass. For both the almandine from glass and from fayalite-sillimanite-quartz the traces of quartz in the garnet could not be eliminated by fine grinding and re-reacting at 900°C, 15 kbar on the iron-wüstite buffer. Synthesis of almandine at a variety of different pressures and temperatures (7–20 kbar, 800–1100°C) gave similar results. However, almandine synthesized as described above but with f_{O_2} buffered by quartz-fayalite-magnetite resulted in a garnet with a slightly larger cell edge ($a = 11.525 - 11.528 \text{ \AA}$) and very slightly increased amounts of additional crystalline phase(s). The only almandine used in this study was that synthesized on the $\text{Fe-Fe}_{1-x}\text{O}$ buffer.

Mössbauer spectra of almandine and ilmenite were obtained at room temperature using a constant acceleration, mechanically driven Mössbauer spectrometer in order to check the starting materials for the presence of Fe^{3+} . Samples of 70–90 mg were used with a 10m Ci^{57}Co in Pd source. Duplicate spectra were recorded in 512 channels of a multichannel analyzer using a velocity increment of 0.03 mm per channel. Counting times were sufficient to obtain several million counts per channel and peak dips of approximately 10^5 counts. The spectra were fitted with lorentzian doublets that in most cases were constrained to equal widths and area for the low- and high-velocity components. Chi-squared and additional goodness-of-fit parameters (Ruby, 1973) were calculated for each fitted spectrum.

The Mössbauer spectrum of ilmenite consists of a single ferrous doublet and a very small, poorly defined ferric doublet that appears in the spectrum as a low intensity "shoulder" on the low velocity part of the ferrous doublet. For the octahedrally coordinated ferrous iron in ilmenite the measured average isomer shift and quadrupole splitting ($\text{IS}_{\text{Fe}^{2+}} = 1.058 \text{ mm/sec}$; $\text{Qs} = 0.637 \text{ mm/sec}$) are similar to previously reported values (Ruby and Shirane, 1961; Syono *et al.*, 1981). Observed peak widths are 0.28 mm/sec. The intensity of the peaks attributable to ferric iron is so low that the location of the ferric doublet had to be constrained in order to obtain convergence in the fitting procedure. The ferric doublet was constrained so as to be consistent with isomer shifts and quadrupole splittings of octahedrally coordinated Fe^{3+} in other similar Fe phases. The relative areas of the ferrous and ferric count dips suggest that approximately $3 \pm 1.5\%$ of the iron is present as Fe^{3+} . A slight, but significant, difference was noted in the areas of the two components of the ferrous doublet. At first this was thought to be the result of

preferred orientation of the platy ilmenite grains. However, similar ferrous doublets with unequal areas are observed even after efforts have been taken to eliminate the preferred orientation. Relaxation of the constraint of equal area results in a slightly better fit to the data but does not change the relative amounts of inferred Fe^{3+} . The relative areas of the ferrous count dips differ by $3 \pm 0.1\%$, and a cause for this difference cannot be determined.

The Mössbauer spectrum of almandine consists of a ferrous doublet that is very widely split in comparison with other ferrous iron silicates and a very small, poorly defined ferric doublet that appears in the spectrum as a low-intensity "shoulder" on the high velocity edge of the low velocity component of the ferrous doublet. For ferrous iron (in the dodecahedral position) the measured average isomer shift and quadrupole splitting ($\text{IS}_{\text{Fe}^{2+}} = 1.299 \text{ mm/sec}$; $\text{Qs} = 3.546 \text{ mm/sec}$) are closely similar to reported values for garnets (Amthauer *et al.*, 1976); however, these values are the first reported for the almandine end member. The observed peak widths are 0.3 mm/sec. The ferric doublet has a measured average isomer shift and quadrupole splitting that appears to be consistent with tetrahedral ferric iron. However, the intensity of the ferric iron count dips is so low that there are large errors in the fitted parameters, and, therefore, the data could also be consistent with octahedrally coordinated Fe^{3+} . For almandine synthesized on the iron-wüstite buffer the relative areas of the ferrous and ferric doublets indicate that $2 \pm 1\%$ of the iron is present as ferric iron. For almandine synthesized on the FMQ buffer somewhat higher Fe^{3+} contents ($4 \pm 1.5\%$) are inferred. This is consistent with the larger cell edge ($a = 11.525 - 11.528 \text{ \AA}$) than for almandine synthesized on $\text{Fe-Fe}_{1-x}\text{O}$ and suggests that the cell edge for almandine reported in a variety of literature sources as 11.526–11.528 (*e.g.*, Robie *et al.*, 1966; Hsu, 1968; Meagher, 1980) was probably determined using almandine containing significant Fe^{3+} . Based on the data described above, the cell edge for almandine is slightly less than 11.521 Å.

Apparatus and experimental procedure

For every experiment, 9–12 mg of the GRAIL assemblage in proportions consistent with the stoichiometry of reaction (2) were ground together and loaded into 1.6 mm diameter $\text{Ag}_{80}\text{Pd}_{20}$ capsules that were sealed by arc welding. The 1.6 mm diameter capsules were loaded into 3 mm diameter Pt capsules along with 150 mg of Fe metal powder and sufficient H_2O to react 75% of the Fe to Fe_{1-x}O . The outer capsules were also sealed by arc welding. For experiments of $\leq 950^\circ\text{C}$ 2–4 wt.% H_2O was added to the reactants in inner capsule to increase reaction rates. The reactants in the inner capsule of experiments above 950°C were loaded dry and the capsules sealed with no special measures taken to eliminate moisture.

All experiments were conducted in piston-cylinder apparatus with 2.54 cm diameter furnace assemblies similar to those described by Johannes (1978) and by Boettcher *et al.* (1981). They consist entirely of NaCl and graphite and differ from those used by Johannes in the following ways: (1) The bottom (piston end) graphite plug extends 3 mm into the internal portion of the assembly. (2) The sample is placed horizontally in the notched top surface of a cylinder of NaCl. (3) The thermocouple ceramic is sheathed by 3 mm diameter MgO tubing that in turn is surrounded by a cylinder of NaCl. Temperature was measured with $\text{Pt}_{100}\text{-Pt}_{90}\text{Rh}_{10}$ thermocouples with no correction for the effect of pressure on emf. We used the piston-in technique by

Table 2. Electron microprobe analyses of ilmenite

Run #	566	581	601	584	588	574	575
SiO_2	0.1	0.1	0.1	0.1	0.2	0.1	0.2
TiO_2	54.5	54.2	53.8	53.5	52.8	52.8	53.0
Al_2O_3	0.0	0.1	0.3	0.4	0.8	0.9	0.9
FeO	46.2	47.3	46.1	46.8	47.5	46.2	46.2
Total	100.8	101.7	100.3	100.8	101.3	100.0	100.3
Si	0.003	0.002	0.002	0.003	0.004	0.002	0.006
Al	0.000	0.003	0.008	0.011	0.020	0.027	0.027
Ti	1.028	1.012	1.019	1.007	0.987	0.999	0.999
Fe	0.970	0.983	0.971	0.980	0.987	0.972	0.968
T(°C)	750	750	900	1000	1050	1100	1100
# points	6	7	7	7	8	7	7

bringing pressure to 10% below that of the final value, increasing the temperature to that desired for the experiment and then increasing the pressure to the final value. During the period over which the temperature was increased, there was a concomitant increase in pressure as a result of thermal expansion of NaCl. However, the piston was always advanced to the final value.

Our furnace assemblies have been calibrated over a wide range of P and T using the melting points of CsCl, LiCl and NaCl (Clark, 1959, as modified by Bohlen and Boettcher, 1982), the reactions albite $\rightleftharpoons$ jadeite + quartz (Hays and Bell, 1973) and ferrosilite $\rightleftharpoons$ fayalite + quartz (Bohlen *et al.*, 1980). These data indicate that our NaCl assemblies require no pressure correction. Nominal pressures are listed in Table 3. The details of the calibration are given by Bohlen and Boettcher (1982).

Experimental products

The products of all experiments were analyzed optically and by X-ray diffraction. Several of the experimental charges were analyzed by electron microprobe. Analyses were obtained using an automated ARL-EMX electron microprobe analyzer with wavelength dispersive ADP, LiF, and TAP crystal spectrometers. Well-analyzed natural almandine-rich garnet (USNM 107105 from the Smithsonian Institution), ilmenite, kyanite, and synthetic andradite were used as standards. An accelerating potential of 15 kV and an emission current of 150 μ A, and a sample current of 0.010–0.012 μ A, were standard operating conditions. Counting times were sufficient to collect >10,000 counts for all major elements in standards and unknowns. Spectrometer data were reduced using the correction procedures of Bence and Albee (1968). The results for sillimanites and ilmenites are given in Tables 1 and 2, respectively. Analyses of garnet were nearly impossible to obtain because of very fine intergrowths of garnet and rutile. Analyses of almandines showed a minimum of 1.5 wt.% TiO_2 apparently the result of intergrown rutile. Neglecting such TiO_2 resulted in garnet formulas that are stoichiometric within analytical uncertainty.

In most cases, reaction direction was obvious upon optical examination of the experimental products. Where changes in the relative proportions of ilmenite–sillimanite–quartz and almandine–rutile were more subtle, the intensities of X-ray peaks of the minerals were used to infer reaction direction. A change of X-ray peak intensities of less than 20% was taken as “no reaction.”

Results and discussion

Results of the experiments are given in Table 3 and in Figure 1. The reversals tightly constrain the equilibrium location and dP/dT slope, providing a sound basis for calculations of metamorphic pressures from natural assemblages of ilmenite– Al_2SiO_5 –quartz–garnet–rutile. The experiments using sillimanite have been carried out almost entirely in the stability field of kyanite. The location of the stable, kyanite-bearing reaction can be accurately calculated from the experimental data and those of Richardson *et al.* (1968). Figure 2 shows the location of the stable kyanite-bearing equilibrium boundary calculated from molar volume data (Robie *et al.*, 1966).

The intersection of the breakdown of staurolite–quartz (Richardson, 1968; Rao and Johannes, 1979) with the GRAIL equilibrium generates additional reactions (Fig. 2). Such equilibria define the lower temperature stability limit of garnet–rutile assemblages in the presence of H_2O vapor. The reactions:

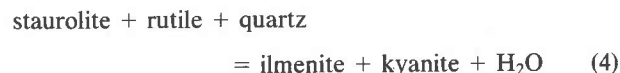
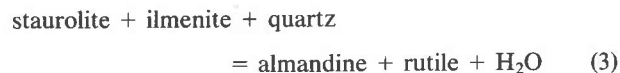
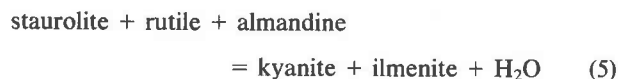


Table 3. Experimental conditions and results

Run #	P(Kbar)	T(°C)	Duration (hrs)	Results
566	9.0	750	70	ISQ(AR)
569	11.0	750	88	ISQ(AR)
571	11.4	750	138.5	ISQAR
581	11.9	750	168.7	ARISQ
570	11.5	800	46	ISQAR
572	11.9	800	68.5	ISQAR
577	12.4	800	97.5	ARISQ
675	12.1	800	141	ARISQ
578	13.0	850	69.3	AR(ISQ)
582	12.6	850	147	ARISQ
678	12.6	850	121.5	AR(ISQ)
679	12.4	850	120.5	ISQ(AR)
559	10.0	900	20.5	ISQ
560	14.0	900	21	AR(ISQ)
563	13.0	900	26	ISQAR
564	15.0	900	26	AR(ISQ)
565	13.4	900	26.5	ARISQ
585	13.0	900	49	ISQAR
586	13.3	900	69	AR(ISQ)
601	13.0	900	70	ISQ(AR)
674	13.1	900	69	ISQ(AR)
587	13.8	950	72	ISQAR
583	14.7	1000	32	AR(ISQ)
584	14.5	1000	41.6	ISQ(AR)
573	15.4	1050	18	AR(ISQ)
576	15.0	1050	25	ISQ(AR)
588	15.2	1050	24	ISQ(AR)
574	15.6	1100	8	ISQ(AR)
575	16.0	1100	8	ARISQ
580	16.2	1100	16.7	AR(ISQ)
598	15.6	1100	18	ISQAR
599	16.0	1100	19	ARISQ
600	15.8	1100	21	ISQAR

Parentheses indicate minor to trace amounts present.
Underlining indicates dominant phases.

are qualitatively located on Figure 2. Uncertainty in the formula and thermodynamic properties of staurolite prevent a quantitative assessment of the dP/dT slopes of reactions (3) and (4). However, these reactions are potentially useful for geobarometry or geothermometry. Assemblages containing both reactants and products of reactions (3) and (4) have been reported in several field areas (Ghent, 1975; Pigage, 1976; Fletcher and Greenwood, 1978; Holdaway, 1978). One additional reaction that emanates from the invariant point involving the GRAIL assemblage is:



We have omitted this reaction from Figure 2 for clarity given that quartz-absent pelitic rocks containing the assemblage appropriate for reaction (5) are practically non-existent.

Geobarometry

Using available volume data (Robie *et al.*, 1966), thermal expansion and compressibility values (Skinner, 1966; Birch, 1966) and the equilibrium curve in Figure 2, we have calculated a P - T - $\log_{10}K$ diagram for GRAIL equilibria (Fig. 3), where $K = (a_{\text{Ilm}})(a_{\text{Al}_2\text{SiO}_5})(a_{\text{Qtz}}^2)/(a_{\text{Alm}})(a_{\text{Ru}}^2)$, the equilibrium constant for reaction (2) where unit activity refers to the pure phase along the univariant equilibrium curve. The $\log_{10}K$ curves were calculated from the expression: $\Delta P = (-RT \ln K)/2.303\Delta V$. The shallow dP/dT slopes of the $\log_{10}K$ curves emphasize the utility of these equilibria for geobarometry. Figure 3 can be used for the evaluation of metamorphic pressures from natural assemblages given (1) the GRAIL assemblage in-

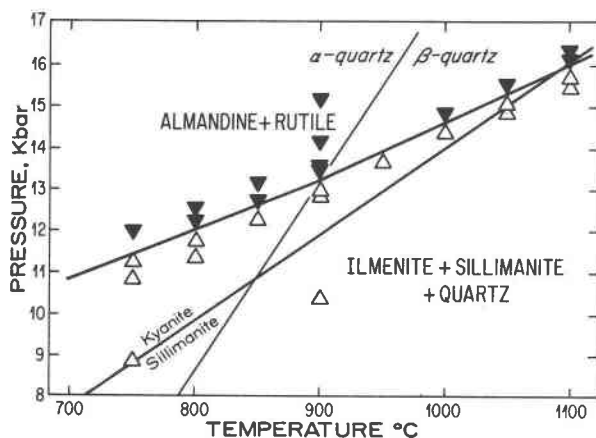


Fig. 1. Pressure-temperature projection showing the relative stabilities of almandine + rutile and ilmenite + sillimanite + quartz. Δ indicates that ilmenite + sillimanite + quartz grew at the expense of almandine + rutile. ∇ indicates that almandine + rutile grew at the expense of ilmenite + sillimanite + quartz. Kyanite-sillimanite and α - β quartz equilibria from Richardson *et al.* (1968) and Cohen and Klement (1967).

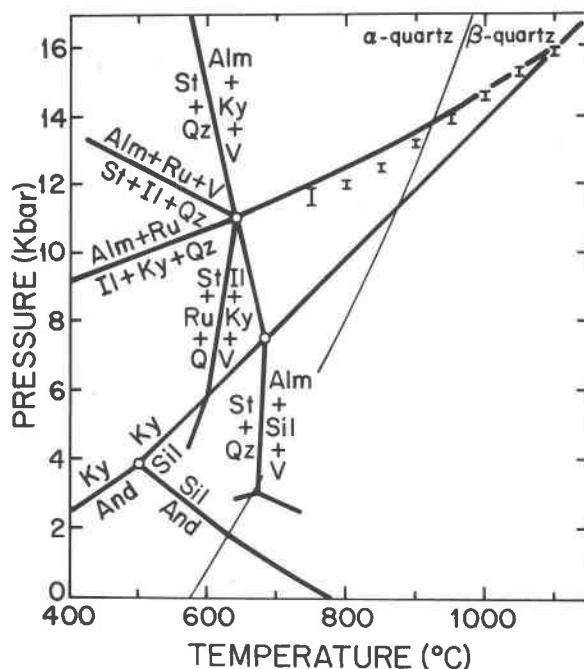


Fig. 2. Pressure-temperature projection showing the relative locations of the stable kyanite-bearing reaction of ilmenite + Al_2SiO_5 + quartz = almandine + rutile. Brackets are experimental reversals for the sillimanite-bearing reaction. Staurolite reactions are from Richardson (1968) and Rao and Johannes (1979). Al_2SiO_5 phase relations from Holdaway (1971). α - β quartz from Cohen and Klement (1967).

ferred to coexist at equilibrium, (2) the compositions of the phases, (3) appropriate solution models for the activity of end-member components in impure minerals, (4) a reasonable estimate of equilibration temperature.

Equilibrium coexistence of the GRAIL assemblage is sometimes difficult to demonstrate. In many rocks one or more of the phases, usually the titanium oxides, are present at levels of less than one modal percent. Additionally, ilmenite may have oxidized during retrogression and/or weathering resulting in the formation of rutile or anatase. Rutile has also been noted as a product of retrogression of titaniferous biotite. Such retrograde development of TiO_2 is usually easily recognizable by textural examination. In our experience the most reliable geobarometry can be obtained from paragneisses in which ilmenite and rutile are present as inclusions in garnet, the oxide inclusions commonly exhibiting grain boundary relations indicative of chemical equilibrium (Vernon, 1975, p. 41). The compositions of the ilmenite and rutile in garnet grains and in the host rock matrix are commonly similar, affording further evidence that the oxide phases and garnet comprised equilibrium assemblages. Relict garnets in some substantially retrogressed rocks may even preserve the former higher grade GRAIL assemblage.

The compositions of quartz, Al_2SiO_5 and rutile com-

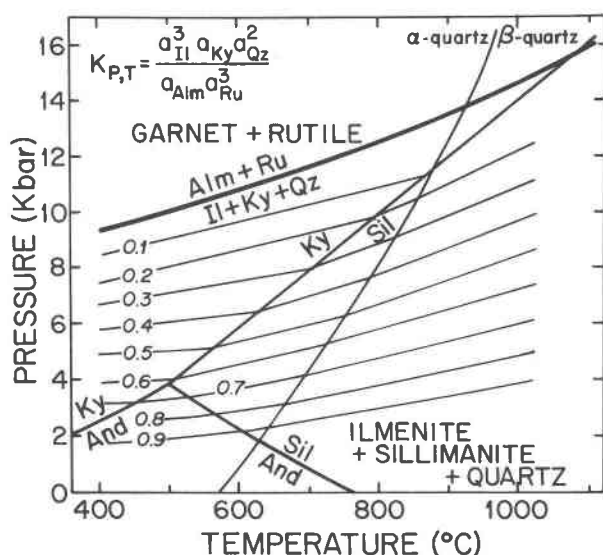


Fig. 3. Pressure-temperature-log K (to base 10) plot for ilmenite- Al_2SiO_5 -quartz-almandine-rutile geobarometer. Al_2SiO_5 phase relations from Holdaway (1971). α - β quartz from Cohen and Klement (1967).

monly differ little from those of end-member components. Rutile with appreciable Nb and Fe have been reported, but application of ideal solution models will not lead to significant errors in calculated pressures. Ilmenite in peraluminous rocks may contain significant proportions of hematite and pyrophanite. Ilmenite-hematite solutions are probably appreciably nonideal at moderate tempera-

tures (*i.e.*, middle amphibolite facies) becoming ideal or nearly so under granulite facies conditions (Anderson and Lindsley, 1981). Hematite-rich ilmenites may not be compatible with almandine-rich garnets, the latter being unstable with respect to oxide-aluminum silicate assemblages at the relatively high f_{O_2} required by hemo-ilmenite. Fe^{3+} enriched ilmenites are probably products of retrograde alteration. In nearly all the cases examined (Table 4), ilmenite in the GRAIL assemblage contained less than 15 mole% hematite and pyrophanite combined, and we have adopted an ideal-solution model for these and other less significant components. It should be noted that Fe-Mn partitioning between ilmenite and garnet is strongly dependent on temperature. When adequately calibrated, Fe-Mn partitioning will provide a useful check on garnet-ilmenite equilibrium relations in natural assemblages.

Garnets in medium-grade rocks commonly exhibit growth zoning whereas those in high-grade paragneisses are usually relatively homogeneous, aside from retrograde rim compositions. In this context accurate geobarometry requires careful assessment of the garnet compositions in equilibrium with the other phases. Zoned garnets that have remained saturated with ilmenite- Al_2SiO_5 -quartz-rutile could conceivably yield information on prograde, peak and retrograde metamorphic pressures.

The solution properties of garnet potentially present an obstacle to accurate geobarometry. In many pelitic rocks, especially those of high metamorphic grade, the garnets are essentially almandine-pyrope solutions with spessartine, grossular and andradite components, together comprising less than 5–15 mole%. Empirical determinations

Table 4. Pressures calculated from assemblages of ilmenite- Al_2SiO_5 -quartz-garnet-rutile

Locality	Reference	Sample No.*	Observed Al-Silicate	Temperature (°C)	Pressure (Kbar)	Other Barometers (Kbar)
Lake Bonaparte, Benson Mines, Adirondacks	Bohlen, unpublished	78-LB-20, 78-Ben-1	Sill	730, 730	7.5, 7.8	7.5**
Western Maine	Evans and Guidotti (1966)	9, 24	Sill	600, 600	6.7, 7.5	
Quesnel Lake, British Columbia	Fletcher and Greenwood (1979)	6, 9, 13	Ky, Ky-Sill, Ky-Sill	680, 680, 680	8.4, 8.4, 7.7	7.6
Esplanade Range, British Columbia	Ghent (1975)	CV-150	Ky	540	7.7	7.9†
South Island, New Zealand	Hattori (1967)	11468	Ky-Sill	620	6.3	6.5
Northern Idaho Batholith	Hietanen (1969)	2127	Ky	650	8.5	
Funeral Mts., Death Valley, California	Labotka (1980)	FML-110	Ky-Sill	660	7.3	7.2
Kilbourne Hole, New Mexico	Padovani and Carter (1977)	4, 18, 51, 54, 57, 62, 68	Sill	800, 800, 800, 800, 800, 800, 800	7.2, 7.3, 8.0, 7.3, 8.1, 7.8, 7.9	
Yale, British Columbia	Pigage (1976)	3, 4, 5	Ky, Ky, Sill	600, 600, 650	7.8, 6.9, 8.0	7.3
Ivrea Zone, N. Italy	Schmidt and Wood (1976)	SD-121, SD-139, SD-430E	Sill	710, 710, 710	7.2, 7.0, 7.4	5.8†
Colton, New York	Stoddard (1976)	C-74A, C-79B1, C-79B2, C-74B, C-79A, C-74, C-629, C-532, C-529	Sill	730, 730, 730, 730, 730, 730, 730	7.5, 7.5, 7.6, 7.3, 7.4, 7.1, 7.2, 7.1, 7.0	5.8†, 7.0††
Central Massachusetts	Tracy (1978)	871, L11y, C26A, M34, 595C	Sill	675, 675, 675, 675, 675	7.0, 6.3, 7.2, 6.5, 5.3	6.8†

*Sample No., Al-silicate, temperature and pressure are listed in corresponding column and row positions.

**Orthopyroxene-olivine-quartz, Bohlen and Boettcher, 1982.

† Plagioclase-garnet- Al_2SiO_5 -quartz, Newton and Haselton, 1981.

†† Orthopyroxene-plagioclase-garnet-quartz, Bohlen et al., 1983.

|| Kyanite-sillimanite at known temperature, Richardson et al., 1968.

of $W_{\text{FeMg}}^{\text{gt}}$ for garnet yield 2580 , 2979 ± 185 , 2580 ± 140 , and 1509 ± 1392 cal/gm atom (Saxena, 1968; Ganguly and Kennedy, 1974; Oka and Matsomoto, 1974; Dahl, 1980), respectively. Experimentally determined values are substantially lower. Kawasaki and Matsui (1977) determined a value of 2120 ± 350 cal/gm-atm at high pressure and temperature. O'Neill and Wood (1979) inferred that Fe-Mg garnet mixing is significantly more ideal at 1000°C than it is in olivine. Heat of solution measurements on olivines by Wood and Kleppa (1981) indicate that W_{FeMg} for olivines is in the range of 1200 cal/gm-atom for Fe-rich compositions. This implies that W_{FeMg} for garnets must be in the range of 500 – 1000 cal/gm-atom. If one accepts Sack's (1980) value of $W_{\text{FeMg}} = 800$ cal/gm-atom for olivines, then W_{FeMg} for garnets of 0 – 300 cal/gm-atom are required by the experimental data. After a review of the available data, Perkins (1979) proposed a T dependent expression for $W_{\text{FeMg}}^{\text{gt}}$ ($3480 - 1.27^\circ\text{C}$) that yields $W_{\text{FeMg}}^{\text{gt}}$ of 2500 ± 100 cal/gm-atom for granulite temperatures. However, in light of the recent experimental data, this expression has been rejected in favor of an ideal mixing model ($W_{\text{FeMg}} = 0$) by Newton and Perkins (1982), although they noted that such a choice is at the lower limit of permissible values. An additional empirical test of $W_{\text{FeMg}}^{\text{gt}}$ can be made by comparing GRAIL barometry with estimates in terranes for which pressures have been reliably established. Choice of $W_{\text{FeMg}}^{\text{gt}}$ below 1000 – 1500 cal/gm-atom yields sillimanite pressures for kyanite-bearing rocks and in a few cases, andalusite pressures for some sillimanite-bearing rocks. In terranes where pressures are well known, such as the Adirondacks (see Bohlen *et al.*, 1982, for a review) empirical evaluations of $W_{\text{FeMg}}^{\text{gt}}$ give values of 2200 – 2500 cal/gm-atom. Therefore, we have adopted the Perkins model for almandine-pyrope because it is consistent with the bulk of empirical data and yields pressures consistent with the appropriate Al_2SiO_5 mineral in all but one of 45 ilmenite- Al_2SiO_5 -quartz-garnet-rutile assemblages evaluated. It should be noted, however, that our conclusion regarding $W_{\text{FeMg}}^{\text{gt}}$ is based primarily on Fe-rich compositions, whereas the data of O'Neill and Wood (1979) were determined for Mg-rich garnets. The apparent discrepancy between the two sets of Fe-Mg mixing properties could be an indication of marked asymmetry of these parameters in Fe-Mg garnets. The Perkins model for almandine-grossular garnets has also been accepted for calculations in this study (see Bohlen *et al.*, 1982, for justification). Spessartine is a significant component of some garnets in peraluminous rocks, but there are few data on the mixing of Fe-Mn and Mg-Mn garnets. For those garnets with significant Mn we have assumed that Fe-Mn garnets mix ideally (Ganguly and Kennedy, 1974) and that interactions of Ca and Mg with Mn are the same as those for Fe. In any case the $\log_{10}K$ -pressure-temperature plot (Fig. 3) derived from the experimental data is not dependent on the garnet mixing models and potential users can make their own choice of solution models for geobarometry applications.

A literature search indicates that the assemblage of ilmenite- Al_2SiO_5 -quartz-garnet-rutile is common, but the compositions of all of the phases are rarely reported. There are a number of terranes that probably contain the assemblage but accessory phases in the rocks are commonly combined in the modes, and there is no distinction between oxides, sulfides, *etc.* As can be seen in this study, it is important that the presence of even trace amounts of a given phase be clearly reported. Pressures have been calculated from 14 areas for which at least garnet analyses are reported (Table 4). Table 4 indicates that the GRAIL geobarometer yields accurate pressures that agree well with a variety of other well-calibrated barometers. Precision of the inferred pressures is also excellent, especially considering that some of the spread may be the result of real pressure variation. With the exception of one assemblage in western Maine (Evans and Guidotti, 1966), pressures inferred from all of the assemblages predict the correct Al_2SiO_5 polymorph. The discrepancy for the Maine assemblage may be the result of a low estimated temperature; increase of the estimated equilibration temperature by 50 – 60°C would eliminate the conflict and still be consistent with other phase relations. Generally the pressures in Table 4 are in agreement with the estimates of the original workers. Our pressure for the Picuris Range, New Mexico (Holdaway, 1978) is about 1 kbar below the value given by Holdaway of 3.7 kbar based on occurrences of Al_2SiO_5 minerals. However, only a garnet analysis (containing 40 mole% spessartine) is available and, therefore, the pressure given is a minimum. The accurate and precise pressures are evidence that generally, on at least the scale of a thin section, all minerals in these pelitic rocks, even those present in very minor to trace amounts, are in equilibrium.

A range of geobarometers applicable to high-grade metamorphic rocks are now available (see Essene, 1982, for a review) but few precise and accurate "sliding" equilibria that are independent of water activities may be used for pressure estimates in medium-grade terranes. Our GRAIL barometer has the advantage that the loci of iso-activity product curves are nearly independent of temperature (Fig. 3). Temperature uncertainties of $\pm 50^\circ\text{C}$ result in maximum errors in inferred pressure of about 0.5 kbar. We suggest that the GRAIL barometer has particular application to Barrovian-style metamorphic terranes. Because the phases involved (other than garnet) depart little from end-member compositions, garnet-rutile assemblages can be used to infer *minimum pressures* for rocks lacking the requisite GRAIL assemblage.

The GRAIL geobarometer may be used to clarify retrograde metamorphic pressure-temperature-time paths. England and Richardson (1977) and Wells (1979) have emphasized the importance of evaluating thermal relaxation histories for understanding the tectonic evolution of metamorphic belts. The oxide phases are known for their reactivity, and for the GRAIL assemblage to remain in equilibrium during retrogression a nearly isobaric cooling

path is required (Fig. 3). Garnet rim compositions are known for several terranes listed in Table 4. The extreme rims are commonly richer in Fe and Mn than internal portions of the garnet. Such rim compositions are considered to result from retrograde adjustments consonant with increased Mn-Fe partitioning between ilmenite, biotite, and garnet. If it is assumed that the garnet rim compositions are in equilibrium with other phases in the rock during retrogression, then retrograde pressures can be evaluated. The $\log_{10}K$ values for the garnet-rim-rutile-ilmenite- Al_2SiO_5 -quartz assemblage are smaller than the $\log K$ values for nonrim garnet compositions. This requires that the retrograde pressure paths be less temperature-dependent than the loci of constant $\log K$ (Fig. 3) which further implies the early retrograde cooling path is nearly isobaric. Similar nearly isobaric retrograde trends have been noted in several metamorphic terranes. The inferred retrograde P - T paths of these terranes are consistent with diminishing heat supply during the waning stages of metamorphism. This suggests, following the thermal models of England and Richardson (1977), that heat from the addition of magma into the crust may be an important component of the heat budget of many metamorphic terranes.

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References

- Birch, F. (1966) Compressibility: elastic constants. In S. P. Clark, Jr., Ed., *Handbook of Physical Constants*, p. 97-174. Geological Society of America Memoir 97.
- Bohlen, S. R. and Boettcher, A. L. (1981) Experimental investigation and geological applications of orthopyroxene-olivine-quartz geobarometry. *American Mineralogist*, 66, 951-965.
- Bohlen, S. R. and Boettcher, A. L. (1982) The quartz $\rightleftharpoons$ coesite transformation: a precise determination and the effects of other components. *Journal of Geophysical Research*, 87, 7073-7078.
- Bohlen, S. R., Essene, E. J., and Boettcher, A. L. (1980) Reinvestigation and application of olivine-quartz-orthopyroxene stability. *Earth and Planetary Science Letters*, 47, 1-10.
- Bohlen, S. R., Wall, V. J., and Boettcher, A. L. (1983) Experimental investigation and application of model garnet granulite equilibria. *Contributions to Mineralogy and Petrology*, 83, 52-61.
- Buddington, A. F. and Lindsley, D. H. (1980) Iron-titanium oxide minerals and their synthetic equivalents. *Journal of Petrology*, 5, 310-357.
- Carmichael, D. M. (1978) Metamorphic bathozones and bathograds: a measure of post-metamorphic uplift and erosion on a regional scale. *American Journal of Science*, 278, 769-797.
- Clark, S. P. (1959) Effect of pressure on the melting points of eight alkali halides. *Journal of Chemistry and Physics*, 31, 1526-1531.
- Cohen, L. H. and Klement, W., Jr. (1967) High-low quartz inversion: determination to 35 kilobars. *Journal of Geophysical Research*, 72, 4245-4251.
- Currie, K. L. (1971) The reaction 3 cordierite = 2 garnet + 4 sillimanite + 5 quartz as a geologic thermometer in the Opinicon Lake region, Ontario. *Contributions to Mineralogy and Petrology*, 33, 215-226.
- Dahl, P. S. (1980) The thermal-compositional dependence of Fe^{2+} - Mg^{2+} distributions between coexisting garnet and clinopyroxene: applications to geothermometry. *American Mineralogist*, 65, 852-866.
- England, P. C. and Richardson, S. W. (1977) The influence of erosion upon the mineral facies of rocks from different metamorphic environments. *Quarterly Journal of the Geological Society of London*, 134, 201-213.
- Essene, E. J. (1982) Geologic thermometry and barometry. In J. M. Ferry, Ed., *Reviews in Mineralogy*, 10, p. 153-206. Mineralogical Society of America, Washington, D.C.
- Evans, B. W. and Guidotti, C. V. (1966) The sillimanite-potash feldspar isograd in western Maine, U.S.A. *Contributions to Mineralogy and Petrology*, 12, 25-62.
- Fletcher, C. J. N. and Greenwood, H. J. (1978) Metamorphism and structure of Penfold Creek area, near Quesnel Lake, British Columbia. *Journal of Petrology*, 20, 743-794.
- Froese, E. (1976) Applications of thermodynamics in metamorphic petrology. Geological Survey of Canada, Paper 75-43.
- Ganguly, J. and Kennedy, G. C. (1974) The energetics of natural garnet solid solution. I. Mixing of the aluminosilicate endmembers. *Contributions to Mineralogy and Petrology*, 48, 137-148.
- Ghent, E. (1975) Temperature, pressure, and mixed-volatile equilibria attending metamorphism of staurolite-kyanite-bearing assemblages, Esplanade Range, British Columbia. *Geological Society of America Bulletin*, 86, 1654-1660.
- Ghent, E. A. (1976) Plagioclase-garnet- Al_2SiO_5 -quartz: a potential geothermometer-geobarometer. *American Mineralogist*, 61, 710-714.
- Goldsmith, J. R. (1980) The melting and breakdown reactions of anorthite at high pressures and temperatures. *American Mineralogist*, 65, 272-284.
- Grambling, J. A. (1981) Kyanite, andalusite, sillimanite, and related mineral assemblages in the Truchas Peaks region, New Mexico. *American Mineralogist*, 66, 702-722.
- Grew, E. S. (1981) Granulite facies metamorphism at Molodzhnaya Station, East Antarctica. *Journal of Petrology*, 22, 297-336.
- Hariya, Y. and Kennedy, G. C. (1968) Equilibrium study of anorthite under high pressure and high temperature. *American Journal of Science*, 266, 193-203.
- Hattori, H. (1967) Occurrence of sillimanite-garnet-biotite gneisses and their significance in metamorphic zoning in South Island, New Zealand. *New Zealand Journal of Geology and Geophysics*, 10, 269-299.
- Hays, J. F. (1967) Lime-alumina-silica. *Carnegie Institution of Washington Year Book*, 65, 234-239.
- Hays, J. F. and Bell, P. M. (1973) Albite-jadeite-quartz equilib-

- rium: a hydrostatic determination. Transactions of the American Geophysical Union, 54, 482.
- Hensen, B. J. and Green, D. H. (1971) Experimental study of the stability of cordierite and garnet in pelitic compositions at high pressures and temperatures. I. Compositions with excess aluminosilicate. Contributions to Mineralogy and Petrology, 33, 309–330.
- Hietanen, A. (1969) Distribution of Fe and Mg between garnet, staurolite and biotite in aluminum-rich schist in various metamorphic zones north of the Idaho Batholith. American Journal of Science, 267, 422–456.
- Holdaway, M. J. (1971) Stability of andalusite and the aluminum silicate phase diagram. American Journal of Science, 271, 97–131.
- Holdaway, M. J. (1978) Significance of chloritoid-bearing and staurolite-bearing rocks in the Picuris Range, New Mexico. Geological Society of America Bulletin, 89, 1404–1414.
- Hsu, L. C. (1968) Selected phase relations in the system Al-Mn-Fe-Si-O-H : a model for garnet equilibria. Journal of Petrology, 9, 40–83.
- Johannes, W. (1978) Pressure comparing experiments with NaCl , AgCl , talc, pyrophyllite assemblages in a piston-cylinder apparatus. Neues Jahrbuch für Mineralogie Monatshefte, 2, 84–92.
- Kawasaki, T. and Matsui, Y. (1977) Partitioning of Fe^{2+} and Mg^{2+} between olivine and garnet. Earth and Planetary Science Letters, 37, 159–166.
- Labotka, T. C. (1980) Petrology of a medium-pressure regional metamorphic terrane, Funeral Mountains, California. American Mineralogist, 65, 670–689.
- Martignole, J. and Sisi, J. C. (1981) Cordierite-garnet- H_2O equilibrium: a geological thermometer, barometer and water fugacity indicator. Contributions to Mineralogy and Petrology, 77, 38–46.
- Meagher, E. P. (1980) Silicate garnets. In P. H. Ribbe, Ed., Reviews in Mineralogy, 5, p. 25–66. Mineralogical Society of America, Washington, D.C.
- Newton, R. C. and Haselton, H. T. (1981) Thermodynamics of the garnet-plagioclase- Al_2SiO_5 -quartz geobarometer. In R. C. Newton, A. Navrotsky, and B. J. Wood, Eds., Thermodynamics of Minerals and Melts, p. 129–145. Springer, New York.
- Newton, R. C. and Perkins, D., III (1982) Thermodynamic calibration of geobarometers for charnockites and basic granulites based on the assemblages garnet-plagioclase-orthopyroxene (clinopyroxene)-quartz with applications to high-grade metamorphism. American Mineralogist 67, 203–222.
- Newton, R. C. and Wood, B. J. (1979) Thermodynamics of water in cordierite and some petrologic consequences of cordierite as a hydrous phase. Contributions to Mineralogy and Petrology, 68, 391–405.
- Oka, Y. and Matsumoto, T. (1974) Study on the compositional dependence of the apparent partition coefficient of iron and magnesium between coexisting garnet and clinopyroxene solid solutions. Contributions to Mineralogy and Petrology, 48, 115–121.
- O'Neill, H. St. C. and Wood, B. J. (1979) An experimental study of Fe-Mg partitioning between garnet and olivine and its calibration as a geothermometer. Contributions to Mineralogy and Petrology, 70, 59–70.
- Padovani, E. R. and Carter, J. L. (1977) Aspects of the deep crustal evolution beneath south central New Mexico. American Geophysical Union Monograph, 20, 19–55.
- Perchuk, L. L., Podlesskii, K. K., and Aranovich, L. Ya. (1981) Calculation of thermodynamic properties of end-member minerals from natural parageneses. In R. C. Newton, A. Navrotsky, and B. J. Woods, Eds., Thermodynamics of Minerals and Melts, p. 111–129. Springer, New York.
- Perkins, D., III (1979) Application of new thermodynamic data to mineral equilibria. Unpublished Ph.D. Thesis, The University of Michigan.
- Pigage, L. C. (1976) Metamorphism of the Settler schist, southwest of Yale, British Columbia. Canadian Journal of Earth Sciences, 13, 405–421.
- Rao, B. B. and Johannes, W. (1979) Further data on the stability of staurolite + quartz and related assemblages. Neues Jahrbuch für Mineralogie, Monatshefte, 10, 437–447.
- Richardson, S. W. (1968) Staurolite stability in a part of the system Fe-Al-Si-O-H . Journal of Petrology, 9, 467–488.
- Richardson, S. W., Bell, P. M., and Gilbert, M. C. (1968) Kyanite-sillimanite equilibrium between 700 and 1500°C. American Journal of Science, 266, 513–541.
- Robie, R. A., Bethke, P. M., Toulmin, M. S., and Edwards, J. L. (1966) X-ray crystallographic data, densities and molar volumes of minerals. In S. P. Clark, Jr., Ed., Handbook of Physical Constants, Geological Society of America Memoir, 97, 27–74.
- Robie, R. A., Hemingway, B. S., and Fisher, J. R. (1978) Thermodynamic properties of minerals and related substances at 298.15K and 1 bar (10^5 Pascals) pressure and at higher temperatures. United States Geological Survey Bulletin, 1452.
- Ruby, S. L. (1973) Why misfit when you already have χ^2 ? Mössbauer Effect Methodology, 8, 263–277.
- Ruby, S. L. and Shirane, G. (1961) Magnetic anomaly in $\text{FeTiO}_3\text{-}\alpha\text{Fe}_2\text{O}_3$ system by Mössbauer effect. Physical Review, 23, 1239–1240.
- Sack, R. O. (1980) Some constraints on the thermodynamic mixing properties of Fe-Mg orthopyroxenes and olivines. Contributions to Mineralogy and Petrology, 71, 237–246.
- Saxena, S. K. (1968) Distribution of iron and magnesium between coexisting garnet and clinopyroxene in rocks of varying metamorphic grade. American Mineralogist, 53, 2018–2024.
- Schmid, R. and Wood, B. J. (1976) Phase relationships in granulitic metapelites from the Ivrea-Verbano Zone (Northern Italy). Contributions to Mineralogy and Petrology, 54, 255–279.
- Skinner, B. J. (1966) Thermal expansion. In S. P. Clark, Jr., Ed., Handbook of Physical Constants. Geological Society of America Memoir, 97, 75–96.
- Spencer, K. J. and Lindsley, D. H. (1981) A solution model for coexisting iron-titanium oxides. American Mineralogist, 66, 1189–1201.
- Stoddard, E. F. (1976) Granulite facies metamorphism in the Colton-Rainbow Falls area, northwest Adirondacks, New York. Unpublished Ph.D. Thesis, University of California, Los Angeles.
- Stormer, J. C., Jr. (1975) A practical two-feldspar geothermometer. American Mineralogist, 60, 667–674.
- Syono, Y., Ito, A., and Morimoto, S. (1981) Systematics of Mössbauer parameters in Fe^{57} -doped titanate and germanate ilmenites. Journal of Physics and Chemistry of Solids, 42, 483–486.
- Thompson, A. B. (1976) Mineral reactions in pelitic rocks. II. Calculation of some P - T - X (Fe-Mg) phase reactions. American Journal of Science, 276, 425–454.

- Tracy, R. J. (1978) High-grade metamorphic reactions and partial melting in pelitic schist, west-central Massachusetts. *American Journal of Science*, 278, 150–178.
- Vernon, R. H. (1975) *Metamorphic Processes*. John Wiley and Sons, New York.
- Vernon, R. H. and Flood, R. H. (1977) Interpretation of metamorphic assemblages containing fibrolitic sillimanite. *Contributions to Mineralogy and Petrology*, 59, 227–235.
- Wall, V. J., Clemens, J. D., Essene, E. J., Treiman, A. F., and Westrum, E. F., Jr. (1980) Thermodynamic properties and phase equilibria for ilmenite (abstr.) *Transactions of the American Geophysical Union*, 46, 1146–1147.
- Wells, P. R. A. (1979) Chemical and thermal evolution of Archaean sialic crust, southern West Greenland. *Journal of Petrology*, 20, 187–226.
- Wood, B. J. and Kleppa, O. J. (1981) Thermochemistry of forsterite-fayalite olivine solutions. *Geochimica Cosmochimica Acta*, 45, 529–534.
- Zen, E. (1973) Thermochemical parameters of minerals from oxygen-buffered hydrothermal equilibrium data: method, application to annite and almandine. *Contributions to Mineralogy and Petrology*, 39, 65–80.

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