Monticellite marble at Cascade Mountain, Adirondack Mountains, New York

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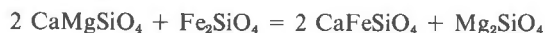*Amherst, Massachusetts 01003*

Abstract

An Adirondack marble contains the assemblage calcite–diopside–forsterite–monticellite, with trace amounts of zincian spinel, titanian andradite, idocrase, and sphalerite. Microprobe analyses indicate that the monticellite and forsterite both have $Mg/(Mg+Fe)$ greater than 0.9, and that monticellite is more iron-rich than coexisting forsterite. Monticellite host grains contain rare microscopic exsolution lamellae of forsterite, a feature noted in only one other terrestrial monticellite occurrence. Diopside is strongly zoned and contains up to 6 weight percent Al_2O_3 and substantial ferric iron, indicating a fassaitic character typical of calc–silicate clinopyroxenes.

Distribution of Fe and Mg among the major silicate minerals indicates that the monticellite-producing reaction must be an Fe–Mg continuous reaction combining the end-member reaction,

$$Mg_2SiO_4 + CaMgSi_2O_6 + 2\ CaCO_3 = 3\ CaMgSiO_4 + 2CO_2$$

with two Fe–Mg exchange equilibria:

$$2\ CaMgSiO_4 + Fe_2SiO_4 = 2\ CaFeSiO_4 + Mg_2SiO_4$$

$$CaMgSi_2O_6 + CaFeSiO_4 = CaFeSi_2O_6 + CaMgSiO_4$$

Calculations suggest that Fe does not lower the reaction temperature significantly. The occurrence of monticellite-free marble in the same outcrops and variable mineral compositions in the calcite–diopside–forsterite–monticellite assemblage implies that these rocks formed in an aCO_2 gradient with aCO_2 probably decreasing from center to edge of the marble layer. $P–T–XCO_2$ relations for the iron-free reaction have been calculated, and suggest that formation of monticellite in the above reaction, under presumed conditions of Adirondack regional metamorphism of 8–10 kbar and about 700°–800°C, requires either great dilution of CO_2 by H_2O in metamorphic fluid, or low aCO_2 under fluid-absent conditions. A possible alternative explanation suggests earlier contact metamorphism at low pressures followed by a later Grenville-age high-pressure regional metamorphism in which the pre-existing high-grade mineral assemblages were not substantially affected.

Introduction

Marble on Cascade Mountain in the Adirondacks near Keene, New York, contains the assemblage calcite–diopside–forsterite–monticellite. This is the only documented occurrence in metamorphic rocks in the eastern United States of monticellite[2], which is usually restricted to contact metamorphic environments

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[2] Choquette (1960, Table 2) lists monticellite in the modes of two quartz-bearing marbles of the Cockeysville Formation in Maryland. G. W. Fisher (personal communication, 1974) has examined these thin sections and believes the mineral is misidentified.

as at Skye (Tilley, 1951), Crestmore (Burnham, 1959), and West Texas (Joesten, 1976). Monticellite, $Ca(Mg,Fe)SiO_4$, is an olivine which typically forms in marbles only in the highest range of metamorphic temperatures, above about 900°C at low pressures, and in rare alkalic and ultramafic rocks and carbonatites (Bowen, 1922; Eckermann, 1948; Sahama and Hytönen, 1957). The occurrence of monticellite at Cascade Mountain is even more striking in that the mineral might have been produced during Precambrian regional metamorphism of the Adirondack massif. A further interesting feature of this occurrence is the presence of forsterite exsolution lamellae in monticellite hosts. Though monticellite and forsterite (Mg_2SiO_4) are known to have a limited mutual miscibility (Warner and Luth, 1973), exsolution features have been previously reported for only one terrestrial occurrence of this mineral pair, in calcsilicate blocks included in norite of the Bushveld Complex (Willemse and Bensch, 1964).

The monticellite-bearing marble crops out on the north flank of Cascade Mountain in the Mt. Marcy quadrangle, which is being remapped by Jaffe (Jaffe and Jaffe, in preparation; Jaffe *et al.,* 1977). It is involved in an isoclinal recumbent fold with adjacent layers of syenitic gneiss and bordering anorthositic gneiss. It is not clear whether or not the marble was intruded by the adjacent gneisses, but it appears that all these rock units have been folded and metamorphosed in the Precambrian Grenville (1100 m.y.) event that affected the Adirondacks and adjacent rocks to the north and west. Some details of the geology of the outcrop area of the marble may be found in Baillieul (1976).

In this paper we describe some of the mineral assemblages and textures in samples of the marble, and present microprobe analyses of the silicate and oxide minerals. The petrology of the monticellite-producing reaction is discussed, and the implications it has for the composition and behavior of the metamorphic fluid are considered. Finally, we note the constraints that this and other Adirondack rocks place on pressure, temperature, and activity of fluid species during metamorphism.

Petrography and mineral chemistry

Mineral assemblages identified in different specimens of the marble include: calcite–forsterite–diopside–magnetite ± spinel; calcite–forsterite–monticellite–diopside–spinel–andradite; and calcite–forsterite–monticellite–diopside–spinel–idocrase.

Diopside is pale green in hand specimen and color-less in thin section. It occurs in rounded isolated grains up to 2 or 3 mm. In hand specimen, forsterite is colorless to pale green where fresh, and dark gray where partially serpentinized. Monticellite is pale brown. Both are colorless in thin section and have a similar size and isolated occurrence as diopside. There are rare small grains of pale green spinel and sphalerite. Both idocrase and andraditic garnet occur as sporadic thin rims on diopside or monticellite grains against calcite. Diopside contains inclusions of spinel, and monticellite contains inclusions of both diopside and spinel. Forsterite appears to be free of inclusions.

All phases in three selected samples were analyzed by electron microprobe. Analyses were made on the MAC microprobe at M.I.T., with operating conditions of 15 kV accelerating potential and sample current of about .025 microamps. Data were corrected using the method of Bence and Albee (1968) and the correction factors of Albee and Ray (1970). Chemical data for monticellite, forsterite, and diopside are presented in Table 1. These phases and others are discussed below.

Forsterite and monticellite

Magnesian olivine ranges in composition from Fo89 to Fo94. The most iron-rich olivine was found in the monticellite-free sample, Ca-22F. There is also a significant amount of iron in the monticellite (Table 1) and the ratio $Fe/(Fe+Mg)$ is higher in monticellite than in coexisting forsterite. Terrestrial occurrences of monticellite + forsterite are very rare—less than a dozen have been found in the literature, of which the majority are igneous. No data exist on compositions of these pairs. However, the Fe–Mg fractionation in the Cascade Mountain occurrence is similar to that found for coexisting fayalitic olivine and magnesian kirschsteinite in Angra dos Reis meteorite (Prinz *et al.,* 1977) and in the Sharps chondrite (Dodd, 1971). Thus, the preferential partitioning of iron into the high-calcium phase is the reverse of fractionation found in most pairs of coexisting low- and high-calcium pyroxenes.

One explanation for this monticellite–forsterite Fe–Mg fractionation may be found in the distribution of cations between $M(1)$ and $M(2)$ sites in the two olivines. Since monticellite $M(2)$ is essentially filled by Ca, all Fe and Mg must be in $M(1)$. On the other hand, in forsterite there is abundant Mg in both $M(1)$ and $M(2)$. Even if forsterite and monticellite contained the same number of atoms of Fe per formula unit, the Fe/Mg ratio of monticellite would be

higher. But there also appears to be an absolute preference of Fe for monticellite, since it contains more Fe atoms per 4 oxygen formula (Table 1). Brown and Prewitt (1973) and Smyth (1975) argue that Fe–Mg ordering in olivines is due to the greater distortion of the $M(1)$ site (Robinson *et al.,* 1971) which causes Fe to prefer $M(1)$. By extension of this argument, Fe might be preferentially partitioned into monticellite $M(1)$, because the monticellite octahedral sites are

larger and more distorted than those in forsterite. While $M(2)$ in monticellite is much larger and more distorted than $M(2)$ in forsterite, monticellite $M(1)$ is larger but only marginally more distorted than $M(1)$ in forsterite. Whether this relative distortion of $M(1)$ sites is enough to be effective is arguable, but the increased size of monticellite $M(1)$ alone might be enough to cause Fe to prefer it.

An important feature of the monticellite is the presence of rare microscopic exsolution lamellae of forsterite (Fig. 1), which are up to about 10 microns thick and are apparently oriented along the (010) planes of the monticellite host. The forsterite composition of these lamellae has been established by electron probe analysis of several larger lamellae, which have the approximate composition $Ca_{0.01}Mg_{1.91}Fe_{0.08}Mn_{0.01}Si_{1.00}O_4$. This is the second reported occurrence of exsolution in terrestrial olivine pairs. Willemse and Bensch (1964) report exsolution lamellae, presumably of forsterite, in monticellite grains in calc–silicate xenoliths in the Bushveld Complex. Dodd (1971) suggests that very small inclusions of ferroan monticellite in olivine hosts in the Sharps chondrite (Section B53) are recrystallized exsolution lamellae. Though Prinz *et al.* (1977) do not state it, a similar interpretation is possible for the magnesian kirschsteinite inclusions in olivine from Angra dos Reis. There is no evidence in the Adirondack marble of any monticellite exsolution from forsterite, nor is any reported by Willemse and Bensch. This discrepancy in host and lamella phase may be due to the difference in Fe/Mg ratio between terrestrial and meteoritic specimens. In other words, the shape of the solvus between forsterite–fayalite and monticellite–kirschsteinite olivines may change significantly with changing Fe/Mg ratio.

Table 1. Microprobe analyses of minerals

| | Ca-22F | Ca-22 | | CL-3a | |
	Fo	Fo	Mo	Fo	Mo
SiO_2	40.79	42.11	37.93	42.42	36.83
TiO_2	0.00	0.00	0.00	0.00	0.01
Al_2O_3	0.00	0.00	0.00	0.00	0.04
Cr_2O_3	0.00	0.00	0.00	0.00	0.06
FeO	5.09	2.85	3.34	3.49	4.47
MnO	0.68	0.05	0.19	0.11	0.50
MgO	52.36	54.25	22.62	54.43	22.76
CaO	0.20	0.16	35.00	0.15	34.99
Total	99.12	99.42	99.08	100.60	99.66
Cations per 4 oxygens					
Si	.999	1.005	1.011	1.003	.986
Al	.000	.000	.000	.000	.000
Ti	.000	.000	.000	.000	.001
Cr	.000	.000	.000	.000	.001
Fe	.104	.057	.074	.069	.100
Mn	.014	.001	.004	.002	.011
Mg	1.876	1.929	.899	1.918	.908
Ca	.005	.004	1.000	.004	1.004
	2.998	2.996	2.988	2.996	3.011
$\frac{Fe}{Fe+Mg}$	.052	.029	.076	.035	.099

Diopsides

|	core	rim	core	rim	core	rim
SiO_2	50.72	52.08	50.73	51.18	49.50	51.19
TiO_2	0.24	0.12	0.71	0.61	0.58	0.23
Al_2O_3	4.07	2.84	4.68	4.12	5.45	3.16
Cr_2O_3	0.03	0.08	0.07	0.07	0.06	0.00
FeO	2.87	2.18	2.20	1.99	2.61	2.12
MnO	0.02	0.00	0.05	0.08	0.17	0.06
MgO	16.05	16.98	15.57	15.34	15.95	16.88
CaO	25.12	25.50	26.03	25.62	25.46	26.43
Na_2O	0.00	0.04	0.01	0.00	0.02	0.00
Total	99.12	99.82	100.05	98.94	99.80	100.07
Cations per 6 oxygens						
Si	1.875	1.905	1.856	1.887	1.822	1.877
Al	.125	.095	.144	.113	.178	.123
	2.000	2.000	2.000	2.000	2.000	2.000
Al	.052	.027	.057	.065	.058	.014
Ti	.006	.003	.019	.016	.016	.006
Cr	.000	.002	.001	.002	.002	.000
Fe	.088	.066	.066	.060	.080	.065
Mn	.000	.000	.001	.002	.005	.002
Mg	.884	.925	.849	.843	.875	.923
	1.030	1.023	.993	.988	1.036	1.010
Ca	.995	.999	1.020	1.012	1.004	1.038
Na	.000	.002	.000	.000	.001	.000
	.995	1.001	1.020	1.012	1.005	1.038
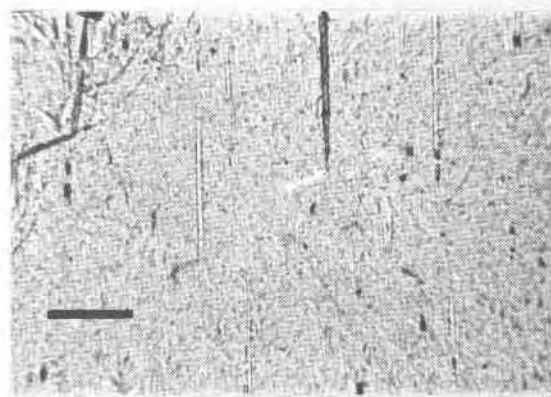
Fig. 1. Photomicrograph of monticellite host (Sample CL-3a) with exsolution lamellae of forsterite probably parallel to (010) of the host. Length of scale bar is 100 microns.

A number of investigators have studied the extent of crystalline solution on the join $CaMgSiO_4$–Mg_2SiO_4 as a function of T and P. The most recent paper, by Warner and Luth (1973), contains a summary of the earlier work. According to Warner and Luth, there is very limited miscibility between monticellite and forsterite below about 1000°C. Limited experimental evidence on the effect of iron upon the phase relations in this system suggests that iron causes the solvus to narrow, similar to its effect upon the miscibility gap in Ca–Fe–Mg pyroxenes. The data of Bowen et al. (1933) indicate complete solid solution at subsolidus conditions down to 700°C between Fe_2SiO_4 and $CaFeSiO_4$. Assuming that there is no significant effect on the phase relations caused by the small amounts of iron in the Cascade Mountain forsterite and monticellite, the data of Warner and Luth (1973, Fig. 4) suggest that these minerals crystallized and exsolved below about 800°C.

Diopside

The diopsides in all three of the analyzed samples are strongly zoned (lower part of Table 1), both in Al content and in the ratio Fe/Mg. Both Al and Fe/Mg decrease regularly and markedly from core to rim. There is similar zoning in Ti, while Ca shows no particular trend. This zoning is most likely due to formation of diopside in a continuous (multivariant) reaction (see Thompson, 1976), in which reactants and products systematically change composition as the reaction progresses. The zoning is apparently not due to the monticellite-forming reaction, because the monticellite-free sample (Ca-22F) shows the same zoning as monticellite-bearing samples.

The diopside analyses in Table 1 show all iron as Fe^{2+}. From the stoichiometry of these minerals, however, as seen in the structural formulas, it is apparent that much of the iron must be in the ferric state. This means that these clinopyroxenes are solid solutions between nearly pure end-member diopside and calcium Tschermak's components. Of the 10–20 percent of Tschermak's substitution, about half is $CaAl_2SiO_6$ and half is $CaFe^{3+}AlSiO_6$. This suggests rather oxidizing conditions during crystallization.

Andraditic garnet and idocrase

Both of these minerals are restricted to reaction rims between diopside or monticellite and calcite. In most cases, they form rims of uniform thickness partially around diopsides, though several examples were observed of andraditic garnet actually replacing part of a diopside crystal, with replacement proceeding more extensively along cleavage traces in the diopside. The garnet is typically honey-yellow and has a very high index of refraction. Preliminary compositions obtained by microprobe show some variation from grain to grain, but all are rather high in titanium (about 1 weight percent). A typical composition is 65 percent andradite and 35 percent grossular with negligible amount of other garnet molecules.

Idocrase, like garnet, occurs in rims adjacent to diopside in the samples examined, though it does occur in discrete grains at other places in the marble (Baillieul, 1976). A probe analysis of idocrase from specimen CL-3a yielded this composition, calculated on an anhydrous basis: $(Ca_{9.78}Mg_{1.72}Fe^{2+}_{0.28}Fe^{3+}_{0.22})$ $(Al_{3.10}Fe^{3+}_{0.80}Ti_{0.10})(Si_{8.67}Al_{0.33})O_{36}$. The ferric iron was estimated assuming a stoichiometric formula of 25 cations and 36 oxygens. Probe analysis for fluorine and chlorine in idocrase suggests that OH/(OH+F+Cl) ranges from 0.81 to 0.89 (Baillieul, 1976), assuming 4 volatile anions in the formula given above. Further, the birefringence of idocrase is very low and some grains are nearly isotropic, suggesting high OH content (Deer et al., 1962).

Spinel

The pale green spinel which occurs sporadically is magnesium- and zinc-rich and poor in iron. Spinel in sample Cl-3a has the composition $(Mg_{0.71}Fe^{2+}_{0.09}Mn_{0.005}Zn_{0.20})(Al_{1.88}Fe^{3+}_{0.12})O_4$, in which Fe^{3+} has been calculated on the basis of a stoichiometric formula of 3 cations per 4 oxygens. Most of the spinel occurs as small (0.5 mm or less) isolated grains, although it has been observed as inclusions in diopside and monticellite. The inclusions do not appear to be systematically different in composition from the isolated grains. The zinc content of the spinel is not surprising in view of its coexistence with sphalerite.

Petrology

Monticellite-producing reaction

The simplest way to view the chemography of the major phases in the marble is in the ternary system CaO–MgO–SiO_2 with excess CO_2, shown in Figure 2a. The arrangement of the phases calcite, diopside, forsterite, and monticellite on this diagram illustrates that the monticellite-forming reaction, in the absence of any other phases, must be:

$$Di + Fo + 2Cc = 3Mo + 2CO_2 \qquad (1)$$

However, the more complicated compositions of the actual minerals (Table 1) and their compositional

variability from sample to sample indicate that this simple graphical analysis is insufficient.

The most important compositional variable, Fe/Mg ratio, may be illustrated in projection. Figure 2a may be expanded into a tetrahedron by adding an FeO apex, and mineral compositions may be projected from calcite onto the SiO_2–FeO–MgO face, because all assemblages contain calcite which is essentially pure $CaCO_3$. Figure 2b shows this projection with mineral compositions illustrated schematically. Relative positions are qualitatively correct but have been exaggerated to emphasize that monticellite is more iron-rich than the diopside and forsterite (+calcite) from which it forms. With progress of the monticellite-producing reaction, the three-phase triangle in Figure 2b must move from more iron-rich to more magnesian compositions. The reaction forming monticellite is therefore an Fe–Mg continuous reaction in which $T_{Mg} > T_{Fe}$. Thus reaction (1) may be considered as a combination of the end-member reaction (1) and the following two Fe–Mg exchange equilibria:
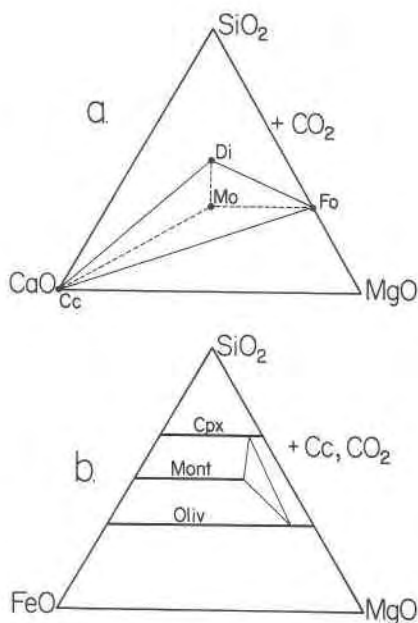

Fig. 2a. The ternary system CaO–MgO–SiO₂ with excess CO₂. Compositions of the phases diopside (Di), forsterite (Fo), calcite (Cc), and monticellite (Mo) are shown to illustrate the monticellite-forming reaction.

·b. Projection from calcite onto the SiO₂–FeO–MgO face in a CaO–MgO–FeO–SiO₂ tetrahedron with excess CO₂. Ranges of olivine, monticellite, and clinopyroxene compositions are shown along with schematic compositions of an equilibrium three-phase assemblage (plus Cc) which is undergoing reaction (1) modified by (2a) and (2b).
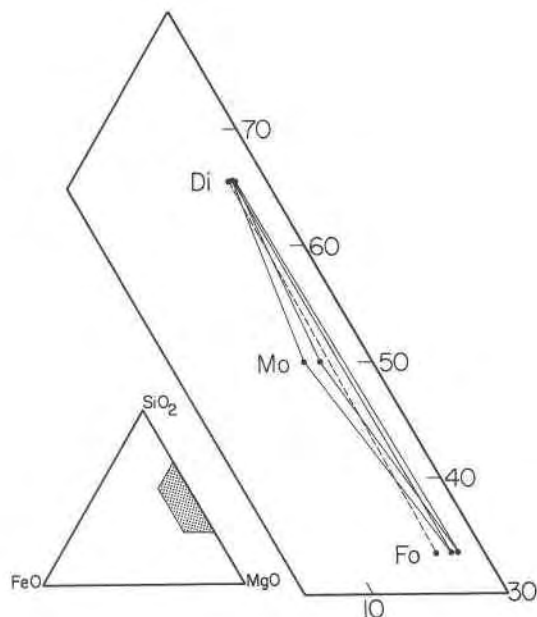

Fig. 3. Compositions of analyzed diopside, forsterite, and monticellite from Cascade Mountain shown on the calcite projection of Fig. 2b. Note that diopside is plotted as if all iron were Fe²⁺, which may not be the case.

$$2\ CaMgSiO_4 + Fe_2SiO_4 =$$
$$2\ CaFeSiO_4 + Mg_2SiO_4 \qquad (2a)$$

$$CaMgSi_2O_6 + CaFeSiO_4 =$$
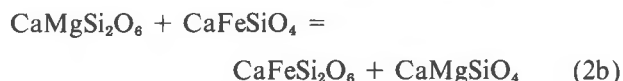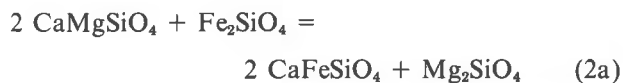$$CaFeSi_2O_6 + CaMgSiO_4 \qquad (2b)$$

Figure 3 illustrates without exaggeration the actual compositions of the analyzed minerals on this calcite projection.

The three analyzed samples were all collected very close to one another, and it is therefore likely that they were metamorphosed at the same temperature and pressure. The discrepancies in mineral assemblage and composition (Fig. 3), which must be due to variations in intensive variables P, T, or fluid composition, are therefore probably due to local variation in activity of CO_2 (aCO_2). The effect of lowered aCO_2 on reaction (1), a simple decarbonation reaction, would be to allow the reaction to proceed at lower temperature (see Kerrick, 1974). It is thus possible that gradients in aCO_2 could produce the variety of compositions and assemblages observed.

An Fe–Mg continuous reaction such as (2) may be portrayed as a reaction loop on an isobaric temperature–composition diagram such as that shown in Figure 4 (for background, see Thompson, 1976). Fig-
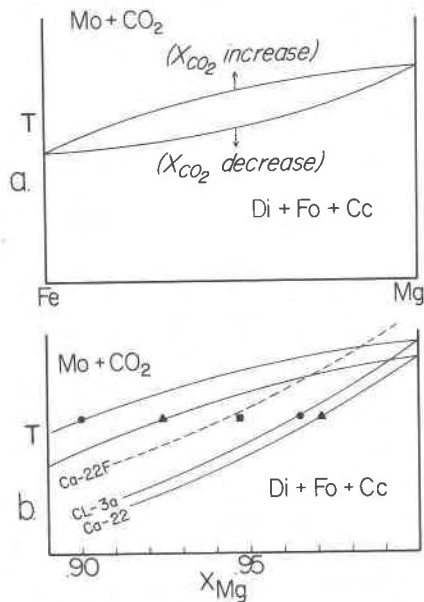
Fig. 4a. Temperature–composition diagram showing the schematic reaction loop for continuous reaction. Note that part of this loop, especially the Fe-rich side, may be metastable relative to other reactions. The arrows on the loop show the effect of raising or lowering the concentration of CO_2 in the fluid.

b. Similar T–X diagram, blown up to show the Mg-rich side, with hypothetical reaction loops for the different but presumably isothermal Cascade Mountain samples. Filled circles indicate compositions of Mo and Fo in sample CL-3a; triangles are for the same phases in Ca-22; the square is forsterite composition in Ca-22F; diopside is ignored for simplification.
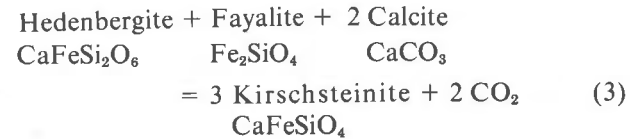
ure 4a illustrates the relative effect on this loop of increase or decrease in aCO_2. Figure 4b shows actual compositions of monticellite and forsterite on opposite sides of the loops (diopside is ignored for simplification). On this plot it is assumed that all samples are isothermal and isobaric. The schematic positions of the reaction loops for each assemblage, functions of aCO_2, are shown in the figure. These relative positions suggest that aCO_2 is lowest for sample Ca-22 and that the reaction has progressed farther in this sample than in CL-3a, which has a slightly higher aCO_2. For sample Ca-22F, the aCO_2 is high enough that the reaction loop has not yet been intersected and the stable assemblage remains Di+Fo+Cc. If the minerals in Ca-22F had been more *magnesian* than the other samples, then the absence of monticellite could have been ascribed to a simple bulk composition effect, that is, that the rock was too magnesian to have encountered the reaction. But the data support the hypothesis that aCO_2 is the controlling physical variable. It must also be noted that the magnitude of

this aCO_2 effect depends upon the temperature difference between the Fe and Mg end-members of reaction (1) or, in other words, upon the steepness of the T–X loops. A small temperature difference, as suggested below, means that very small variations in aCO_2 could produce the observed effects illustrated in Figure 4b.

Estimation of conditions of metamorphism

The most effective method of estimating metamorphic conditions is to apply the results of relevant experimental work to the natural assemblages. Unfortunately, very little experimental work has been done on monticellite-related reactions, and only that of Kushiro and Yoder (1964) at elevated pressures. The only experiments on reaction (1) in the system $CaO–MgO–SiO_2–CO_2$ are those of Walter (1963) at pressures of less than one kbar. In addition, there is no experimental evidence bearing on the effect of Fe in lowering the temperature of reaction (1).

However, the hypothetical equilibrium temperature of the iron analogue of reaction (1), *i.e.*,

Hedenbergite + Fayalite + 2 Calcite
$CaFeSi_2O_6$ Fe_2SiO_4 $CaCO_3$

$$= 3 \text{ Kirschsteinite} + 2\,CO_2 \qquad (3)$$
$$CaFeSiO_4$$

can be calculated from known and estimated thermochemical data. The relation

$$T_{eq,1\,bar} = \Delta \bar{H}^0_{Fe} / \Delta \bar{S}^0_{Fe} \qquad (4)$$

can be used to estimate the temperature of reaction (3) at one bar. Entropies for fayalite, calcite, and CO_2 were taken from Robie and Waldbaum (1968), while those for hedenbergite and kirschsteinite had to be calculated according to the method described by Cantor (1977); these values enabled $\Delta \bar{S}^0_{Fe}$ to be calculated. $\Delta \bar{H}^0_{Fe}$ was then estimated from the Fe–Mg fractionation of phases in the Cascade Mountain samples (data in Table 1). The temperature estimate for reaction (3) at one bar is 435°C, as compared to an estimated temperature for reaction (1) of 500°C at one bar (from data of Walter, 1963). Though this temperature estimate may have considerable uncertainty, it is considered to provide a reasonable approximation of the effect of iron on reaction (1). Note that the presence of substantial CaTs component in the pyroxene (Table 1) will tend to displace the reaction to higher temperature, at least in part offsetting the temperature effect of iron. Based upon the estimation that the Fe end-member reaction is probably no more than 100°C below the Mg end-member at one

bar, the effect of the small amount of iron in the Cascade Mountain samples will be ignored, and further estimates of physical conditions will be based upon the simplifying assumption that the system is iron-free.

It is clear from Walter's (1963) experimental determination of reaction (1), fluid-saturated with $XCO_2 \cong 1.0$ in the fluid, that the reaction cannot occur at geologically reasonable temperatures at pressures above one kbar if Pfluid = Ptotal and the fluid is rich in CO_2. This is why monticellite is typically restricted to very shallow contact-metamorphosed rocks, *e.g.* Tilley (1951), Burnham (1959), Joesten (1976). There are two ways to lower the reaction temperature at elevated pressures. The first is to assume that fluid pressure is less than solid pressure and that the fluid is pure or nearly pure CO_2. Examination of Walter's (1963) data suggests that, for regional metamorphic conditions thought to have prevailed in the Adirondack massif (*i.e.,* 700–800°C and about 8 kbar, see below), fluid pressure would have had to have been less than about 10 percent of total solid pressure in this case.

The second way to lower the temperature is to assume that fluid pressure equals solid pressure but that CO_2 is diluted in the fluid by H_2O or other species. A similar explanation to explain wollastonite in Adirondack marbles was given by Valley and Essene (1977). The possibility that CO_2 was significantly diluted by F or Cl has been discounted, because of the apparent high OH/(Cl + F) ratio in idocrase. F can be strongly fractionated into solid phases, as shown by Munoz and Ludington (1974, 1977), suggesting that the fluid may have been much poorer in F than the idocrase.

The alternative that fluid pressure equalled total solid pressure but that CO_2 was diluted in the fluid by H_2O can be evaluated quantitatively. P–T–XCO_2 relations for reaction (1) in the system CaO–MgO–SiO_2–CO_2–H_2O have been calculated at pressures up to 10 kbar and temperatures to 1000°C, as described in the Appendix. It is clear from these calculations that, above 5 kbar, XCO_2 must be less than about 0.1 for the monticellite-forming reaction to occur at reasonable temperatures. At the presumed conditions of Adirondack metamorphism, XCO_2 might have been 0.01 or less, and the fluid phase would have been very nearly pure H_2O.

Some independent evidence exists regarding the temperature and pressure of Adirondack metamorphism. Bohlen and Essene (1977a, b) have given estimates of conditions in the center of the Adirondack massif of about 700–800°C and 8 ± 1 kbar. Phase assemblages in orthoferrosilite microperthite gneiss less than 5 kilometers from the Cascade Mountain locality (Jaffe *et al.,* 1978) suggest metamorphic pressures of at least 9 kbar at 800°C or 7 kbar at 600°C, but certainly not more than 12 kbar, based upon olivine–orthopyroxene Fe–Mg fractionation at XFe>0.9 (Wood, 1975). Further, the coexistence of orthopyroxene with K–feldspar and the absence of biotite and of migmatitic segregations in such rocks of granitic composition under these conditions implies either a very low XH$_2$O in a coexisting fluid phase or, more probably, a very low aH$_2$O under fluid-absent conditions. If the monticellite assemblage was produced during regional metamorphism under these conditions, then the considerations discussed above dictate two extreme possibilities: (1) that the marble at Cascade Mountain was suffused with a fluid phase very rich in H_2O as compared to that, if any, in the surrounding rocks; or (2) that no fluid phase was present and that the monticellite assemblage was controlled by a very low aCO$_2$ in a diffusional gradient. The diffusion of CO_2 through the Adirondack terrain has been proposed by Taylor (1968) to explain the oxygen isotope composition of Adirondack igneous and metasedimentary rocks.

The difficulties inherent in postulating a regional metamorphic origin of monticellite make it tempting to argue that the marble was contact metamorphosed at low pressure by syenitic or anorthosite magma (Isachsen, 1975) and later remetamorphosed at high pressure. Berg (1977, p. 400) cites Buddington (1968) and others in support of the suggestion that the anorthosites of eastern North America were emplaced at relatively shallow depths (as little as 12 to 18 kilometers) into low-grade country rocks. Berg speculates that those south of the Grenville front, such as the Adirondack massif, were later regionally metamorphosed at significantly greater depths, wiping out much of the evidence of their earlier history. A major problem in applying this interpretation to the Cascade Mountain occurrence is an apparent lack of recrystallization and retrogression of the supposed original contact metamorphic assemblage, which might be expected to occur during granulite facies regional metamorphism. Furthermore, anorthosite intrusion at depths as shallow as 12 to 18 kilometers would still be at pressures rather high for production of monticellite, though it would slightly ease the problems of fluid behavior noted above.

The present geologic evidence, therefore, indicates that the Cascade Mountain monticellite occurrence is

more likely to be of regional than contact metamorphic origin, even though regional metamorphic origin requires unusual composition or behavior of metamorphic fluid. On the other hand, an origin in contact metamorphism and survival of the assemblage through later regional metamorphism cannot be ruled out. Further elucidation of the geology of the area is clearly necessary for firmer conclusions to be drawn.

Appendix

Preliminary P–T–XCO_2 relations have been calculated for reaction (1) in the system CaO–MgO–SiO_2–CO_2–H_2O. The method of calculation involved the "equilibrium constant approach," as discussed by Kerrick and Slaughter (1976). Experimental data for reaction (1) (Walter, 1963, Table 1) for runs at 800°C and above were plotted on a $\ln K$ vs. $1/T$ diagram to derive ΔH_r^0 and ΔS_r^0. Because all the run data are at pressures of 500 bars or less, correction for non-ideal mixing in fluid was made using the data of Ryzhenko and Malinin (1971). For extrapolation above 2000 bars (see below), ideal mixing was assumed and the fugacity coefficients of Burnham and Wall (unpublished) were used, as suggested by Ohmoto and Kerrick (1977, p. 1033) and by Slaughter et al. (1976). Calculations were done using the following equilibrium relation:

$$0 = \Delta G_r = \Delta H_r^0 - T\Delta S_r^0 + P\Delta V_s^0 + RTn CO_2 \ln fCO_2$$
$$(A1)$$

When rearranged, this becomes:

$$T = (\Delta H_r^0 + P\Delta V_s^0)/(\Delta S_r^0 - Rn CO_2 \ln fCO_2) \quad (A2)$$

As noted above, ΔH_r^0 and ΔS_r^0 were derived from Walter's (1963) data. ΔV_s^0 data were taken from Robie et al. (1967). Isobaric T–XCO_2 sections and P–T locations of reaction (1) at various $XCO_2 < 1.0$ have been calculated from equation (A2).

We are aware of the considerable uncertainty in the above calculations, especially in the derivation of ΔH_r^0 and ΔS_r^0 from Walter's experiments using the equilibrium constant method (see Kerrick and Slaughter, 1976). To indicate the magnitude of uncertainty, maximum and minimum ΔH_r^0 calculated from Walter's data were −57.4 kcal and −51.3 kcal, respectively; maximum and minimum ΔS_r^0 were 74.1 gibbs and 68.6 gibbs. It was considered important, however, to calculate and extrapolate reaction (1) in P–T–XCO_2 space in order to provide at least qualitative estimates of the effects of variable fluid composition and pressure.

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