Akermanite in the Cascade Slide Xenolith and Its Significance for Regional Metamorphism in the Adirondacks*

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Abstract. Akermanite (Ak_{90}) coexists with monticellite (Mo_{92}) and wollastonite (Wo_{99}) in an unusual calc-silicate xenolith in anorthosite at Cascade Slide in the Adirondack Mountains, New York. Experimental results bearing on the stability of akermanite have been evaluated through calculations based on thermochemical data and by chemical analysis of experimental products (Yoder 1975). A temperature of $750° \pm 30°$ C and a pressure less than 7 kb are inferred. These estimates are in agreement with the conditions of regional metamorphism previously inferred from other nearby rock types. When errors are considered, all existing data show that the Cascade Slide mineral assemblages last equilibrated at a slightly higher pressure of 7.4 ± 1 kb and at a temperature of $750° \pm 30°$ C during regional granulite facies metamorphism. The exotic mineralogy at Cascade Slide (akermanite, monticellite, cuspidine and wilkeite) was stabilized by low carbon dioxide fugacity. Posttectonic anorthosite intrusion is ruled out by the absence of a preserved contact aureole.

Introduction

An unusual occurrence of akermanite coexisting with monticellite and wollastonite has been found in a zoned xenolith of marble and calc-silicate at Cascade Slide within the anorthosite massif of the Adirondack Highlands. Although this xenolith contains a diverse suite of minerals that are typical of the sanidinite facies, previous estimates of metamorphic grade in all other rocks of the Adirondack Highlands show equilibration in the granulite facies. We have exam-

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ined the stability of akermanite-bearing assemblages in order to determine whether the xenolith last equilibrated in a post-tectonic aureole, during syntectonic regional metamorphism, or during pre-tectonic contact metamorphism. This question is critical to resolving the many conflicting theories of anorthosite genesis (de Waard 1969a) and the possibility of polymetamorphism in the Adirondacks.

Cascade Slide is located on the north side of Cascade Mountain above the outlet of Upper Cascade Lake in North Central Mt. Marcy Quadrangle, New York. Several blocks of metasediment are found as inclusions in anorthosite on Cascade Mountain. The largest is exposed in Cascade Slide with outcrop measuring about 30×200 m. This body has been previously investigated because of its unusual mineralogy (Emmons 1842; Kemp 1920; Baillieul 1976; Valley and Essene 1977, 1979; Tracy et al. 1978), but its metamorphic significance has not been completely understood. The writers have located two smaller marble xenoliths nearby, but neither contains comparable mineralogies.

Widespread evidence of assimilated metasediment can often be found on mountain tops in the vicinity of Cascade Mountain (Kemp 1920; Isachsen and Fisher 1970). This relationship suggests that this area was near the top of the anorthosite intrusion that engulfed xenoliths and roof pendants of orginally overlying rock units. At contacts there is always a silicated zone that may be as thin as 15 cm or as thick as 6 m separating the anorthosite from marble. One or more concentric zones are observed, with varying assemblages of: grossular-andradite, wollastonite, calcite, clinopyroxene, quartz or magnetite. It is likely that many of the compositional zones found at Cascade Slide, including the akermanite unit, represent varying degrees of metasomatic interaction between marble and anorthosite. However, the contact relationships are partially obscured by cover and it
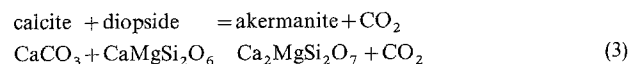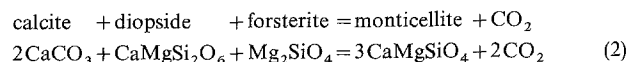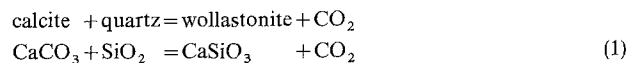
is also possible that the body is a synform as proposed by Baillieul (1976) based on detailed mapping. Some compositional banding in the calc-silicates could represent original sedimentary layers.

The granulite facies metamorphism of the Adirondack Highlands has been extensively studied (Buddington 1939; de Waard 1969b; Valley and Bohlen 1979). The overprint of this 1 b.y. Grenville event is so strong that sediments have completely recrystallized. Even dry, refractory igneous rocks have largely recrystallized and now contain garnets and/or pyroxenes of metamorphic composition (Bohlen and Essene 1978). Recent results (Bohlen et al. 1980b; Valley and Essene 1980) indicate a gradual increase in metamorphic grade across the Adirondacks from 6 ± 1 kb, $650° \pm 30°$ C at the amphibolite-granulite facies boundary in the northwest to 8 ± 1 kb, $750° \pm 30°$ C in the Central Adirondack Highlands. Temperatures of regional metamorphism have been contoured across the Adirondacks from K-feldspar-plagioclase and magnetite-ilmenite thermometry (Bohlen and Essene 1977; Bohlen et al. 1980b). The 700° and 750° C isotherms form roughly concentric curves around the anorthosite massif with higher temperatures toward the center. If the minerals at Cascade Slide equilibrated during regional metamorphism then these isotherms would lead one to predict a temperature slightly in excess of 750° C.

Metamorphic pressure in the Adirondack Highlands is restricted by widespread occurrences of sillimanite that require pressures less than 9 kb at 700°–750° C (Newton 1966a; Richardson et al. 1968; Holdaway 1971). Such pressures are consistent with the assemblage fayalite + quartz in the Au Sable Quadrangle (20 km NNE of Cascade Slide), which yields a pressure less than 9.5 ± 1 kb (Bohlen et al. 1980a) when the effects of impurities in the olivine are considered. In addition, scattered occurrences of iron-rich orthopyroxene restrict minimum pressures. Jaffe et al. (1978) report Fs_{95} in charnockites 8 km to the west of Cascade Slide that restricts pressures to more than 7.8 ± 1 kb when the effects of impurities are properly modeled (Bohlen et al. 1980a). Unfortunately neither sillimanite nor olivine + quartz has been found within the anorthosite massif. Thus, there is a possibility that pressures might be somewhat higher in Mt. Marcy Quadrangle. Jaffe et al. (1978) estimate pressures to be 8.5 to 11.5 kb at 750° C based on their interpretation of ferrosilite and fayalite + quartz assemblages, significantly overlapping the stability of kyanite. It will be shown, however, that if akermanite equilibrated during regional metamorphism, then its presence at Cascade Slide can be used to restrict these higher pressures, requiring metamorphism within the sillimanite field.

Melilite group minerals can form at high temperatures and low pressures by the contact metamorphism of impure limestone (Tilley 1929; Burnham 1959; Joesten 1974). At Scawt Hill in Ireland, melilite, larnite, merwinite and spurrite are developed at the contact of dolerite and chalk (Tilley 1929). At Crestmore, California, melilite is associated with many minerals that are also found at Cascade Slide, including grossular, diopside, wollastonite, vesuvianite, monticellite, cuspidine, forsterite, perovskite and spinel at the contact of limestone and quartz monzonite porphyry (Burnham 1959). Relatively pure akermanite is reported by Schaller (1916) at Mt. Vesuvius, where it occurs in metamorphosed blocks of impure limestone. In this study we report the first occurrence of akermanite in a high-grade regionally metamorphosed terrane and discuss its stability.

Akermanite, monticellite and sometimes wollastonite are generally considered to be index minerals of the sanidinite facies (Bowen 1940; Turner 1967). They are so characteristic that Winkler (1976) has proposed the terms monticellite-melilite zone and tilleyite-spurrite zone for low and high temperature subdivisions of the sanidinite facies. However, many studies have shown the importance of mixed volatiles in metamorphism (Greenwood 1967; Kerrick 1974) and because these minerals may form through volatilization reactions their stability cannot be considered in terms of pressure and temperature alone. Important reactions limiting their stability are:

calcite + quartz = wollastonite + CO_2

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2 \tag{1}$$

calcite + diopside + forsterite = monticellite + CO_2

$$2CaCO_3 + CaMgSi_2O_6 + Mg_2SiO_4 = 3CaMgSiO_4 + 2CO_2 \tag{2}$$

calcite + diopside = akermanite + CO_2

$$CaCO_3 + CaMgSi_2O_6 = Ca_2MgSi_2O_7 + CO_2 \tag{3}$$

In each reaction higher CO_2 pressure tends to stabilize the reactants while a decrease in CO_2 pressure stabilizes the products, wollastonite, monticellite, or akermanite. At 8 kb, the lithostatic pressure inferred for regional metamorphism of the Adirondack Highlands, these reactions require temperatures of 1,010°, 1,150°, and 1,150° C respectively if lithostatic pressure is equal to CO_2 pressure (calculations based on experiments by Walter 1963; Greenwood 1967; Yoder 1975). Because these temperatures are 200° to 400° C higher than other estimates for the Adirondacks and would cause massive in situ melting in adjacent feldspathic rocks for which there is no evidence, it has been suggested that lower values of CO_2 pressure are likely (Valley and Essene 1977; Tracy et al. 1978). This could have resulted from dilution by other fluids,

such as H_2O or CH_4, or from the absence of a free metamorphic fluid such that CO_2 activities were buffered by solid phases only (Valley and Essene 1977, 1979). These two possibilities should always be considered when working with volatilization reactions, especially in the granulite facies, and will be the subject of a second paper by the authors on Cascade Slide. A third possibility, that these minerals were stabilized during pre- or post-tectonic contact metamorphism, at much lower lithostatic pressure, is inconsistent with other solid-solid equilibria at Cascade Slide, as will be shown in this paper. Thus Bowen's (1940) index minerals for marbles are of little use in determining either metamorphic temperature or facies unless the fugacity of CO_2 can be defined.

Mineralogy and Texture

Mineral assemblages from the calc-silicate bodies on Cascade Mountain are listed in Table 1. Only those minerals are listed that are inferred to be in chemical equilibrium from the criteria described below. Common minerals include calcite (often sky-blue in hand specimen), pyroxene (Di_{97-50}), garnet (Gr_{80-40}), wollastonite, monticellite, scapolite (Me_{40-80}), magnetite, K-feldspar and plagioclase. Less commonly, assemblages may contain forsterite, akermanite, spinel, tremolite, quartz, sphene, tourmaline, apatite, sphalerite, pyrite, pyrrhotite, galena, perovskite, harkerite, cuspidine, wilkeite and vesuvianite. Phlogopite and graphite have been reported in float at Cascade Slide (Baillieul 1976) but have not yet been found in place. This paper is the first report of akermanite, cuspidine and wilkeite in the Adirondacks and, to the writers' knowledge, in any granulite facies terrane.

Mineral textures in Adirondack marbles and calc-silicates typically indicate metamorphic annealing, often with 120° grain boundary angles. The domain of a thin section is assumed to represent equilibrium except in banded rocks or where minerals are zoned. Equilibrium assemblages have not been inferred across bands of

different mineralogy because of the possibility that gradients in chemical potentials exist. Equilibrium has been assumed within individual bands that are likely to represent domains of constant chemical potential in the absence of mineral zoning. Retrograde textures such as rimming or exsolution that are easily recognized elsewhere in Adirondack marbles (Valley and Essene 1980) have been avoided. Many cuspidine-bearing samples, including LP 77-210-10, contain 30% alteration that is fine grained and chemically heterogeneous at the scale of microprobe analysis. This alteration does not appear to have formed at the expense of any of the minerals that were analyzed, except sometimes wollastonite (Fig. 1b), and probably indicates the former presence of additional minerals that may have been stable at the peak of metamorphism. Powder X-ray diffraction and qualitative electron microprobe analysis of a few areas of alteration have failed to reveal the identify of such former minerals.

Two generations of wollastonite and monticellite occur with occasional crystals of akermanite. Coarse, discrete grains of each mineral (Fig. 1a, b) are found in thin section along with a fine-grained, graphic intergrowth. The intergrowths consist of wollastonite and monticellite in a symplectic texture (Fig. 1c). It is assumed that the coarse grains of wollastonite and monticellite were in equilibrium with akermanite at the peak of metamorphism, but the intergrowths may represent back-reaction of akermanite. Similar intergrowths from carbonate xenoliths in gabbro of the Bushveld Complex are reported by Willemse and Bensch (1964) and interpreted to represent retrograde reaction of akermanitic melilite. The same conclusion was made by Harker and Tuttle (1956) for intergrowths at Crestmore, although Burnham (1959) interprets them as a metasomatic replacement of preexisting intergrowths of monticellite with spurrite, merwinite or cuspidine.

Akermanite Stability in the System CaO—MgO—SiO_2

An estimate of pressure and temperature at Cascade Slide may be obtained from solid-solid reactions involving akermanite. Five applicable reactions have

Table 1. Mineral assemblages identified in thin section from Cascade Mt. The * indicates minerals that have been quantitatively analyzed. Approximate compositions when given were determined by energy dispersive analysis. LP samples are from this study; CL is from Tracy et al. (1978) and Cl is from Baillieul (1976). Mineral abbreviations are: Cc = calcite; Cpx = clinopyroxene; Fo = forsterite; Gn = garnet; Mo = monticellite; Wo = wollastonite

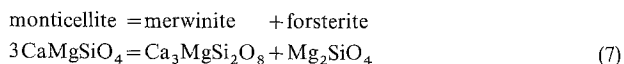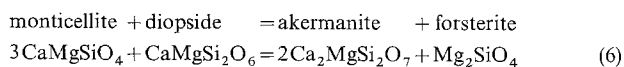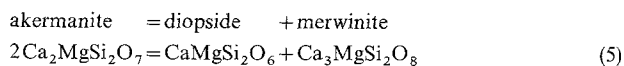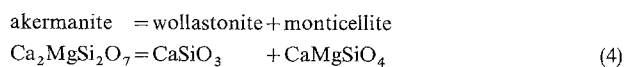|	Cc	Cpx	Mo	Fo	Wo	Gn	
LP 77-201	x	x*	x*	x*			spinel*, wilkeite, sphalerite
LP 77-201-1	x						tremolite*, tourmaline
LP 77-201-2	x	x			x	x	
LP 77-201-5	x	x	x				spinel, apatite, vesuvianite
LP 77-210-1		x					magnetite
LP 77-210-5	x	x				x	pyrrhotite
LP 77-210-10		x*	x*		x*	x*	akermanite*, cuspidine*
LP 78-210-6	x	x				x	garnet-clinopyroxene, symplectite
LP 201-3	x	x				x	quartz, sphene
LP 201-3a		x				x*	quartz, sphene, plagioclase, K-feldspar, apatite
LP 201-3b	x	x					sphalerite, pyrite
LP 201-3c	x	x					sphalerite, pyrite, pyrrhotite
LP 201-34		x				x*	quartz, K-feldspar, plagioclase, sphene, apatite
LP 201-4	x	x	x			x	spinel
Cl-1h							harkerite, perovskite
CL-3a	x	x	x*	x*			spinel*, vesuvianite*
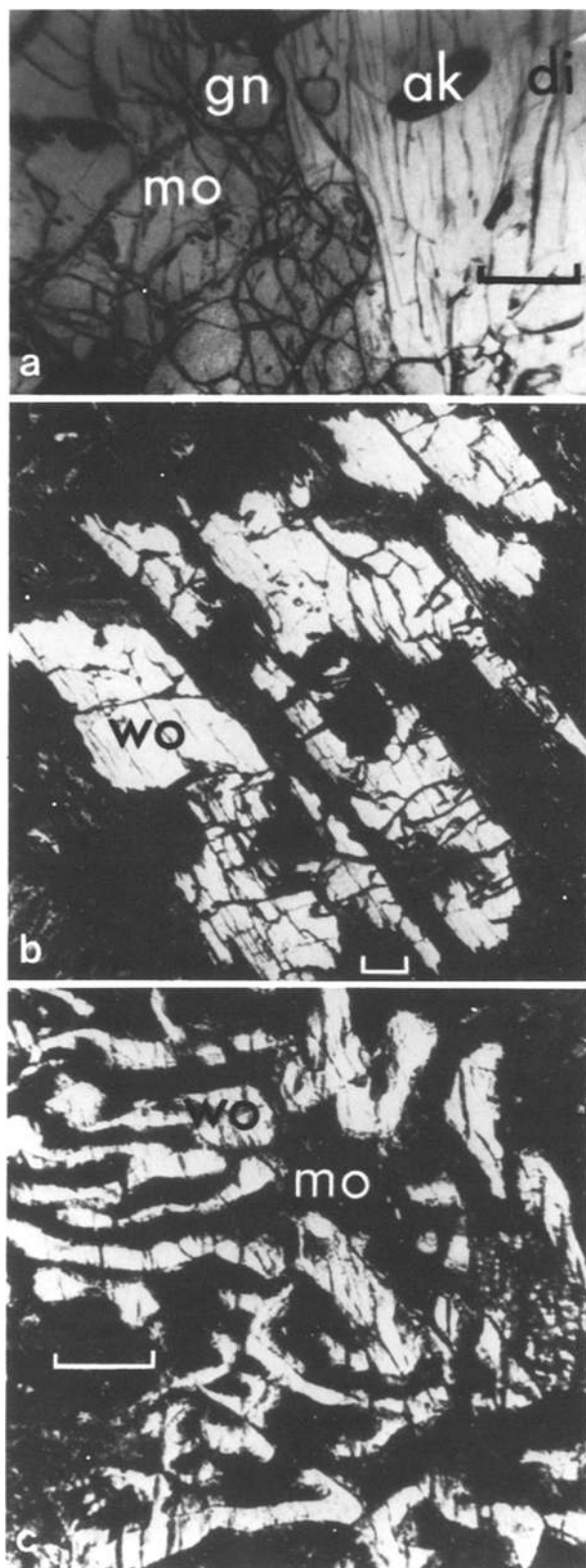
Fig. 1. a Photomicrograph of LP 77-210-10 showing coexisting akermanite, monticellite, diopside and garnet. Scale bar is 1,000 μm. Elsewhere in this thin section are cuspidine and wollastonite. Analyses of these minerals are in Table 4. **b and c** Photomicrographs of LP 78-210-10-2. This sample was collected within one meter of LP 77-210-10 from the same rock unit and is mineralogically similar although the wollastonite-monticellite intergrowths are better developed. Figure 1 b shows primary, coarse, optically continuous wollastonite that is broken with fine-grained, heterogeneous alteration along fractures. Scale bar is 200 μm. Figure 1 c shows a fine-grained intergrowth of optically continuous monticellite and wollastonite. Scale bar is 100 μm. Note the 5 × magnification over Fig. 1 b

been experimentally calibrated in the system CaO—MgO—SiO_2:

akermanite = wollastonite + monticellite
$$Ca_2MgSi_2O_7 = CaSiO_3 \quad + CaMgSiO_4 \tag{4}$$

akermanite = diopside + merwinite
$$2Ca_2MgSi_2O_7 = CaMgSi_2O_6 + Ca_3MgSi_2O_8 \tag{5}$$

monticellite + diopside = akermanite + forsterite
$$3CaMgSiO_4 + CaMgSi_2O_6 = 2Ca_2MgSi_2O_7 + Mg_2SiO_4 \tag{6}$$

monticellite = merwinite + forsterite
$$3CaMgSiO_4 = Ca_3MgSi_2O_8 + Mg_2SiO_4 \tag{7}$$

wollastonite + monticellite = diopside + merwinite
$$2CaSiO_3 \quad + 2CaMgSiO_4 = CaMgSi_2O_6 + Ca_3MgSi_2O_8 \tag{8}$$

These reactions are plotted in Fig. 2 along with the reversals of Harker and Tuttle (1956) and Yoder (1975) for reaction (4), Kushiro and Yoder (1964) and Yoder (1975) for reaction (5), Walter (1963) and Yoder (1968) for reaction (6), Yoder (1968) for reaction (7), and Yoder (1975) for reaction (8). Because coexisting akermanite + wollastonite + monticellite are found at Cascade Slide, the $P-T$ conditions must lie along reaction (4) but at lower pressure than the invariant point [Fo].

The $P-T$ location of all reactions in Fig. 2 have been calculated by the computer program EQUILI (Wall and Essene 1972) from the relation:

$$\Delta G_r(P_2 T_2) - \Delta G_r(P_1 T_1) = -\int_{T_1}^{T_2} \Delta S_r \, dT + \int_{P_1}^{P_2} \Delta V_r \, dP. \tag{9}$$

Details of this program are described elsewhere (Valley and Essene 1980). Necessary entropy data are given in Table 2. Values of V_{298} are taken when available from Robie et al. (1978) except for merwinite which is from Moore and Araki (1972). Thermal expansion is calculated from data in Skinner (1966) and compressibility from Birch (1966). When not available these values are estimated from data on structurally and chemically related minerals.

The experimentally determined reaction slopes in Fig. 2 are generally consistent with calculated slopes except for reactions (5) and (6). For reaction (5) the calculated slope is $+131°/kb$ whereas the experimental reversals require a slope of $+85°/kb$. A possible explanation of this discrepancy is that solid solution at high temperatures has shifted the experimental reaction relative to end-member minerals. This explanation has also been proposed by Helgeson et al. (1978) to explain inconsistencies between their thermodynamic data and Yoder's (1968) experiments for reaction (6). For example, if the diopside and merwinite grown in the experiments of Yoder (1975) were mutu-
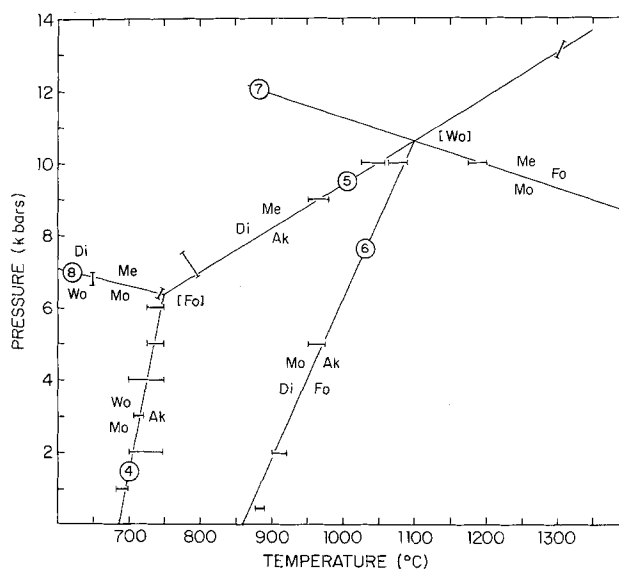

Fig. 2. Pressure-temperature diagram of reactions (4) through (8) for end-member compositions in the ideal system CaO—MgO—SiO_2

ally soluble then the experimentally determined equilibrium for reaction (5) will be shifted to lower pressures. If the experimentally grown akermanite is a solid solution (within the system CaO—MgO—SiO_2), the reaction will be shifted to higher pressures. Thus significant solid solution could explain the difference between the calculated and experimental slope. An alternative explanation for this discrepancy is that errors in entropy and/or volume result in an error in the calculated slope. Increase of calculated ΔV_r by 0.75 J/bars (from -2.11 to -1.36) or decrease in ΔS_r by 8.8 J/mol°K (from -16.0 to -24.8) would be required to account for the disagreement. Such a change in ΔS_r would correspond to a 1–3% change in S_T for either merwinite or akermanite. Such an error is not unlikely as the heat capacities of merwinite and akermanite have only been measured above 50°K. If the volume of merwinite given by Robie et al. (1978) (10.44 J/bar) is used rather than that of Moore and Araki (1972) (9.848 J/bar), then much of the discrepancy is removed. Moore and Araki summarize five other studies consistent with their own careful measurements, whereas Robie et al. estimated volume from density data and Robie now accepts the Moore and Araki value (Robie, personal communication, 1979). Thus, the volume data of Moore and Araki are to be preferred and assignment of the slope discrepancy to errors in the volume of merwinite alone cannot be justified. The calculated slope for reaction (5) will be more accurately estimated when the heat capacities of merwinite and akermanite have been measured to low temperatures, thereby decreasing uncertainties in the entropy data base.

Table 2. Volume and entropy of minerals used in EQUILI: V°_{298} in cm^3/mol; $S^\circ_T - S^\circ_{298} = A \cdot \ln T + B \cdot 10^{-3} \cdot T + C \cdot 10^5 T^{-2} + D$ (T in $^\circ K$, S in cal/mol·$^\circ$). Note: to convert to S.I. units as is done in the text, divide V by 10 and multiply S by 4.1840

	V°_{298}	Source	S°_{298}	Source	A	B	C	D	Source
Akermanite	92.81	(1)	50.031	(1)	60.972092	10.781864	6.3927813	-357.76	(1)
Anorthite	100.79	(1)	47.63	(1)	36.177765	40.583145	-9.3403101	-210.03	(1)
Calcite	36.934	(1)	21.92	(1)	24.597229	5.6011763	2.918417	-145.09	(1)
Diopside	66.09	(1)	34.106	(2)	56.563293	5.5108109	12.942201	-335.71	(1)
Forsterite	43.79	(1)	22.49	(2)	35.966522	6.6885138	4.6139383	-212.13	(1)
Grossular	125.30	(1)	60.96	(3)	107.96191	13.708772	16.051285	-637.33	(3)
Merwinite	98.48	(6)	60.499	(1)	73.798569	11.307795	7.7449579	-432.57	(1)
Monticellite	51.36	(1)	25.64	(4)	34.322296	9.1385698	3.7102203	-202.46	(4)
Quartz	22.688	(1)	9.909	(1)	11.100000	8.3889999	1.3310003	- 67.24	(1)
Wollastonite	39.93	(1)	19.37	(5)	26.386215	3.8636436	3.1771917	-155.05	(1)

Sources: (1) Robie et al. (1978); (2) Robie (pers. comm., 1979); (3) Westrum et al. (1979); (4) $S_{Mo} = {}^1/_2 (S_{Forsterite} + S_{Ca\text{-}olivine})$; (5) Haas et al. (1979); (6) Moore and Araki (1972)

Because the location of reaction (5) is critical to restricting pressures at Cascade Slide, the possibility of solid solution in experimental run products was carefully investigated. The run products in experiments reported by Yoder (1975) were not analyzed by electron microprobe. Dr. Yoder was contacted concerning analysis of these run products and he has kindly provided the products of 33 capsules for reactions (4) and (5). Several of the run products were coarse enough to analyze and the results show that the products are stoichiometric within analytical errors (Table 3). The phases analyzed were crystalline diopside, akermanite and merwinite, from 5 to 50 μm in diameter. The coarsest of these, merwinite, contained visible fluid inclusions. Slightly low analytical totals (97.5–99.2%) are attributed to the small grain size and to these inclusions. Thus Yoder's (1975) experiments appear to be applicable to the endmember reaction (5) and will be used in this paper in preference to calculated curves.

The conclusion that akermanite + diopside + merwinite show no mutual solid solution at the relevant temperatures can be used to make a qualitative evaluation of the importance of solid-solution for reaction (6). Forsterite and monticellite show 3–4% mutual solid solution across an approximately symmetric solvus at 10 kb, 1,100° C (Warner and Luth 1973). If diopside and akermanite solutions in forsterite and monticellite are assumed to be negligible then the shift of Yoder's (1968) experiments relative to the end-member reaction can be calculated. Because the stoichiometry of reaction (6) involves 3 moles of monticellite reacting to 1 mole of forsterite, the resulting equilibrium coefficient will be less than unity and the experimental curve will be at higher temperatures than the end-member reaction. This location of the end-member reaction (6) at lower temperatures than the experiments is the opposite of the conclusion of Helgeson (1978) that the end-member reaction is lo-

Table 3. Electron microprobe analyses of experimental run products from Yoder (1975). Abbreviations are: Ak = akermanite; Di = diopside; Me = merwinite. All runs were with excess H$_2$O. Experimental conditions were: run 83, 880° C, 8.0 kb; runs 28 and 29, 750° C, 6.5 kb

	Ak 83	Me 28	Di 28	Me 29	Di 29
SiO$_2$	43.31	35.29	54.04	35.47	54.51
MgO	15.17	12.24	18.33	12.25	18.31
CaO	40.71	49.97	25.67	50.46	25.84
SUM	99.19	97.50	98.04	98.19	98.66
Si	1.992	1.978	1.985	1.974	1.994
Mg	1.024	1.022	1.004	1.017	0.994
Ca	1.986	3.000	1.011	3.009	1.010
O	6.994	7.978	5.985	7.974	5.992

cated some 400° C above Yoder's reversals. Helgeson chose the value of ΔG°_f for monticellite that is reported in Robie et al. (1978). Valley and Essene (1979) have found that values of ΔG°_f derived from Yoder's experiments on reaction (4) are more consistent with other monticellite experiments (Walter 1963). We propose that in many cases more accurate ΔG°_f (and hence ΔH°_f) can be derived from carefully reversed solid-solid experiments where potential solid solutions have been evaluated. In the case of invariant points [Fo] and [Wo] in Fig. 1, this calculation of ΔG°_f requires knowledge of ΔG°_f for only two minerals to uniquely fix the value of ΔG°_f for the remaining four phases.

Effect of Solid Solution on Akermanite Equilibria

The extent of solid solution in certain critical minerals was evaluated by wavelength-dispersive electron microprobe analysis (Table 4). Minerals are normalized around expected cations, assuming no vacancies, which permits estimation of Fe^{3+}. The details of anal-

Table 4. Electron microprobe analysis of minerals from Cascade Slide

	LP 201-3a Gn	LP 201-34 Gn	LP 77-201 Di	LP 77-201 Mo	LP 77-201 Fo	LP 77-201 Spinel	LP 77-210-10 Gn	LP 77-210-10 Ak	LP 77-210-10 Mo	LP 77-210-10 Wo	LP 77-210-10 Di	LP 77-210-10 Cusp
SiO_2	38.85	38.96	50.63	37.13	41.30	≤0.05	37.18	44.07	38.40	51.81	55.06	32.77
TiO_2	0.28	0.27	0.44	≤0.05	0.05	≤0.05	1.55	0.05	0.05	≤0.05	0.08	0.08
Al_2O_3	18.71	17.84	4.28	≤0.05	≤0.05	60.29	8.24	0.33	0.03	≤0.05	0.48	≤0.05
Fe_2O_3[b]	4.55	6.38	0.00	0.00	0.00	7.45	17.80	0.00	0.00	≤0.05	0.89	≤0.05
FeO[b]	2.54	2.05	1.86	3.99	3.37	2.05	0.00	0.47	3.92	≤0.05	0.00	≤0.05
MnO	0.25	0.31	≤0.05	0.45	0.38	0.23	0.10	0.11	0.84	<0.05	≤0.05	≤0.05
MgO	0.22	0.18	16.53	23.61	54.68	18.85	0.68	12.87	22.16	0.07	17.98	0.08
CaO	34.52	33.76	25.93	35.15	0.26	≤0.05	34.53	40.09	36.50	48.38	26.71	61.00
Na_2O	—	—	—	—	—	—	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05	≤0.05
ZnO	—	—	≤0.05	0.10	0.05	11.28	0.06	1.56	0.17	0.12	0.10	0.14
Cl	—	—	—	—	—	—	—	—	—	—	—	≤0.05
F	—	—	—	—	—	—	—	—	—	—	—	10.06
H_2O[b]	—	—	—	—	—	—	—	—	—	—	—	0.15
SUM[a]	99.94	99.75	99.67	100.43	100.09	100.15	100.14	99.52	102.07	100.39	101.30	100.10
O[b]	12.000	12.000	5.943	3.977	3.982	4.002	12.007	7.045	4.006	3.000	5.992	7.041
Si	2.982	3.013	1.841	0.978	0.981	0.001	2.986	2.034	1.004	0.999	1.969	1.988
Al	0.018	0.000	0.159	≤0.001	≤0.001	1.853	0.014	0.000	0.000	≤0.001	0.020	≤0.003
Al	1.675	1.627	0.025	0.000	0.000	—	0.765	0.018	0.001	0.000	0.000	0.000
Fe^{3+}[b]	0.307	0.321	0.000	0.000	0.000	0.147	1.077	0.000	0.000	≤0.001	0.024	≤0.002
Fe^{2+}[b]	0.120	0.184	0.057	0.088	0.067	0.045	0.000	0.018	0.086	≤0.001	0.000	≤0.002
Ti	0.018	0.015	0.011	≤0.001	0.001	≤0.001	0.094	0.002	0.001	≤0.001	0.002	0.003
Mg	0.025	0.021	0.896	0.928	1.936	0.733	0.082	0.886	0.864	0.002	0.958	0.007
Mn	0.016	0.020	≤0.002	0.010	0.008	0.005	0.006	0.004	0.019	≤0.001	≤0.002	≤0.002
Zn	—	—	≤0.002	0.002	0.001	0.217	0.004	0.054	0.003	0.002	0.003	0.006
Ca	2.839	2.797	1.010	0.993	0.006	≤0.001	2.971	1.984	1.023	0.998	1.023	3.986
Na	—	—	—	—	—	—	≤0.004	≤0.003	≤0.001	≤0.001	≤0.001	≤0.003
Cl	—	—	—	—	—	—	—	—	—	—	—	≤0.002
F	—	—	—	—	—	—	—	—	—	—	—	1.940
OH[b]	—	—	—	—	—	—	—	—	—	—	—	0.060
	α_{Gr} =0.594	α_{Gr} =0.544	α_{Di} =0.906	α_{Mo} =0.921	α_{Fo} =0.920	α_{Sp} =0.629		α_{Ak} =0.902	α_{Mo} =0.887	α_{Wo} =0.996	α_{Di} =0.970	

[a] Adjusted for Fe_2O_3, F=O and H_2O
[b] Calculated from normalized formula

ysis and normalization are discussed elsewhere (Valley and Essene 1980).

It is significant to note that in sample LP 77-210-10, which contains akermanite coexisting with five other minerals, all phases are near to end-member compositions except garnet. Thus, end-member reactions involving any of these phases will approximate their stability and only small corrections are necessary for solid solution. It will be shown below that such corrections can be modeled for nearly end-member phases, but that the lack of activity coefficient data could introduce large errors for phases that deviate greatly from end-member composition.

It is also significant that elements are highly fractionated among the minerals of LP 77-210-10. The

ions Fe^{3+}, Ti, and Al are strongly concentrated in garnet, whereas akermanite concentrates Zn and monticellite concentrates Mn and Fe^{2+}. Thus Zn stabilizes akermanite and shifts reaction (4) to significantly lower temperatures but Mn and Fe^{2+} have a somewhat compensatory effect. It becomes very important to consider all substitutions when minerals show such large fractionation of elements, particularly for solid-solid equilibria with small values of ΔV_r and/or ΔS_r.

The change in pressure of a reaction due to substitutions can be calculated from the relation:

$$-\Delta P \Delta V = R \cdot T \cdot \ln K \qquad (10)$$

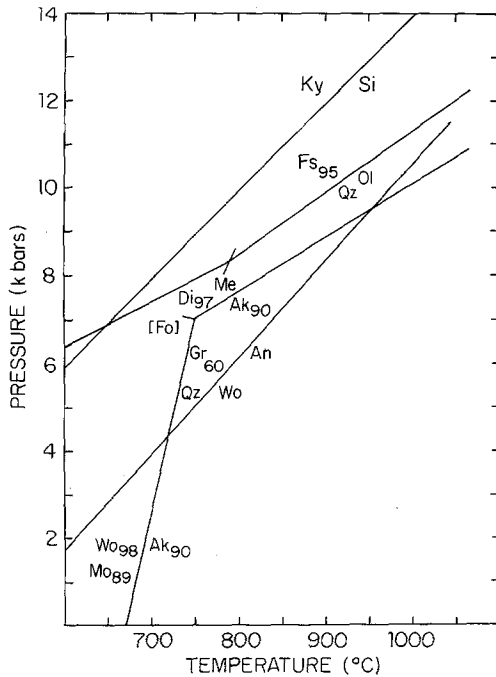where K is the equilibrium constant. Because the nec-

Fig. 3. Pressure-temperature diagram of reactions adjusted for mineral activities appropriate to this study: wollastonite (0.98)+monticellite (0.89)=akermanite (0.90); akermanite (0.90)=diopside (0.97)+merwinite; grossular (0.60)+quartz=wollastonite+anorthite; ferrosilite (mole fraction=0.95)=olivine+quartz; kyanite=sillimanite

essary activity vs. composition relations have not been experimentally measured, activities have been calculated using a modified version of the ideal ionic model (Kerrick and Darken 1975), considering independent substitutions on a site-by-site basis such that:

$$\alpha_{Ak} = \alpha^{melilite}_{Ca_2MgSi_2O_7} = (X_{Ca})^2(X_{Mg}) \tag{11}$$

$$\alpha_{Mo} = \alpha^{monticellite}_{CaMgSiO_4} = (X_{Ca})(X_{Mg}) \tag{12}$$

$$\alpha_{Mo} = \alpha^{wollastonite}_{CaSiO_3} = (X_{Ca}) \tag{13}$$

$$\alpha_{Di} = \alpha^{clinopyroxene}_{CaMgSiO_6} = (X_{Ca})(X_{Mg}) \tag{14}$$

$$\alpha_{Gr} = \alpha^{garnet}_{Ca_3Al_2Si_3O_{12}} = (X_{Ca})^3(X_{Al})^2 \tag{15}$$

In using this model the authors assume ideal mixing and take into account ordering and coupled substitutions to the extent that they are known. Tetrahedral substitution of Al for Si is ignored on the basis that it is not independent, but rather is coupled by charge considerations to substitutions of other cations amounting to local charge balance. This model is supported for diopside-tchermakite solid solution by experiments of Wood (1976), who shows that activities of $CaAlAlSiO_6$ in clinopyroxene are approximately equal to the mole fractions of $CaAlAlSiO_6$.

Reactions (4) and (5) are plotted (Fig. 3) using the activities calculated in Table 4 for actual mineral compositions. The kyanite-sillimanite boundary

(Newton 1966a; Richardson et al. 1968; Holdaway 1971) and the maximum stability of the Fs_{95} analyzed by Jaffe et al. (1978) are shown for comparison. The pressure change of reaction (4) corresponds to a temperature shift of $-14°$ C at point [Fo]. Because merwinite has not been found at Cascade Slide, its activity is set equal to one and a maximum shift for reaction (5) is calculated to be $+0.6$ kb at [Fo]. If merwinite should take up some Zn, Mn or Fe in equilibrium with akermanite, diopside and monticellite, this effect will be diminished. The combined effect of these shifts is to move point [Fo] from 6.4 kb, 750°C to 7.0 kb, 750° C. The principal errors in calculation of the shift of this invariant point are in the activity models used. It is believed that the magnitude of such errors is not large in this case where phases are near to end-member composition. Although such error cannot be rigorously evaluated, the authors feel that uncertainties of ± 1 kb and $\pm 30°$ C are conservatively large.

Other Equilibria

The conditions of metamorphism at Cascade Slide are also restricted by assemblages of grossular-rich garnet + quartz and by forsterite + monticellite. Garnet is restricted by:

grossular + quartz = wollastonite + anorthite

$$Ca_3Al_2Si_3O_{12} + SiO_2 = 2CaSiO_3 + CaAl_2Si_2O_8 \tag{16}$$
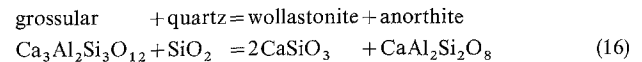
Grossular-rich garnet + quartz are found at Cascade Slide, but not coexisting with wollastonite + anorthite. Garnet + quartz will nevertheless provide a minimum pressure at known temperature if α_{Gr} is known. A maximum stability for the Cascade Slide garnets ($\alpha_{Gr}=0.6$) is plotted in Fig. 3 assuming that the activities of anorthite and wollastonite equal one. Data on the end-member reaction are from experiments by Newton (1966b) and Boettcher (1970). At 750° C the Cascade Slide garnet-quartz assemblage requires $P > 5$ kb.

The solvus relations between monticellite and forsterite offer a potential geothermometer. This relationship has been experimentally and theoretically investigated in several studies that are summarized by Warner and Luth (1973). In the ideal $CaMgSiO_4 - Mg_2SiO_4$ system, Warner and Luth report very limited solid solution of about 1 mole% each of forsterite in monticellite and monticellite in forsterite at 800° C, 10 kb. This solid solution increases to 5% at 1,200° C and is nearly independent of pressure variation from 1 to 10 kb. Monticellite coexists with forsterite at Cascade Slide, but the presence of Fe and Mn precludes direct application of the solvus. The analysis

of primary contiguous grains from sample LP 77-201 is given in Table 4 where Fe is the largest additional component with 8.5% kirschsteinite ($CaFeSiO_4$) substitution in monticellite and 3.3% fayalite substitution in olivine. Similar analyses are reported by Tracy et al. (1978) who also describe occasional fine forsterite lamellae in monticellite. Such lamellae are found in the analyzed monticellite of this study but no attempt was made to reintegrate them as they represent less than 1% of the host. The effect of Fe and Mn on solvus compositions has not been experimentally evaluated, but the partitioning of Fe into monticellite over forsterite suggests that the effect in the $Ca_2SiO_4 - Fe_2SiO_4 - Mg_2SiO_4$ ternary could be significant. In the absence of experimental data, all that can be concluded is that these coexisting compositions are consistent with equilibration at relatively low temperature, i.e. $T \leqq 800°$ C.

Discussion

The results of all the systems studied give a self-consistent, well constrained estimate for the conditions of metamorphism at Cascade Slide. The chemically analyzed assemblage akermanite + monticellite + wollastonite indicates $T = 750 \pm 30°$ C, in agreement with the regional temperature contours of Bohlen et al. (1980b). At 750° C the analyzed akermanite indicates $P \leqq 7.0 \pm 1$ kb and, because there is no reason to expect extreme pressure gradients in the granulite facies, the presence of an iron-rich orthopyroxene (Fs_{95}, 8 km away) restricts $P \geqq 7.8 \pm 1$ kb. These pressure and temperature results are consistent with the less restrictive assemblages of grossular + quartz and monticellite + forsterite and indicate metamorphic conditions in the sillimanite field of 7.4 ± 1 kb and $750 \pm 30°$ C.

These results indicate metamorphism at the peak of the Grenville orogeny and preclude a high-temperature and/or low-pressure contact metamorphic event for the last equilibration of these rocks. Two theories for the timing of anorthosite intrusion are consistent with this conclusion: (1) the Adirondack anorthosite intruded pre-tectonically, and the resulting contact aureole was overprinted by the later granulite facies event, or (2) the anorthosite intruded syn-tectonically with contact temperatures equal to those of the regional metamorphism. The agreement of pressures and temperatures at Cascade Slide with the regional trend argues against a third possibility, post-metamorphic anorthosite intrusion. Pre- or syn-metamorphic intrusion is consistent with the structural interpretation of McLelland (1979) in the Southern Adirondacks.

The close agreement of the pressure and temperature estimates for Cascade Slide provides one of the best known points on a granulite facies geotherm. It is thus tempting to speculate about the heat source of this event which took place several hundred degrees above the average geotherm at 1 b.y. The correlation of high pressures and high temperatures seen in the Central Adirondack Highlands suggests that post-metamorphic domical uplift has been important. Similar, and possibly related uplift is operating in the Adirondacks today (Isachsen and Wold 1977). Such a theory is consistent with either theory 1 or 2 of anorthosite timing. Alternatively, if the anorthosite intruded syn-tectonically (theory 2), a significant amount of energy would have been provided by the large 10,000 km^3 body of anorthositic magma, which coexisting igneous pyroxenes indicate was 1,100° C upon intrusion (Bohlen and Essene 1978). These high igneous temperatures would have been dissipated by the cooler country rock to form a regional temperature aureole. This is consistent with geophysical data showing a low gravity and magnetic anomaly for approximately the same region as is outlined by the 700° C isotherm (Isachsen et al. 1979). These gravity and magnetic measurements do not vary over areas with and without outcropping anorthosite and could indicate that shallowly buried anorthosite correlates with the 700° C isotherm. The final resolution of this question may ultimately have to wait until direct dates are obtained, perhaps from Nd/Sm isotopes, which will resolve the question of timing for anorthosite intrusion.

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