

Reactions among sodic, calcic, and ferromagnesian amphiboles, sodic pyroxene, and deerite in high-pressure metamorphosed ironstone, Siphnos, Greece

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ABSTRACT

Sodic actinolite, ferri-winchite, cummingtonite, crossite, and riebeckite occur in a metamorphosed ironstone from Siphnos, Greece, containing in addition deerite, quartz, magnetite, almandine, and aegirine-augite. Saliient petrographic features are the following: idio-blastic sodic actinolite cores occur in large prisms of cummingtonite; cummingtonite crystal margins are replaced and overgrown by homoaxial sodic amphibole and, less abundantly, by sodic actinolite-winchite; internal *S* surfaces of garnet porphyroblasts are composed of aegirine-augite, deerite, and quartz; schistose rock matrix is composed predominantly of sodic amphibole, aegirine-augite, deerite, magnetite, and quartz; and deerite is partially replaced by magnetite, quartz, sodic amphibole, and ferri-winchite, and, later, by cronstedtite and hematite.

These relationships are explained in terms of model hydration reactions consuming cummingtonite, quartz, and components of aegirine-augite and producing sodic and calcic amphibole. Three reactions, all proceeding toward dehydration, can be written between deerite and other minerals in the rock. A calculated *P-T* phase diagram shows that all observed reactions can be explained by a metamorphic path of isothermal decompression, in agreement with independent geologic evidence.

The occurrence in one rock of sodic, calcic, and ferromagnesian amphiboles requires an unusual whole-rock composition but not necessarily high pressure—even though this rock experienced *P-T* conditions within the stability fields of deerite and jadeite + quartz. The coexistence of cummingtonite and aegirine-augite at modest metamorphic temperatures does, however, require high pressure. Despite considerable compositional variability among the amphiboles, the results of microprobe analysis are indicative of the extent of mutual solubility between Ca, Na, and (very roughly) Fe on M(4), for conditions of approximately 15 kbar and 460°C. Ferri-winchite or sodic actinolite (depending on *P-T*) and riebeckite or crossite (depending on μ_{FeAl}) are alternates respectively in a stable three-amphibole paragenesis.

INTRODUCTION

In a recent review of amphibole composition space (Robinson et al., 1982), only two examples of analyzed coexisting sodic and ferromagnesian amphibole were brought to light. Clearly, the bulk-rock compositions and/or environmental conditions necessary for such pairs are seldom present. However, both riebeckite and grunerite-cummingtonite are relatively common in metamorphosed iron-formations (Klein, 1982), and so it is not surprising to find further examples of this mineral pair emerging from studies of such rock types. For example, coexisting riebeckite, cummingtonite, and actinolite were recently reported in banded iron formation from Wisconsin (Kimball and Spear, 1984). The present paper describes a rock containing riebeckite, crossite, cummingtonite, actinolite, and ferri-winchite collected among high-pressure metamorphosed ironstones on the Cycladic island of Siphnos, Greece. These amphiboles occur together with aegirine-

augite, almandine, deerite, magnetite, and quartz. Some of the net-transfer reactions that can be written among these phases can be shown on textural grounds to have progressed, and an attempt is made here to estimate the attendant physical conditions. This appears to be the first description of a rock containing members of all four of the principal monoclinic amphibole groups (Leake, 1978).

HIGH-PRESSURE METAMORPHISM ON SIPHNOS

The sample described in this paper was collected from the metamorphosed ironstone outcrops overlooking Vroulidia Bay, close to the northern tip of the island of Siphnos (Fig. 1), in the group of Aegean islands known as the Cyclades. Deerite from this locality (no. 352, Matthews and Schliestedt, 1984, Fig. 2) was described by Schliestedt (1978). The northern part of the island of Siphnos is underlain by a coherent high-pressure metamorphic terrane, consisting of sequences of glaucophane-rich meta-

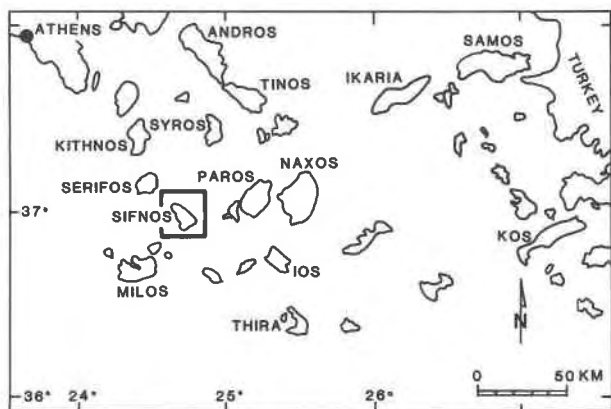


Fig. 1. Location map of the Cycladic Islands.

basites, eclogites, jadeite gneisses, metapelites, marbles, and metacherts. This blueschist-facies metamorphism has been dated as middle Eocene (about 42 Ma, Altherr et al., 1979). A later, Barrovian-style metamorphism took place in the Cycladic Islands in the early Miocene (20–25 Ma, Altherr et al., 1979). This metamorphism overprinted the high-pressure metamorphic rocks with greenschist-facies assemblages in the center and south of Siphnos, but had much less effect in the north (Okrusch et al., 1978; Schliestedt, 1980).

Minimum metamorphic conditions of $470 \pm 30^\circ\text{C}$ and 16 ± 3 kbar were estimated from mineral assemblages and compositions for the high-pressure metamorphic rocks at the north end of the island (Okrusch et al., 1978; Schliestedt, 1980). Fractionation of oxygen isotopes among minerals from northern Siphnos gave an average equilibration temperature of 455°C (Matthews and Schliestedt, 1984). The greenschist overprint in central Siphnos was apparently accompanied by a systematic enrichment in ^{18}O due to infiltration by CO_2 -enriched aqueous solutions (Matthews and Schliestedt, 1984).

Metamorphic parageneses developed at Vroulidia Bay comprise various equilibrium combinations of sodic pyroxene, almandine, glaucophane, actinolite, epidote, paragonite, and phengite (Schliestedt, 1980)—in other words, a high-temperature subfacies of the blueschist facies, bordering on the eclogite facies. During decompression, jadeite in metakeratophyres partially back-reacted to albite, aegirine, and white mica, and garnet and glaucophane to chlorite (Okrusch et al., 1978).

PETROGRAPHY OF METAMORPHOSED IRONSTONE SAMPLE CY-20

Red almandine garnet and black sodic amphibole (crossite-riebeckite) are megascopically prominent in the ironstones at Vroulidia Bay. In addition to these minerals, sample CY-20 contains quartz (~40%), aegirine-augite (~10%), magnetite (~10%), cummingtonite (~5%), deerite (~3%), sodic actinolite-ferri-winchite (~3%), apatite, and biotite (both <1%).

The rock possesses a schistosity defined by mineral lay-

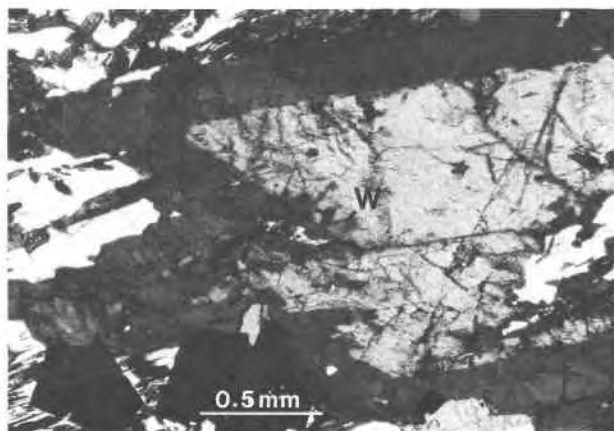
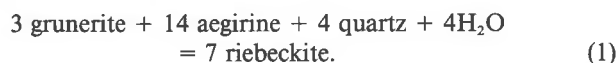


Fig. 2. Photomicrograph (plane light) of sodic amphibole (dark gray) marginal to cummingtonite (light gray) with minor winchite (W). Also present are magnetite, quartz, and aegirine-augite.

ering and alignment of deerite, aegirine-augite, cummingtonite, and sodic amphibole. Garnet (~5 mm in diameter), magnetite, and some of the larger sodic amphibole prisms (~1 cm) have overgrown the schistosity. In contrast to deerite and aegirine-augite, sodic amphibole occurs almost exclusively outside the garnet porphyroblasts. Where determined, it exhibits crossite optics (O.A.P. \perp (010), Y approx. $\parallel c$; X pale tan, Y blue, Z violet) and considerable variation in color and birefringence. Cummingtonite forms prisms up to 15 mm in length, all of which have been partially replaced around the margins by homoaxial sodic amphibole (Fig. 2), and to a lesser degree by sodic actinolite-ferri-winchite. The (100) polysynthetic twinning of the cummingtonite has in some cases been inherited by the sodic amphibole. The contact between the two amphiboles is sharp, relatively straight in sections along c but irregular in sections normal to c . Sodic actinolite (X colorless, Y pale green, Z pale blue-green) occurs as idiomorphic inclusions (up to $1.0 \times 0.2 \times 0.2$ mm) in the cummingtonite and sodic amphibole (Fig. 3); sodic actinolite-ferri-winchite occurs as irregular patchy intergrowths with the sodic amphibole rimming the cummingtonite. Needles of deerite ($2 \times 0.1 \times 0.1$ mm) locally have been replaced by quartz, magnetite, ferri-winchite, and crossite (Fig. 4). A late-stage partial alteration of deerite produced hematite and cronstedtite. Magnetite is mostly in the form of octahedra up to 0.5 mm in cross section; it has undergone partial alteration to hematite.

PETROGRAPHIC INTERPRETATION

The partial replacement of cummingtonite by sodic amphibole can be interpreted in terms of progress of the model reaction



The participation of sodic pyroxene is inferred on mass-balance grounds and from the much higher ratio of sodic

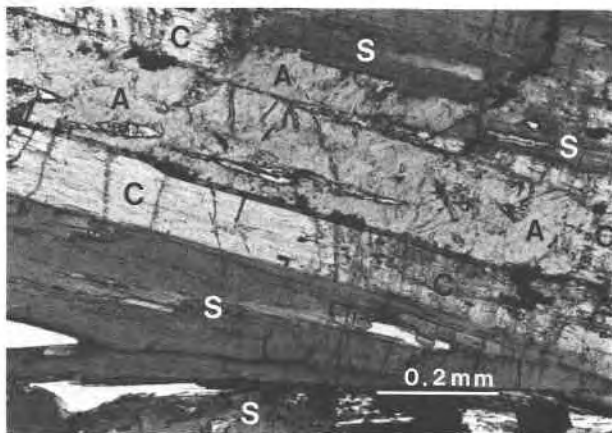


Fig. 3. Photomicrograph (plane light) of 1-mm-long idio-blastic actinolite (A, also Table 1, analysis 3) enclosed in cummingtonite (C) with sodic amphibole (S) margins. Quartz and magnetite are present in the matrix.

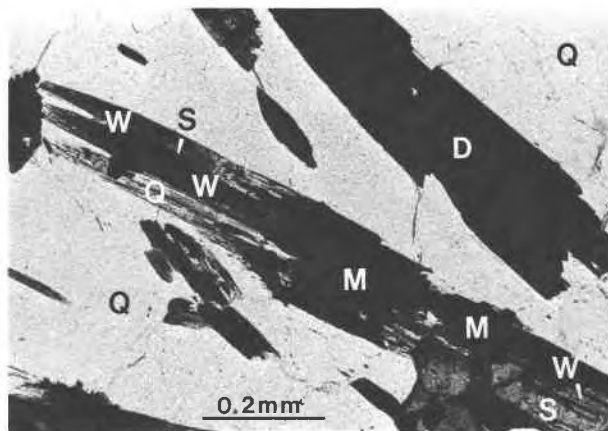
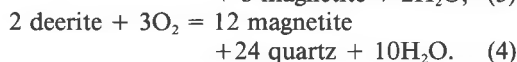
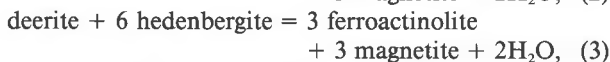
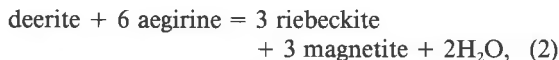


Fig. 4. Photomicrograph (plane light) of pseudomorph of magnetite (M), quartz (Q), ferri-winchite (W), and sodic amphibole (S) after deerite (D). Matrix is quartz.

pyroxene to sodic amphibole inside as compared to outside the garnet porphyroblasts. Because of the presence of components other than FeO , NaFeO_2 , SiO_2 , and H_2O , Reaction 1 has a variance greater than one.

The partial replacement of deerite [$\text{Fe}_{12}^{2+}\text{Fe}_6^{3+}\text{Si}_{12}\text{O}_{40}(\text{OH})_{10}$] by quartz, magnetite, crossite, and ferri-winchite can be modeled by at least three reactions:



The amount of progress of Reaction 4, if any, is not known. Reactions 2, 3, and 4 differ from 1 in evolving rather than consuming H_2O . Reactions 2 and 3 are, of course, different ways of expressing an energy balance among phase components in deerite, aegirine-augite, ferri-winchite, crossite, magnetite, and H_2O . By the same token, Reaction 1 could be changed to



The amount of calcic amphibole produced by Reaction 5 was considerably less than the amount of sodic amphibole produced by Reaction 1, however.

Whereas the ferromagnesian and sodic amphiboles are in an obvious reaction relationship, the possibility of local (micrometer-scale) exchange and net-transfer equilibrium among the sodic, calcic, and ferromagnesian amphiboles and other minerals can still be entertained. The compositions of the minerals in CY-20 have been determined by microprobe analysis and are discussed in the next section. The analyses provide further clues to the petrologic

history of the area based on this sample and to the relations among the amphiboles.

MINERAL COMPOSITIONS

The microprobe analyses were obtained with an automated ARL EMX-SM using natural mineral standards and on-line Bence-Albee matrix-correction procedures. Spot analyses of amphibole and pyroxene are plotted in Figure 5 through 8, and selected spot analyses or average compositions are set down in Table 1.

The choice of a normalization scheme for microprobe analyses of Fe-rich amphiboles is unavoidably somewhat arbitrary. For the cummingtonites and sodic amphiboles, the formulae and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios were calculated on the basis of 23 oxygens (anhydrous) and 15 cations, not including K. For the actinolites and winchites, 23 oxygens were balanced against 15.1 cations, not including K. The reasons for these choices are as follows: (a) in the presence of cummingtonite, normalization of total cations less Ca, Na, and K to 13 is obviously inappropriate—when this is done, 75% of the sodic, sodic-calcic, and calcic amphiboles have cation totals less than 15; (b) in a rock containing riebeckite and crossite, normalization on a totally Fe^{2+} basis [which maximizes A-site occupancy and Fe^{2+} on M(4)] is equally inappropriate; (c) average Si contents (based on 15 cations) of 7.95 for the cummingtonites and 7.91 for the sodic amphiboles suggest an upper limit on A-site occupancy of 0.09 and 0.17 atoms, respectively; (d) actinolites and winchites normalized to 15 cations in most cases have insufficient Al to bring the tetrahedral cation sum to 8.0; the choice of the 15.1 cation sum eliminates the need to have tetrahedral Fe^{3+} and represents a compromise between the 15.0 cation assumption and the all- Fe^{2+} assumption (with cation totals of 15.17 to 15.53). As a result, calculated $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios and Fe^{2+} on M(4) (cummingtonite solid solution) are very uncertain, particularly in the actinolites and winchites.

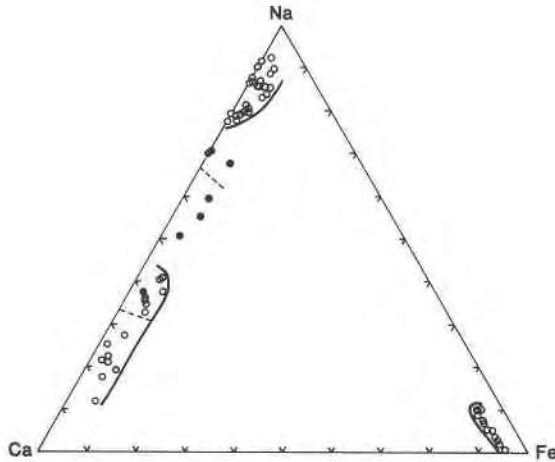


Fig. 5. Na, Ca, and Fe proportions in M(4) of CY-20 amphiboles. All analyses plotted as circles, except amphibole in pseudomorphs after deerite (dots). Analyses of physical mixtures have been excluded. Solid-solution limits correspond to the high-pressure metamorphism, stage 5, Table 2. Note that Fe on M(4) of the calcic, sodic-calcic, and sodic amphiboles is highly uncertain. Dashed lines are the limits of winchite composition.

Fe^{2+} and Fe^{3+} in sodic pyroxene was assigned by assuming a formula of 4 cations and 6 oxygens.

Cummingtonite. On the 15-cation basis, Si per formula unit (pfu) was found to range from 7.87 to 8.03 and averaged 7.95. The ratio $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ varies from 0.61 to 0.66 (av. 0.63), and so compositions do not quite extend into the grunerite range. Whereas the content of Ca is small and fairly uniform from point to point [0.10 atoms pfu, or about 5% actinolite component (Fig. 5)], the content of Na varies from 0.01 to 0.20 pfu (Table 1), that is, from 0.5% to 10% of the sodic amphibole component (Fig. 5). Since this Na shows little or no correlation with the small amounts of Al (Fig. 6) and correlates positively with

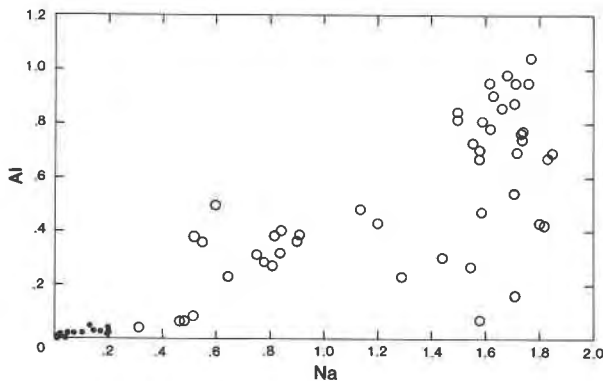


Fig. 6. Correlation between total Al and total Na per formula unit for all analyzed amphibole spots. Note that 0.1 atoms of Na in actinolite and winchite have been assigned to the A site. Dots: cummingtonite; circles: actinolite, winchite, and sodic amphibole.

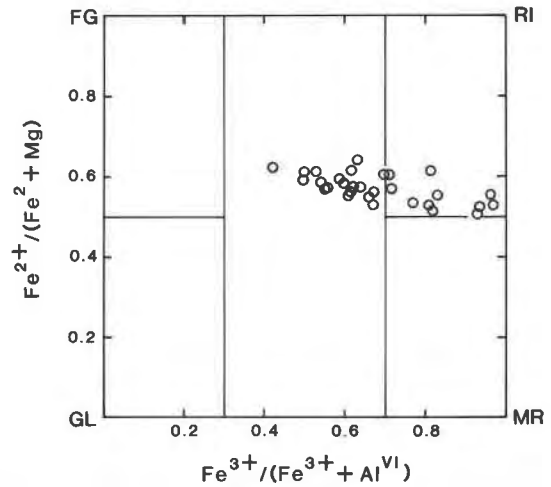


Fig. 7. Compositions of sodic amphiboles in CY-20.

calculated Fe^{3+} (not plotted), the dissolved sodic amphibole component may be regarded as riebeckite. The presence of cummingtonite locally almost free of Na suggests that some may have grown initially in the absence of sodic amphibole (or at least in an environment of very low potential of the riebeckite component). There is a further possibility that it grew initially in an environment almost lacking in Na, that is, that the Na was introduced metasomatically during the early stages of the metamorphism. Others (e.g., Reinecke, 1983) have suggested Na uptake during diagenesis, however. For a metasedimentary rock rich in Fe, the cummingtonite is unusually low in Mn. This is a property shared by all the amphiboles in the sample. Figure 5 indicates that the composition of cummingtonite in equilibrium with both calcic and sodic amphibole may be expressed in terms of M(4) occupancy as $\text{Ca}_{0.12}\text{Na}_{0.20}(\text{Fe},\text{Mg})_{1.68}$.

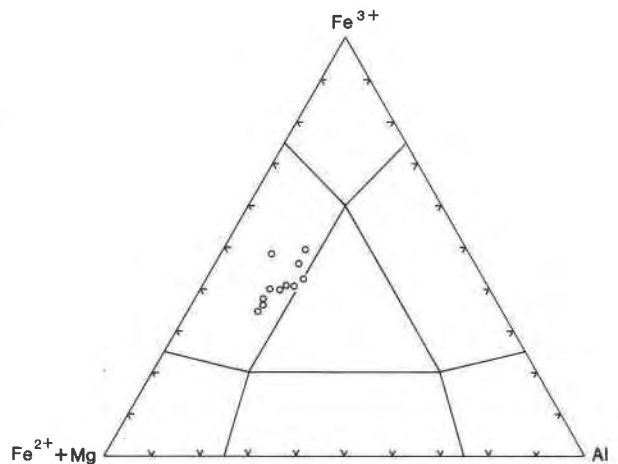


Fig. 8. Composition of sodic pyroxene in CY-20 in terms of M(1) occupancy.

Table 1. Compositions of minerals in meta-ironstone CY-20

	1	2	3	4	5	6	7	8	9	10	11
	(Weight percent)										
SiO ₂	52.6	52.1	54.1	53.1	54.9	53.9	52.7	53.2	37.5	34.3	0.0
TiO ₂	0.00	0.00	n.d.	0.00	0.00	0.00	n.d.	0.00	0.00	0.7	0.07
Al ₂ O ₃	0.06	0.15	0.36	1.74	4.48	0.40	2.8	3.93	19.8	0.65	0.00
Fe ₂ O ₃ *	0.0	2.9	2.5	5.8	9.7	14.0	8.0	14.5	1.8	20.8	69.0
FeO	35.0	32.2	19.3	18.2	15.8	15.3	17.9	7.2	32.7	38.5	31.1
MgO	10.5	10.2	11.1	9.53	6.09	7.56	7.67	3.72	0.64	0.62	0.00
MnO	0.05	0.06	0.05	0.01	0.02	0.17	0.12	0.05	0.7	0.24	0.0
CaO	0.51	0.57	9.4	7.66	1.59	1.42	5.64	10.2	7.7	0.02	0.00
Na ₂ O	0.03	0.69	1.7	2.76	6.18	5.51	3.97	7.9	0.00	0.00	0.00
K ₂ O	0.00	0.01	n.d.	0.07	0.02	0.02	n.d.	0.00	0.00	0.00	0.00
H ₂ O**	1.96	1.98	2.04	2.04	2.07	2.03	2.03	—	—	4.23	—
Total	100.71	100.86	100.55	100.91	100.85	100.31	100.83	100.70	100.84	100.06	100.17
	Cations per formula unit										
Si	8.02	7.93	7.97	7.82	7.96	7.98	7.78	1.996	3.02	12.1	0.000
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.00	0.2	0.002
Al	0.01	0.03	0.06	0.30	0.77	0.07	0.49	0.174	1.88	0.3	0.000
Fe ³⁺	0.00	0.33	0.28	0.64	1.05	1.56	0.89	0.409	0.11	5.5	2.000
Fe ²⁺	4.47	4.10	2.38	2.24	1.92	1.89	2.21	0.226	2.20	11.5	1.000
Mg	2.39	2.31	2.44	2.09	1.31	1.67	1.69	0.208	0.08	0.3	0.000
Mn	0.01	0.01	0.01	0.00	0.00	0.02	0.01	0.002	0.05	0.1	0.000
Ca	0.08	0.09	1.48	1.21	0.25	0.23	0.89	0.410	0.66	0.0	0.000
Na	0.01	0.20	0.48	0.79	1.74	1.58	1.14	0.575	0.00	0.0	0.000
K	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.000	0.00	0.0	0.000
H**	2.00	2.00	2.00	2.00	2.00	2.00	2.00	—	—	10.0	—

Note: (1) cummingtonite, least sodic; (2) cummingtonite, most sodic; (3) actinolite, inclusion in cummingtonite; (4) ferri-winchite, typical; (5) crossite, typical; (6) riebeckite, least aluminous; (7) ferri-winchite, replacing deerite; (8) aegirine-augite, typical; (9) garnet, average; (10) deerite, average (normalized to 30 cations); (11) magnetite, average; n.d. = not determined. Cations normalized as described in the text.

* Fe₂O₃ computed from formula.

** H₂O from formula.

Actinolite and ferri-winchite. The calculated formula content of Si averages 7.79 and ranges between 7.52 and 7.96; these numbers are lower than in the cummingtonites and sodic amphiboles, but not low enough for some to be classed as barroisite (although unanalyzed grains may extend into that range). The series is continuous from sodic actinolite with 0.22 Na on M(4) (plus 0.1 Na on the A site) to Na-rich ferri-winchite and calcic riebeckite (Fig. 5). The least-sodic actinolite analyzed (Table 1, analysis 3) was a crystal totally enclosed in cummingtonite (Fig. 3). The Na-rich ferri-winchites occur in pseudomorphs after deerite and formed late in the metamorphic history of the rock, probably under higher *T/P* conditions than the other amphiboles—hence they are excluded from the one-phase compositional areas in Figure 5. A plot of literature data in Maresch et al. (1982, Fig. 2) shows that large contents of Fe²⁺ and Fe³⁺ favor a narrower miscibility gap between calcic and sodic amphibole. Thus, we might expect the occurrence of ferri-winchite to turn out to be more common than aluminowinchite (e.g., Klein, 1969; Katagas, 1974; Green and Spiller, 1977). The ratio Fe³⁺/(Fe³⁺ + Al^{VI}), calculated on the 15.1-cation basis, ranges from 0.70 to 1.0 and averages 0.86. Therefore, as in the case of cummingtonite, the Na on M(4) is primarily associated with solution of a riebeckite rather than glaucophane component. That the great excess of Na on M(4) over Al^{VI} is not purely an artifact of the normalization scheme adopted here can be seen in Figure 6, which plots total Al vs. total Na, both of which are virtually unaffected

by the choice of normalization. The possibility exists, then, although it needs independent confirmation, that the ratio of the components riebeckite/glaucophane in sodic actinolite and in winchite is as high, if not higher, than in the coexisting sodic amphibole. It is customarily thought that an increase in the potential of the exchange component FeAl₁ favors sodic over calcic amphibole (e.g., Brown, 1974). The calculated amount of cummingtonite solid solution [Fe²⁺ on M(4)] is largely an artifact of the normalization procedure (Fig. 5); for example, the limits are about 2 and 15%, respectively, when calculated on the 15-cation and all-Fe²⁺ bases. Calculated ratios of Fe²⁺/(Fe²⁺ + Mg) fall in the range 0.47 to 0.72, with lower values being more typical of the actinolites.

Sodic amphibole. The occupancy of the M(4) site by Na is between 77 and 93% (Fig. 5), and miscibility is greater in the direction of actinolite than cummingtonite. It should be noted, then, that not *all* the calculated Mg and Fe²⁺ in the Miyashiro diagram (Fig. 7) are components of sodic amphibole endmembers. This diagram shows that compositions in terms of Fe³⁺/(Fe³⁺ + Al^{VI}) extend across much of the crossite and riebeckite fields, but that Fe²⁺/(Fe²⁺ + Mg) varies only within the range 0.65 to 0.51. The calculated average content of Si is 7.91, with a range from 7.81 to 8.00. The differences in the ratio Fe²⁺/(Fe²⁺ + Mg) among the amphibole species are somewhat blurred by computation problems, although one can detect an increase in the sequence: actinolite < riebeckite < crossite < cummingtonite, with winchite overlapping the sodic

amphiboles. This variation between the monoclinic amphibole groups is consistent with the known Fe and Mg site preferences (e.g., Hawthorne, 1983) and the blockage of these cations by Na and Ca on M(4) and Al and Fe³⁺ on M(2).

Aegirine-augite. The average composition is $Jd_{1.5}Ac_{4.1}Aug_{4.4}$, the "augite" component including < 1% of both ferrosilite and CATS endmembers. The compositions in terms of the M(1) sites are shown in Figure 8. Matrix pyroxene is slightly less acmitic than pyroxene enclosed in garnet porphyroblasts. This is consistent with the greater observed consumption of aegirine through progress of Reaction 1 as compared to consumption of hedenbergite through Reaction 5.

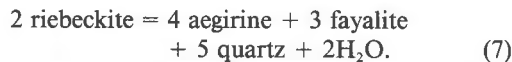
Other minerals in CY-20. The composition of garnet averages $Alm_{73.5}Py_{2.6}Sp_{1.6}Gro_{16.8}And_{3.5}$. Zoning is present but was not studied in detail. The deerite in CY-20 is very close to the endmember composition (Table 1). It is very similar to the analyses by Schliestedt (1978, 1980), all of which show extremely low MnO. The content of TiO₂ varies from 0.3 to 2.0%. Magnetite is effectively pure Fe₃O₄ (Table 1). Small amounts of an Fe-rich biotite occur in association with garnet. Microprobe analyses were unsuccessful owing to pervasive partial chloritization. The identification of cronstedtite was based on microprobe analyses, the average of eight spots giving the formula $(Ca_{0.04}Mg_{0.14}Fe_{3.82}^{2+}Fe_{2.0}^{3+})(Si_{1.42}Al_{0.17}Fe_{2.41}^{3+})O_{9.71}(OH)_8$.

PETROGENESIS

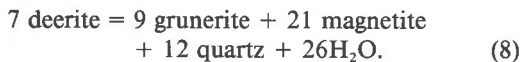
Reaction 1, which determines the limit of stability of riebeckite at high pressure (Fig. 9), is generated by the intersection of the grunerite breakdown reaction



and a low-pressure breakdown reaction of riebeckite (which is metastable above about 600°C with respect to a complex arfvedsonitic amphibole, Ernst, 1962; Owen, 1985):



The intersection at high pressure of the ferrosilite-forming breakdown reactions of grunerite and deerite, respectively (not shown on Fig. 9), generates Reaction 8, which represents the upper-temperature limit of stability of deerite over most of the metamorphic range (Fig. 9):



Reaction 8 has a positive dP/dT slope, and its intersection with Reaction 1 generates an invariant point at which deerite + grunerite + aegirine + riebeckite + magnetite + quartz + H₂O are stable. Reaction 2, with relatively small dP/dT slope, emerges from this invariant point. The P - T locations of these invariant and univariant assemblages in the system Na₂O-FeO-Fe₂O₃-SiO₂-H₂O has been computed (Fig. 9), using the program PT-SYSTEM written by T. H. Brown and E. H. Perkins (U.B.C. Vancouver). The thermodynamic data file used in the calculations is avail-

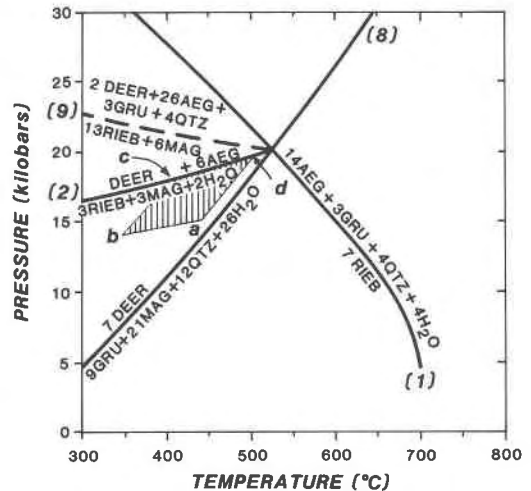


Fig. 9. Calculated locations of reactions (as numbered in the text) among pure phases deerite, grunerite, riebeckite, aegirine, quartz, magnetite, and H₂O. Possible locations of the compositionally displaced invariant point are inside the ruled area *abcd*. Corners *a*, *b*, *c*, and *d* correspond to invariant point locations for pure deerite, quartz, magnetite, and H₂O, together with aegirine activity = 0.2 throughout, riebeckite activity = 0.1, 0.1, 0.04, and 0.04, respectively, and grunerite activity = 0.65, 0.05, 0.05, and 0.65, respectively. Dashed curve is the H₂O-absent reaction.

able from the author. This file contains internally consistent data for minerals in the system FeO-Fe₂O₃-SiO₂-H₂O (R. G. Berman and M. Engi, unpubl.), and enthalpies for riebeckite, deerite, and grunerite based on experiments by Ernst (1962), Lattard and Schreyer (1981), and Evans and Engi (1984). An improved version of Figure 9 will be possible upon completion of work on the low- T heat capacities of deerite and grunerite (E. F. Westrum, unpubl.) and on a redetermination of Reaction 7 (C. Owen, in progress).

In the Al₂O₃- and MgO-free system, the invariant point is calculated to be at 525°C and 20 kbar. In the complex natural system, the univariant curves and the invariant point gain one or more degrees of freedom. A realistic calculation of the compositionally induced shift in the invariant point is rendered difficult by the variation in compositions of the minerals in CY-20, particularly of the sodic amphibole, and by the uncertainty in activity-composition relations of the amphiboles. An attempt has nevertheless been made in Figure 9. The relocated invariant point is believed to lie within the area *abcd*. This area is defined by adopting extreme possible activities of 0.05 ($a = X_{Fe}$, no cation ordering) and 0.65 ($a = X_{Fe}$) for grunerite, activities of 0.1 (an intermediate Al-free riebeckite) and 0.04 (average crossite) for riebeckite, and an activity of 0.2 for aegirine (average composition, Fig. 8). Area *abcd* encompasses the suggested P - T conditions for the high-pressure metamorphism in northern Siphnos of approximately 460°C and 16 kbar.

An independent estimate of the location of Reaction 2 in natural ironstones (between 9 and 15 kbar at 400°C)

Table 2. Probable sequence of equilibrium assemblages

Time sequence	Minerals	Comments
1	<i>qtz mag riebeckite ank chlo</i>	low grade
2	<i>qtz mag riebeckite act deer chlo</i>	prograde, blueschist facies
3	<i>qtz mag aegirine act deer chlo riebeckite</i>	$P >$ Reaction 2; H ₂ O exhausted?
4	<i>qtz mag aegirine act deer gt cum</i>	Reaction 9
5	<i>qtz mag aegirine Na-act deer gt cum riebeckite</i>	invariant point; metamorphic maximum
6	<i>qtz mag aegirine win (deer) gt (cum) riebeckite</i>	P declining
7	<i>qtz hematite (aegirine) (win) (deer) (gt) (cum) riebeckite chlo cronstedtite</i>	very late

Note: Minerals in italics are hypothetical; those in parentheses are relic phases. Abbreviations: qtz = quartz; mag = magnetite; hem = hematite; riebeckite = riebeckite-crossite; act = actinolite; cum = cummingtonite; win = winchite; aeg = aegirine; deer = deerite; chl = chlorite; gt = garnet; cron = cronstedtite.

may be obtained by noting the presence of deerite + aegirine in the Franciscan ironstones at Laytonville (Wood, 1982) and the alternative, lower-pressure assemblage riebeckite + magnetite in the Shuksan ironstones (Brown, 1974; Brown and O'Neil, 1982; Owen, 1981).

Figure 9 shows that the reaction relationships observed petrographically in sample CY-20, modeled by Reactions 1 and 2, can be explained in terms of a decompression path. It is reasonable to suppose that these reactions proceeded simultaneously and that the "invariant" assemblage (deerite + aegirine-augite + riebeckite + cummingtonite + magnetite + quartz) existed stably over a modest range in P and T , the increase in variance coming from the additional components CaO, MgO, and Al₂O₃. Since Reactions 1 and 2 involve both hydration and dehydration, they cannot have been driven by an infiltrating fluid. The pressure decline as the driving force is consistent with the Tertiary metamorphic history of Siphnos, which involved the overprint of greenschist on blueschist facies assemblages (Okrusch et al., 1978; Schliestedt, 1980). Table 2 represents an attempt to provide a probable sequence of equilibrium assemblages for the ironstone during its entire metamorphic history. An isochemical history is assumed only for convenience. The phases listed for the early prograde high P - T portion are highly conjectural. From near the highest pressure of metamorphism, the appearance of phases is consistent with the petrography and the phase diagram (allowing for the extra components).

Since the sodic and sodic-calcic amphiboles joined the ferromagnesian and calcic amphiboles as a result of a decline in pressure, it seems unreasonable to argue that the coexistence of calcic, sodic, and ferromagnesian amphiboles in CY-20 was due to unusually high pressure. Conditions for coexisting actinolite, cummingtonite, and riebeckite in the Jackson County Iron Formation, Wisconsin, were estimated to be 3.5 kbar and 550°C (Kimball and Spear, 1984). The necessary circumstances are me-

dium grades of metamorphism imposed on a chemical sediment of unusual bulk composition. On the other hand, the association of cummingtonite with aegirine-augite does require either relatively high pressures or temperatures (Fig. 9). The possible role of mass transfer (of Na⁺ for example) during diagenesis or metamorphism is another question. Exchange equilibrium, particularly along vectors AlFe₋₁ and NaAl(CaMg)₋₁, less so along FeMg₋₁, was clearly never attained on a thin-section scale. However, local equilibrium among up to three amphibole species (cummingtonite + sodic amphibole + actinolite or ferri-winchite) was reached at least for a time during the rock's history.

ACKNOWLEDGMENTS

This study was supported by the National Science Foundation (Grant EAR 83-05902). The author is much indebted to M. Schliestedt and R. Altherr for a guided tour of Syros and Siphnos and to R. G. Berman and M. Engi for assistance with phase-equilibrium computations. Critical reviews of the manuscript by P. Misch, C. Owen, J. M. Rice, and P. Robinson are greatly appreciated.

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MANUSCRIPT RECEIVED MARCH 29, 1985

MANUSCRIPT ACCEPTED MAY 16, 1986