

COEXISTING SODIC AMPHIBOLES AND SODIC PYROXENES FROM BLUESCHIST FACIES METAMORPHIC ROCKS

HITOSHI ONUKI

Tohoku University, Sendai, Japan

AND

W. G. ERNST

University of California, Los Angeles, California, 90024

ABSTRACT

Two pairs of coexisting riebeckites and aegirines, and their parent metacherts from near Laytonville, California, were analyzed by conventional gravimetric techniques. In combination with previously available data these analyses show clearly that, under blueschist facies metamorphic conditions, solid solution among sodic amphiboles extends from near glaucophane towards magnesioriebeckite and riebeckite compositions; no solvus exists in this mineral group. Sodic pyroxenes exhibit a wide range of solid solutions from jadeite to acmite and diopside; if a solvus exists in this series, it lies at Fe³⁺-poor compositions of limited range between jadeite and omphacite.

Cation proportions, structural site geometries and ionic sizes are compatible with concentration of manganese in the octahedral *M*(1) + *M*(3) sites of sodic amphiboles investigated but in the 8-fold coordinated *M*(2) positions of the sodic pyroxenes. The partitionings of (Fe²⁺ + Mn)/Mg and of (Fe³⁺ + Ti)/Al for the two pairs of coexisting iron-rich sodic amphiboles and sodic pyroxenes, and for five other aluminous and/or magnesian pairs from blueschist facies rocks of diverse compositions from the California Coast Ranges and the Sanbagawa terrane of Shikoku, Japan, are systematic; the first case is regular but complex, probably reflecting a three- or four-site versus a two-site cation exchange model, whereas the second is essentially ion-for-ion, indicating single-site participation by each phase in the equilibrium. In all examples, the bigger Fe²⁺ cations tend to be concentrated in the sodic amphibole relative to the more magnesian coexisting Na-pyroxene; in general, Fe³⁺ is favored over Al in the sodic amphibole, whereas the associated sodic pyroxene typically is more aluminous.

INTRODUCTION

Sodic amphiboles and sodic pyroxenes are common minerals in metamorphic rocks of the blueschist facies. Recently, a wealth of new analytical data, documenting solid solution relations within each of these two mineral groups has become available (Miyashiro and Iwasaki, 1957; Banno, 1959; Iwasaki, 1960; Ernst, 1964; Essene and Fyfe, 1967; Borg, 1967; Coleman and Clark, 1968; Coleman and Papike, 1968; Ernst and others, in press). Although compositional variations among the sodic amphibole end members glaucophane, $\circ\text{Na}_2\text{Mg}_3\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$ ¹ riebeckite, $\circ\text{Na}_2\text{Fe}_3^{+2}\text{Fe}_2^{+3}\text{Si}_8\text{O}_{22}(\text{OH})_2$, and magnesioriebeckite, $\circ\text{Na}_2\text{Mg}_3\text{Fe}_2^{+3}\text{Si}_8\text{O}_{22}$, are well demonstrated, blueschist pyroxenes approximating acmite (aegirine), Na-Fe³⁺Si₂O₆, have not been chemically analyzed previously. Such sodic pyroxenes are fairly common in metacherts from the Franciscan terrane of the California Coast Ranges and the Outer Metamorphic Belt of Japan, where they typically are associated with riebeckitic or magnesioriebeckitic amphiboles.

In part to remedy this lack of chemical data, pairs of coexisting sodic pyroxenes and sodic amphiboles were analyzed gravimetrically from two Franciscan siliceous schists. The host rocks, exposed in a small riprap quarry situated within a landslide five miles south of Laytonville, California, directly north of U.S. highway 101 (Chesterman, 1966) were also analyzed. The locality is notable for the occurrence of the new minerals deerite, howieite and zussmanite (Agrell and others, 1965).

¹The large 10–12 fold coordinated A structural site of amphiboles is unoccupied in sodic varieties; the symbol \circ indicates this vacancy here and in Figure 1.

Combined with five previously investigated sodic amphiboles and sodic pyroxenes from Shikoku and western California, it is now possible to examine element partitioning in the coexisting single- and double-chain Na-silicates. This study also utilizes appropriate crystal structure refinements, most of which have become available only recently (Whittaker, 1949; Prewitt and Burnham, 1966; Clark and Papike, 1968; Papike and Clark, 1968; see also Colville and Gibbs, 1965). The interested reader is referred to these papers for descriptions of the structures and the site terminology.

PETROLOGY OF THE INVESTIGATED ROCKS

The sodic amphibole + sodic pyroxene-bearing rocks studied are all metasedimentary. Modes are presented in Table 1. The pair of newly analyzed rocks from Laytonville are metachert (LO-1) and siliceous ferruginous shale (LO-3), as are the two specimens from eastern Shikoku (E-7 and E-2017). In contrast, three other rocks from the Californian Diablo Range (X-1 and X-3) and its northern extension (G-119) represent tuffaceous and subarkosic meta-graywackes. The principal contrast in phase assemblages among the various samples involves the hydrous Ca-Al-silicates: piemontite occurs in one of the Japanese specimens (E-2017), whereas the three Californian metaclastics carry lawsonite. Otherwise the rocks have quite similar mineralogies, the remaining differences being attributable to variable phase proportions, and to contrasts in compositions of the solid solutions.

The rocks all exhibit weakly to intensely developed schistosity paralleling a somewhat vague or irregular compositional layering. Sodic amphiboles and sodic pyroxenes

TABLE 1. MODES OF SODIC AMPHIBOLE + SODIC PYROXENE-BEARING METASEDIMENTS

Sample no.	LO-1	LO-3	E-7	E-2017	X-1	X-53	G-119
Quartz	81.8	58.0	79.0	52.9	5	20	21
Na-amphibole	8.6	24.9	5.4	21.4	34	8	24
Na-pyroxene	5.7	5.1	4.0	3.0	29	30	30
Stilpnomelane	0.3	4.1	0.0	0.0	0	4	5
White mica	0.0	0.0	0.6	12.1	0	0	5
Chlorite	0.0	0.0	0.1	tr	0	0	0
Garnet	1.0	5.0	6.1	2.0	0	0	0
Piemontite	0.0	0.0	0.0	3.9	0	0	0
Lawsonite	0.0	0.0	0.0	0.0	24	30	10
Others ^a	2.6	2.9	4.8	4.7	8	8	5

LO-1, LO-3, metachert and siliceous metashale from near Laytonville, Calif., (present study).

E-7, E-2017, siliceous schists from the Kôtu-Bizan District Eastern Shikoku (Iwasaki, 1963; Ernst, 1964).

X-1, X-53, metaclastic rocks from Pacheco Pass, Calif., (Ernst and others, in press).

G-119, metaclastic rock from Goat Mountain, Calif., (Ernst and others, in press).

^a others=iron oxides, clay, carbonate, carbonaceous matter and very fine-grained matrix.

show preferred orientations lying within the plane of foliation defined by alignment of the white mica, chlorite, stilpnomelane and minor clay minerals. Grain sizes of the chief phases range from less than 0.2 to more than 1.5 mm. Quartz and garnet tend to be equigranular and fine-grained (0.02–1.0 mm), whereas sheaves of sodic amphibole and sodic pyroxene (\pm stilpnomelane) are acicular and in some cases are intimately intergrown; the chain silicates range from very finely fibrous to prismatic crystals exceeding 1.5 mm in length. Layered silicates form individual flakes a tenth of a millimeter or so in maximum dimension, but mainly are intimately intergrown in a finely dispersed matrix.

Bulk chemical analyses of the two Laytonville rocks (LO-1 and LO-3) are presented in Table 2, along with analyses of the spilitic, tuffaceous metagraywacke (X-1) and a subarkosic metagraywacke (G-119) from the Diablo Range and its northern extension. Supporting the model data, these analyses demonstrate that wide ranges in rock bulk compositions have produced rather comparable mineral assemblages. It should be noted in passing that although most Sanbagawa and Franciscan metacherty sediments, including siliceous shales, are rich in K_2O relative to Na_2O (Iwasaki, 1963, Table 6; Bailey and others, 1964, Tables 9 and 10), certain others contain larger amounts of soda than potash (Coleman and Lee, 1963, Table 5; Ernst, 1965, Table 11; this study, Table 2).

MINERAL CHEMISTRY

Coexisting sodic amphiboles and sodic pyroxenes were concentrated from crushed aliquots of the two investigated Laytonville rocks using a magnetic separator and heavy liquids. Analyzed separates of the sodic amphiboles exceed 98.5 percent purity, but the presence of fine-grained inclusions of quartz and an unidentified phase in the sodic pyroxenes reduced the purity in these samples to barely 98 per-

cent. Table 3 presents the chemical results. Cation proportions based on structural formulas are given in Table 4; for pyroxenes, the calculations were based on six oxygens, whereas for amphiboles, cation proportions were based on 23 oxygens (assuming 2 OH per formula unit, as discussed by Miyashiro, 1957). The suffixes Am (= sodic amphibole) and Px (= sodic pyroxene) are used throughout the text, tables and figures to indicate the mineral of a particular rock—thus LO-3Am refers to the sodic amphibole of rock LO-3.

As evident from Fig. 1, the newly analyzed amphiboles are both riebeckites, employing Deer and others' (1963, Fig. 82) terminological modification of the classification scheme proposed by Miyashiro (1957). Each specimen exhibits insufficient H_2O in the chemical analysis to provide two OH^- per formula unit. A similar relationship was noted by Whittaker (1949), Ernst (1960), Coleman and Papike (1968), and in fact by numerous investigators of ferric iron-bearing amphiboles. Barnes (1930) showed that oxyamphiboles can be produced by heating ferrous analogues in air; in this case dehydrogenation is accompanied by an increase in Fe^{3+}/Fe^{2+} ratio to maintain overall charge balance. Inasmuch as cations residing in the amphibole $M(1)$ and $M(3)$ octahedral sites are bonded to the occupant of site O(3) (typically hydroxyl), the preferential stripping of electrons from such adjacent iron cations to preserve local charge balance in hydrogen-deficient am-

TABLE 2. BULK CHEMICAL ANALYSES OF SODIC AMPHIBOLE + SODIC PYROXENE-BEARING CALIFORNIAN METASEDIMENTS

Sample no.	LO-1	LO-3	X-1	G-119
Oxide				
SiO ₂	84.98	65.28	51.71	68.15
TiO ₂	0.22	0.38	1.12	0.33
Al ₂ O ₃	0.39	3.45	18.21	12.75
Fe ₂ O ₃	6.01	9.21	1.41	3.37
FeO	5.13	10.68	4.86	1.90
MnO	0.05	3.43	0.12	0.08
MgO	0.02	0.35	4.20	0.77
CaO	0.31	1.33	6.96	3.91
Na ₂ O	1.76	2.66	6.15	4.55
K ₂ O	0.10	0.69	0.05	0.73
H ₂ O(+)	0.78	1.09	4.43	2.73
H ₂ O(-)	0.18	0.73	0.11	0.30
P ₂ O ₅	0.03	0.54	0.12	0.07
CO ₂	—	—	0.45	0.04
Total	99.96	99.82	99.90	99.68
Analyst	H. Onuki			

LO-1, LO-3, metachert and siliceous metashale from near Laytonville, Calif. (present study).

X-1, metaclastic rock from Pacheco Pass, Calif. (Ernst and others, in press, Table 7).

G-119, metaclastic rock from Goat Mountain, Calif. (Ernst and others, in press, Table 6).

TABLE 3. CHEMICAL COMPOSITIONS OF COEXISTING SODIC AMPHIBOLES AND SODIC PYROXENES FROM BLUESCHIST FACIES METAMORPHIC ROCKS

Sample no.	LO-1Am LO-1Px		LO-3Am LO-3Px		E-7Am E-7Px		E-2017Am E-2017Px		X-1Am X-1Px		X-53Am X-53Px		G-119Am G-119Px	
Oxide														
SiO ₂	52.05	51.66	51.97	51.20	55.62	52.47	55.56	52.26	55.04	56.60	54.51	55.94	54.50	59.37
TiO ₂	0.44	0.24	0.19	0.21	0.26	0.10	0.13	0.15	1.03	0.63	1.39	1.25	1.00	0.08
Al ₂ O ₃	0.40	0.57	2.01	2.11	4.54	6.98	6.71	8.59	9.68	19.04	12.14	20.17	12.27	22.72
Fe ₂ O ₃	16.57	30.49	14.14	23.29	12.99	17.39	9.16	12.54	2.87	3.70	2.01	2.56	2.59	1.41
FeO	21.77	2.98	19.59	5.21	3.53	1.25	5.53	1.17	11.64	1.55	11.07	1.76	11.36	0.29
MnO	0.13	0.10	3.00	3.71	1.25	1.07	0.63	0.90	0.19	0.05	0.15	0.08	0.19	0.06
MgO	0.36	0.29	0.48	1.05	11.98	4.88	12.35	5.22	8.11	2.02	7.14	1.38	6.86	0.38
CaO	0.15	1.83	0.75	3.70	1.95	6.87	2.15	9.77	1.64	3.28	2.60	4.29	1.69	2.39
Na ₂ O	6.29	11.66	5.83	9.41	5.58	8.51	5.78	7.55	6.87	12.57	6.15	12.16	6.58	12.12
K ₂ O	0.20	0.12	0.34	0.18	0.36	0.28	0.20	Tr	0.06	0.11	0.08	0.15	0.42	0.56
H ₂ O(+)	1.49	0.07	1.78	0.05	1.96	0.43	1.93	1.55	2.79	—	2.71	0.21	2.19	0.24
H ₂ O(-)	0.04		0.20		0.00	0.00	0.00	0.13	0.20	—	0.19		0.05	0.39
Total	99.89	100.01	100.28	100.12	100.02	100.23	100.13	99.83	100.12	99.55	100.14	99.94	99.70	100.01
Analyst	H. Onuki				H. Haramura				H. Onuki					

LO-1Am, LO-1Px, LO-3Am, LO-3Px, (this study)
 E-7Am, Miyashiro and Iwasaki (1957, Table 3)
 E-7Px, Banno, 1959 (Table 1, no. 2)
 E-2017Am, Iwasaki (1960, Table 1, no. II)
 E-2017Px, Iwasaki (1960, Table 3, no. IV)
 X-1Am, X-53Am, G-119Am, Ernst and others (in press, Table 32)
 X-1Px, X-53Px, G-119Px, Ernst and others (in press, Table 33).

phiboles might be expected. However, crystal structure studies by Whittaker (1949), Colville and Gibbs (1965 and pers. commun., 1969) and by Papike and Clark (1968) have demonstrated a preference of the *M*(2) amphibole octahedral site for the smaller ferric iron and aluminum, relative to the bigger Fe²⁺ and Mg ions. Similar conclusions were made by Burns and Prentice (1968) from a study of the crocidolite infrared spectra. The *M*(2) site is adjacent *M*(4) which, in the sodic amphiboles, is occupied by a large, monovalent cation. Therefore the concentration of trivalent cations in *M*(2) of Na-amphibole probably reflects a tendency towards maintaining local charge balance among neighboring cations rather than between the *M* strip and coordinating layer of anions.¹

¹ Although the *M*(1) cation also shows anions with the occupant of *M*(4), there are four *M*(4)-*O*-*M*(2) bonds in contrast with only two *M*(4)-*O*-*M*(1) bonds.

The analyzed pyroxenes coexisting with the riebeckites are both aegirines, or aegirine-augites (see Fig. 2) using the somewhat similar classifications by Essene and Fyfe (1967), Clark and Papike (1968) and Coleman and Clark (1968). End member proportions according to Banno's (1959) method of calculation are Ac_{89.8}Aug_{8.0}Jd_{2.2} and Ac_{73.7}Aug_{17.7}Jd_{8.6} for samples LO-1Px and LO-3Px respectively. Both the aegirine and riebeckite from LO-3 exhibit an unusually high concentration of manganese, reflecting the high bulk rock MnO content as seen in Table 2 (3.43 weight percent). Evidently the manganese resides principally in the large 8-fold coordinated *M*(2) site in the sodic pyroxene LO-3Px, whereas it is distributed among the smaller octahedral *M*(1) + *M*(3) (but no *M*(2)?) sites in the sodic amphibole of samples LO-3Am, judging from cation sums listed in Table 4. This reasoning satisfactorily accounts for compositional relations in the sodic amphiboles and sodic

TABLE 4. CATION PROPORTIONS OF COEXISTING SODIC AMPHIBOLES AND SODIC PYROXENES FROM BLUESCHIST FACIES METAMORPHIC ROCKS

Sample no.	LO-1Am LO-3Am E-7Am E-2107Am X-1Am X-53Am G-119Am							LO-1Px LO-3Px E-7Px E-2017Px X-1Px X-53Px G-119Px														
Cation-site																						
IV {Si Al}	8.020	7.966	7.80	7.74	7.795	7.661	7.669	1.996	1.983	1.94	1.94	1.974	1.948	2.024	0.004	0.017	0.06	0.06	0.026	0.052	0.000	
	0.000	0.034	0.20	0.26	0.205	0.339	0.331															
VI {Al Ti Fe ³⁺ Fe ²⁺ Mg Mn}	0.072	0.329	0.55	0.84	1.408	1.668	1.701	0.022	0.079	0.25	0.32	0.755	0.774	0.911	0.007	0.006	0.00	0.00	0.017	0.033	0.002	
	1.915	1.631	1.36	0.96	0.304	0.215	0.274	0.883	0.677	0.48	0.35	0.097	0.067	0.036	2.796	2.511	0.41	0.64	1.374	1.296	1.332	
	0.083	0.110	2.50	2.56	1.722	1.505	1.448	0.017	0.061	0.27	0.29	0.106	0.072	0.019	0.017	0.390	0.15	0.07	0.023	0.018	0.022	
	0.017	0.390	0.15	0.07	0.023	0.018	0.022															
	Total VI	4.934	4.993	5.00	5.08	4.941	4.869	4.883	1.025	0.991	1.03	1.00	1.020	0.997	0.976							
	VIII {Mn Ca Na K}	0.025	0.123	0.29	0.32	0.249	0.391	0.255	0.003	0.122	0.03	0.03	0.001	0.002	0.002	0.076	0.154	0.27	0.39	0.123	0.160	0.087
1.877		1.733	1.52	1.56	1.883	1.673	1.792	0.872	0.706	0.62	0.54	0.848	0.820	0.800	0.039	0.067	0.07	0.04	0.010	0.015	0.078	
0.039		0.067	0.07	0.04	0.010	0.015	0.078	0.006	0.009	0.01	0.00	0.005	0.007	0.024								
Total VIII		1.941	1.923	1.88	1.92	2.142	2.079	2.125	0.957	0.991	0.93	0.96	0.977	0.989	0.913							

pyroxenes investigated, but may not be applicable to certain other chain silicates. For instance, Klein (1964, p. 969) showed that manganese is located in $M(4)$ in members of the cummingtonite-grunerite series; similar conclusions may be drawn from the electron microprobe data presented by Ross and others (1968).

Compositions of five other metamorphic pairs of single- and double-chain Na-silicates from rocks of the California Coast Ranges and the Outer Metamorphic Belt of Japan previously described are also listed in Table 3; Table 4 presents the corresponding cation proportions. The analytical data of these two tables indicate a wide range of compositions for coexisting sodic amphiboles and sodic pyrox-

enes. As was apparent from the four new mineral analyses, these additional ten support the idea that manganese is predominantly eight-fold coordinated in Na-pyroxenes, whereas it occupies chiefly octahedral sites in Na-amphiboles (see Table 4). Smith and Albee (1967) have demonstrated that Mn^{3+} , which is favored over Mn^{2+} by a high chemical potential of oxygen, is preferentially incorporated in the epidote-type structure relative to chain silicates; therefore, the presence of only minor amounts of manganese in the sodic amphibole and sodic pyroxene associated with piemontite in sample E-2017 may reflect a high oxidation state (hence an elevated Mn^{3+}/Mn^{2+} ratio) for this rock.

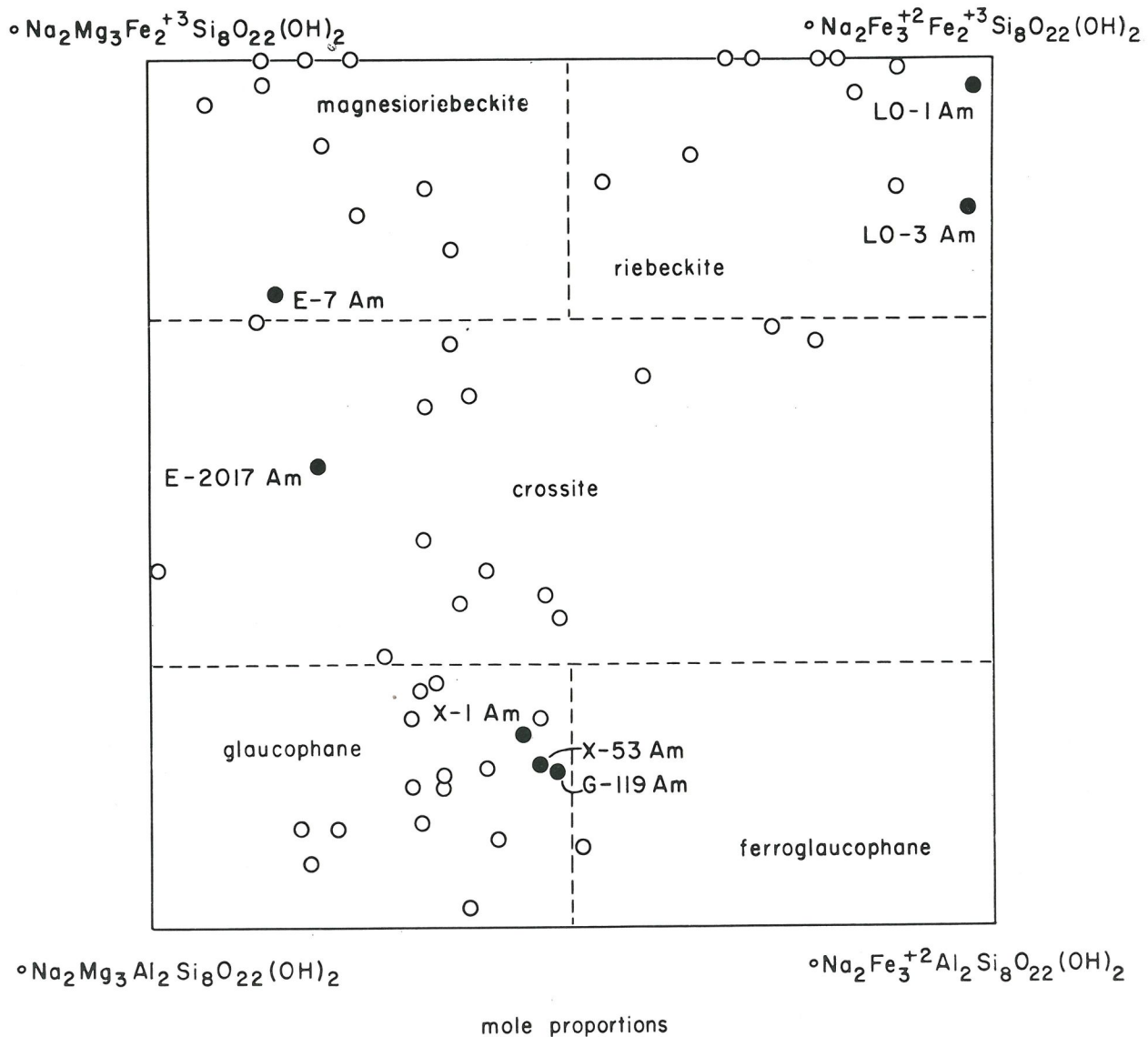


FIG. 1. Compositions from the literature of amphiboles closely approaching the glaucophane-ferroglaucophane-magnesioriebeckite-riebeckite series, determined by conventional gravimetric methods. All samples illustrated are from low-grade schists or feebly recrystallized sediments. Specimens represented by black circles have been investigated in this study. Classification employed is that of Miyashiro (1957), modified slightly by Deer and others (1963, Fig. 82).

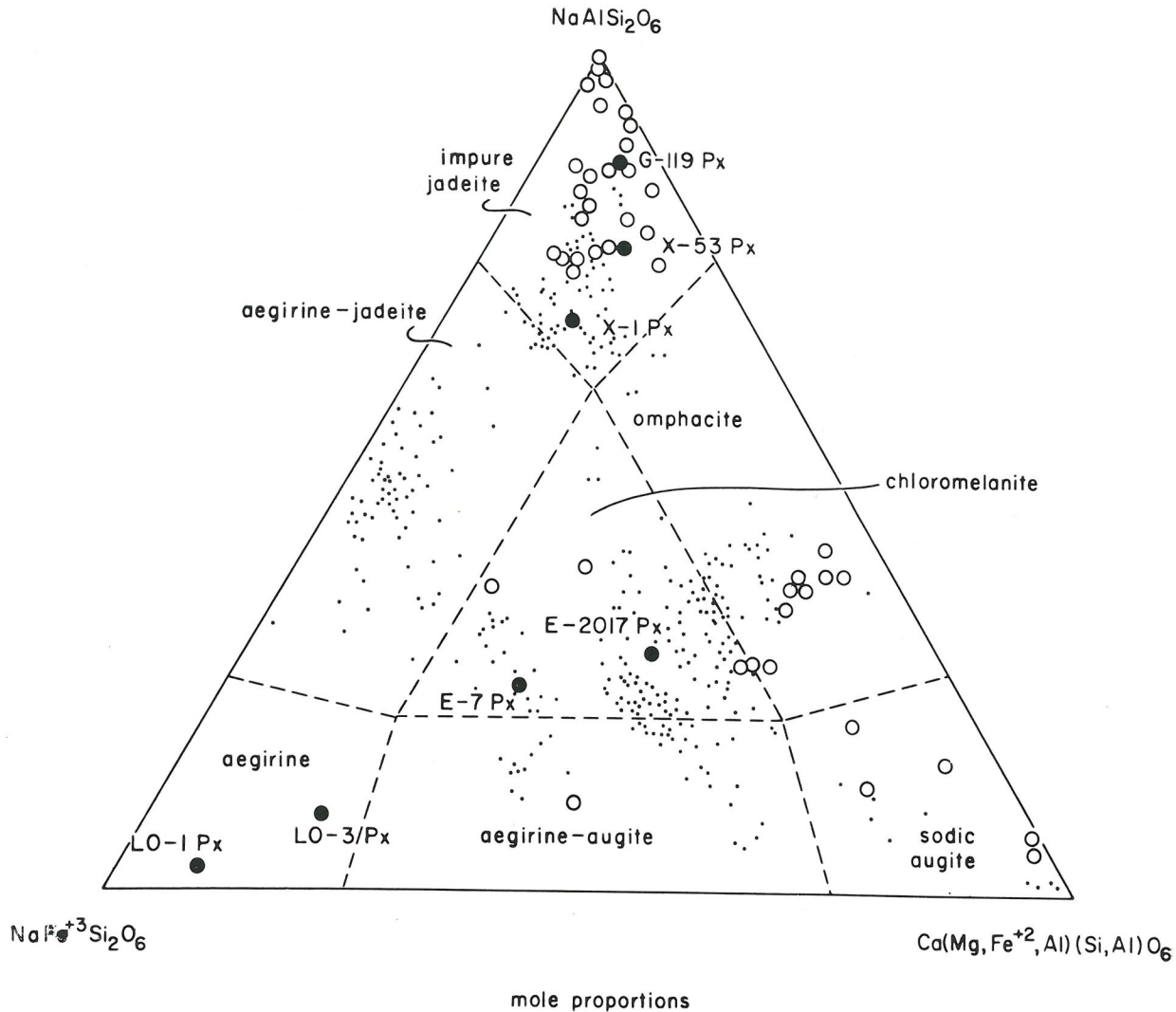


FIG. 2. Compositions from the literature of pyroxenes closely approaching the acmite-jadeite-augite series; circles represent conventional gravimetric analyses, dots indicate partial microprobe analyses. Samples illustrated are predominantly from low-grade metamorphic environments. Specimens represented by black circles have been investigated in this study. Classification employed is that of Essene and Fyfe (1967).

COMPOSITIONAL RANGES OF METAMORPHIC SODIC AMPHIBOLES AND SODIC PYROXENES

Chemical variations among sodic amphiboles from weakly recrystallized and low-grade metamorphic rocks are shown in Figure 1; the data are taken principally from Ernst (1960), Colville and others (1966), Coleman and Papike (1968), Ernst and others (in press) and the present study (see also Borg, 1967). As is well known, solid solution is essentially complete among glaucophane, magnesio-riebeckite and riebeckite. There is, however, apparently only limited natural solid solution towards ferroglaucophane. Evidently appropriate rock bulk compositions crystallize to condensed assemblages containing albite, iron oxide and quartz rather than ${}^{\circ}\text{Na}_2\text{Fe}_3^{+2}\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$ -bearing associations under physical conditions of low-grade metamor-

phism. Whatever the reason for the apparent nonoccurrence of end member ferroglaucophane, it is clear from Figure 1 that a solvus does not exist among the low-grade metamorphic sodic amphiboles. Such a relationship also has been documented experimentally (Ernst, 1963).

Figure 2 illustrates chemical variation among Na-Ca clinopyroxenes from blueschist-type metamorphic environments; the data are taken principally from Essene and Fyfe (1967), Seki and Onuki (1967), Coleman and Clark (1968), and Ernst and others (in press), as well as from the present investigations. Dobretsov (1962) postulated the existence of a solvus between omphacite (intermediate Di-Jd solid solution) and jadeitic pyroxene; chemical and crystallographic data presented by Coleman and Clark (1968, p. 48) are compatible with such a miscibility gap in

the region between approximately $\text{Di}_{55}\text{Jd}_{45}$ and $\text{Di}_{25}\text{Jd}_{75}$. However, chemical analyses of sodic pyroxenes—some of which come from igneous rocks—presented by Iwasaki (1963, Fig. 17), Seki and Onuki (1967) and Essene and Fyfe (1967, especially their Fig. 10, not shown in Fig. 2 of the present paper) tend to support the concept of more nearly complete solid solution in this compositional region. From high-pressure experimental phase equilibrium work, Bell and Davis (1965, 1967) concluded that a broad miscibility gap exists between jadeite and diopside; however, using similar techniques, Kushiro (1965) produced a wide compositional range of one-phase omphacite solid solutions employing bulk compositions lying along the $\text{NaAlSi}_3\text{O}_8$ — $\text{CaMgSi}_2\text{O}_6$ join. In any case, it seems clear from Figure 2 that although solid solution is extensive, few omphacites lack essential amounts of ferric iron ($\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ component). Thus the question of a solvus in the Na-Ca pyroxenes is unresolved, but if a miscibility gap occurs, its compositional width is evidently rather narrow.

Coleman and Papike (1968, Fig. 3) and Coleman and Clark (1968, Fig. 1) demonstrated a close relationship between the compositions of the host rocks and those of the chain silicates produced. In addition, Ernst and others (in press, Figs. 48–50) have shown that, even considering rocks of essentially the same bulk composition, small but systematic contrasts in the chemistry of chain silicates from Shikoku and California are recognizable: in particular, Franciscan sodic amphiboles and sodic pyroxenes are enriched in aluminum compared to the more iron-rich Sanbagawa equivalents. Such differences are attributed to relatively higher pressures and/or lower temperatures of California Coast Range metamorphism, compared to those operating during recrystallization of the Outer Metamorphic Belt of Japan (Ernst and others, in press).

Miyashiro (1967) has pointed out that relatively high chemical potentials of oxygen and sodium in through-going solutions would favor production of sodic amphiboles and sodic pyroxenes in ferruginous rocks poor in aluminum, such as cherts; in more aluminous rocks, the effects of high μ_{Na} probably would be obscured by the growth of alkali feldspar, white mica, or possibly blue-green hornblende. Where the chemical potential of oxygen is low, Miyashiro (1967) suggested that magnetite would not react with the sodic solutions. However, elevated values of μ_{Na} would cause the crystallization of a more ferrous sodic amphibole, arfvedsonite, and/or aegirine even at low oxidation states, as indicated by experimentally determined phase relations (see Ernst, 1962). Hence in either an oxidizing or a reducing environment, high μ_{Na} ought to be reflected by the presence of sodic chain silicates in Al-poor, iron-rich siliceous rocks. The lack of evidence for soda metasomatism under some conditions of elevated μ_{Na} suggests the possibility that the original rocks possessed the requisite bulk compositions, including relatively high Fe_2O_3 and Na_2O contents.

It is evident from both natural occurrences and low-and

high-pressure phase equilibrium studies (Ernst, 1962; Yagi, 1966; Gilbert, 1967; Bailey, 1969) that riebeckite-arfvedsonite solid solutions and aegirine are stable at intermediate oxidation states under magmatic as well as submagmatic P - T conditions. The two newly-analyzed riebeckites have K_2O contents of 0.20 and 0.34, whereas the aegirines contain 0.12 and 0.18 weight percents potash. In contrast, the six riebeckite-arfvedsonites from igneous rocks quoted by Deer and others (1963, Table 54) range from 1.42 to 2.10 and average 1.69 weight percent potash; the six igneous aegirines listed by these authors (Deer and others, 1963, Table 12) for which K_2O analyses are given range from 0.14 to 0.35 and average 0.24 weight percent. Obviously the large 10–12 fold coordinated A site in sodic amphiboles allows the accommodation of considerable amounts of potassium; sodic pyroxenes have no equivalent structural position, hence such minerals incorporate only trace amounts of potassium. K_2O is abundant in alkalic igneous rocks, whereas it is a very minor constituent in metacherts and in many metagraywackes and metabasalts, so the characteristic concentration of potassium in igneous riebeckite-arfvedsonites compared to metamorphic analogues may be either a function of rock bulk composition or of contrasting P - T conditions of formation (or both).

ELEMENT FRACTIONATIONS BETWEEN COEXISTING SODIC AMPHIBOLES AND SODIC PYROXENES

Let us consider the equilibrium partitioning of a pair of cations between two coexisting minerals. We will disregard the *intracrystalline* effects of contrasting structural sites, and merely relate the *intercrystalline*, or over-all, fractionation to an exchange equation of the type

$$lA_{Am} + mB_{Px} = lB_{Am} + mA_{Px}, \quad (1)$$

where A and B represent the chemical species involved, such as Fe^{2+} and Mg, and l and m indicate the number of moles exchanged. Remember that, for the case considered, clin amphibole-clinopyroxene equilibrium, two multisite phases are involved; we have lumped both energetically different sites, and the contrasting numbers of exchangeable cations participating in each site. Dividing equation (1) by l (letting $n = m/l$), the equilibrium is related to the universal gas constant, R , the absolute temperature, T , activities, a , and the standard free energy change, ΔG° , by the mass action law:

$$-\Delta G^\circ = RT \ln \left(\frac{a_B}{a_A} \right)_{Am} \left(\frac{a_A}{a_B} \right)_{Px}^n. \quad (2)$$

If we make the further simplifying assumption that the activity coefficients of the species A and B in both chain silicates are of unit value, then we may replace the activity quotient above by a readily measurable mole fraction quotient defined as equal to the equilibrium constant, K_D :

$$\exp(-\Delta G^\circ/RT) = \left(\frac{X_B}{X_A} \right)_{Am} \left(\frac{X_A}{X_B} \right)_{Px}^n \equiv K_D, \quad (3)$$

$$K_D \left(\frac{X_B}{X_A} \right)_{Px}^n = \left(\frac{X_B}{X_A} \right)_{Am}. \quad (4)$$

TABLE 5. SOME AVERAGE METAL-OXYGEN BOND DISTANCES AND CATION SITE OCCUPANCIES IN SODIC AMPHIBOLES AND SODIC PYROXENES

Magnesioriebeckite ^a	Jadeite ^d
$M(1) = 2.11 \text{ \AA} (0.72 \text{ Mg}; 0.28 \text{ Fe})$	$M 1 = 1.928 \text{ \AA} (0.99 \text{ Al}; 0.01 \text{ Mg})$
$M(2) = 2.07 \text{ \AA} (0.02 \text{ Al}; 0.33 \text{ Mg}; 0.65 \text{ Fe})$	$M 2 = 2.469 \text{ \AA} (0.98 \text{ Na}; 0.02 \text{ Ca})$
$M(3) = 2.11 \text{ \AA} (0.72 \text{ Mg}; 0.28 \text{ Fe})$	Omphacite ^e
$M(4) = 2.54 \text{ \AA} (0.69 \text{ Na}; 0.06 \text{ K}; 0.09 \text{ Ca}; 0.12 \text{ Mg})$	
Riebeckite ^b	
$M(1) = 2.113 \text{ \AA} (\sim 1.0 \text{ Fe}^{2+})$	$M 1 \begin{cases} = 1.94 \text{ \AA} (0.95 \text{ Al}; 0.05 \text{ Fe}) \\ = 1.95 \text{ \AA} (0.82 \text{ Al}; 0.18 \text{ Fe}) \\ = 2.07 \text{ \AA} (0.81 \text{ Mg}; 0.19 \text{ Fe}) \\ = 2.10 \text{ \AA} (0.80 \text{ Mg}; 0.20 \text{ Fe}) \end{cases}$
$M(2) = 2.034 \text{ \AA} (\sim 1.0 \text{ Fe}^{2+})$	
$M(3) = 2.113 \text{ \AA} (\sim 0.25 \text{ Al}; 0.5 \text{ Fe}^{2+}; 0.25 \text{ Li})$	$M 2 \begin{cases} = 2.44 \text{ \AA} (0.64 \text{ Na}; 0.36 \text{ Ca}) \\ = 2.47 \text{ \AA} (0.36 \text{ Na}; 0.64 \text{ Ca}) \\ = 2.50 \text{ \AA} (0.64 \text{ Na}; 0.36 \text{ Ca}) \\ = 2.55 \text{ \AA} (0.03 \text{ Na}; 0.97 \text{ Ca}) \end{cases}$
$M(4) = 2.561 \text{ \AA} (\sim 1.0 \text{ Na})$	
Glaucofane ^c	
$M(1) = 2.087 \text{ \AA} (0.84 \text{ Mg}; 0.16 \text{ Fe}^{2+})$	
$M(2) = 1.943 \text{ \AA} (0.91 \text{ Al}; 0.09 \text{ Fe}^{3+})$	
$M(3) = 2.094 \text{ \AA} (0.71 \text{ Mg}; 0.29 \text{ Fe}^{2+})$	
$M(4) = 2.498 \text{ \AA} (0.98 \text{ Na}; 0.02 \text{ Ca})$	

^a Whittaker (1949, p. 315, 316)

^b Colville and Gibbs (1965 and pers. commun., 1969)

^c Papike and Clark (1968, Table 7)

^d Prewitt and Burnham (1966, p. 958 and Table 6)

^e Clark and Papike (1968, Table 10)

^f Octahedral coordination for sodic amphibole $M(1)$, $M(2)$ and $M(3)$, sodic pyroxene $M(1)$; eight-fold coordination for sodic amphibole $M(4)$, sodic pyroxene $M(2)$.

A straight line is defined by equation (4) on a log-log plot of $(X_B/X_A)_{Am}$ as the ordinate versus $(X_B/X_A)_{Px}$ as the abscissa, provided that the values of K_D and n are not a function of composition for one or both of the participating phases. Setting the $(X_B/X_A)_{Px}$ at unit value, K_D is obtained by reading off the value of the ordinate intercept $(X_B/X_A)_{Am}$. The slope of the line is n .

Where a simple ion-for-ion exchange takes place, such as

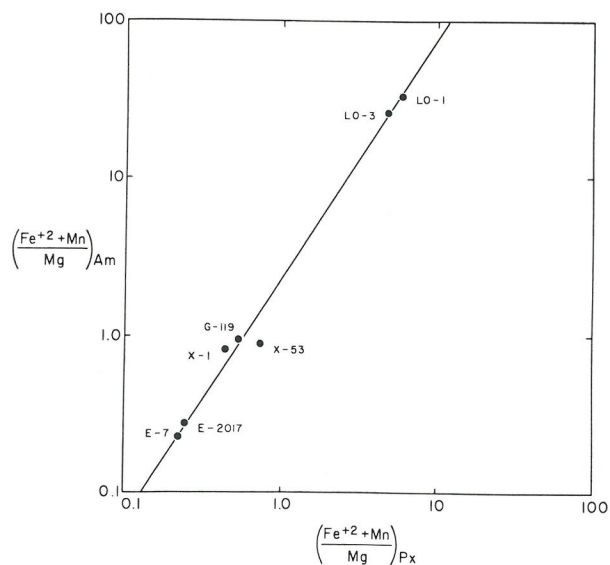


FIG. 3. Partitioning of $(\text{Fe}^{2+} + \text{Mn})/\text{Mg}$ between coexisting sodic amphiboles and sodic pyroxenes, blueschist facies rocks. Ratios are based on atomic proportions. $K_D = 2.3$, $n = 1.5$.

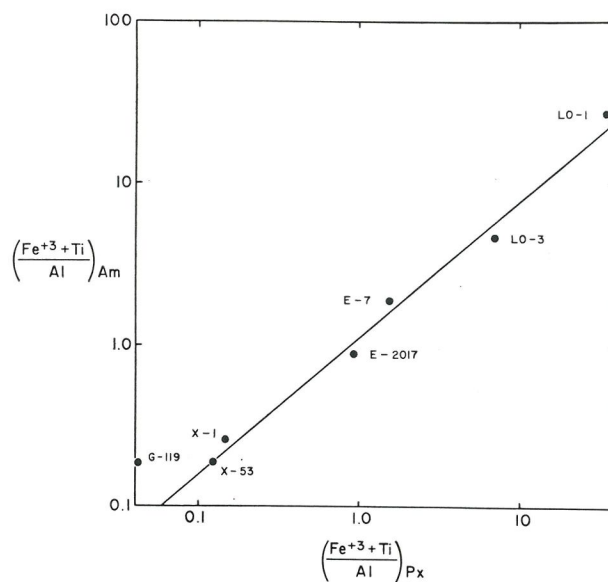


FIG. 4. Partitioning of $(\text{Fe}^{3+} + \text{Ti})/\text{Al}$ between coexisting sodic amphiboles and sodic pyroxenes, blueschist facies rocks. Ratios are based on atomic proportions. $K_D = 1.2$, $n = 0.9$.

in the case of perfect intracrystalline disorder or equilibrium between single-site phases, the slope is 45° and n is unity. However, the $M(1)$, $M(2)$, $M(3)$ and $M(4)$ sites in sodic amphiboles differ geometrically (hence probably energetically also) from one another, and so do $M1$ and $M2$ positions in sodic pyroxenes, as is evident from Table 5. It is, of course, true that in some cases where different sites carry identical cations, bond lengths may be quite comparable, as in members of the tremolite-actinolite and cummingtonite-grunerite series (e.g., Zussman, 1955; Ghose, 1959; Ghose and Hellner, 1961; Fischer, 1966; see also Table 5 of the present report). Nevertheless, the tolerances—or compliances—of different structural positions for the various cations must contrast markedly, or observed cation ordering would be inexplicable. Such compliances undoubtedly are a complex function of structural geometry, cation size, and the necessity of approximating local charge balance. Hence in general, for such at least partially ordered phases, more complicated exchange equilibria are to be expected. The structural complexities of Na-amphiboles and Na-pyroxenes require that eight specific exchange equilibria (five of which are independent) be written to describe fractionation between a four-site and a two-site mineral, and the limited amounts of data presently available do not warrant such treatment.¹ For simpler systems, the reader is referred to pioneering quantitative investigations by Mueller (1962), Matsui and Banno (1965), Grover and Orville (1969) and Thompson (1969).

¹ For equilibrium between a phase containing x energetically distinct structural sites, and a second phase containing y such positions, the total number of partition coefficients required to specify the exchange equilibrium is xy , of which $x + y - 1$ are independent.

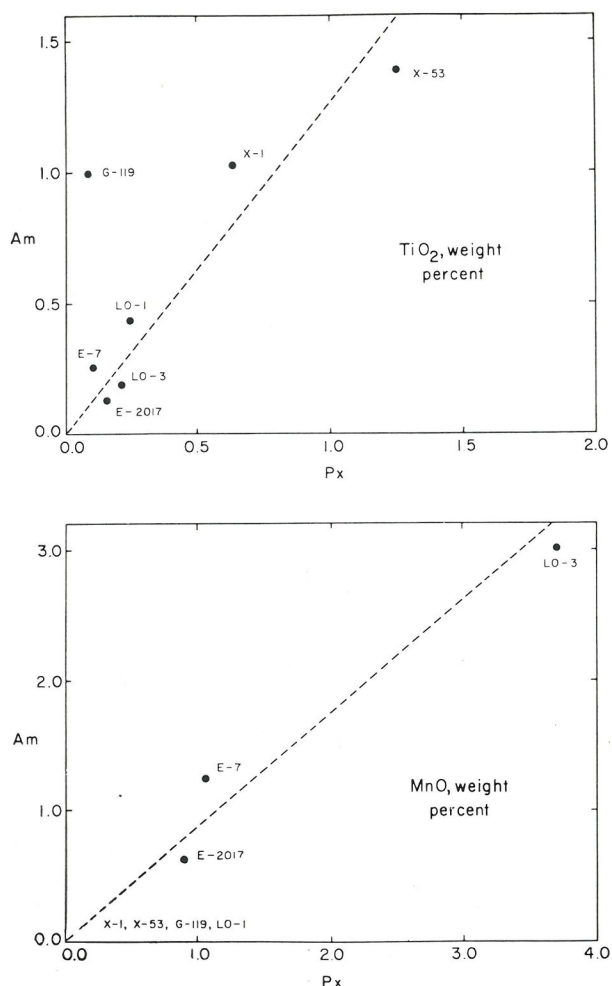


FIG. 5. Partitioning of TiO_2 and of MnO between coexisting sodic amphiboles and sodic pyroxenes, blueschist facies rocks.

The distribution of $(\text{Fe}^{2+} + \text{Mn})$ versus Mg in the seven coexisting sodic amphiboles and sodic pyroxenes studied in this investigation is illustrated in Figure 3. The corresponding fractionation of $(\text{Fe}^{3+} + \text{Ti})$ versus Al is presented in Figure 4 (total aluminum rather than Al^{VI} was employed because the analyzed concentrates of LO-1Am and G-119Px evidently contained minor inclusions of quartz, which in turn would have introduced a small error into the calculation of Al^{IV} , hence Al^{VI} , for these specimens). Cations were divided into these groupings based on charges, and on six-fold coordinated ionic radii taken from Shannon and Prewitt (*in press*, Table 1: $\text{Al} = 0.530$, $\text{Ti} = 0.605$, $\text{Fe}^{3+} = 0.645$, $\text{Mg} = 0.720$, $\text{Fe}^{2+} = 0.770$, $\text{Mn}^{+2} = 0.820 \text{ \AA}$).

First let us consider distribution of the divalent cations. The value of K_D of 2.3 indicates that magnesium is enriched in the $M1$ positions of Na-pyroxene relative to the Na-amphibole (Fig. 3). The roles played by amphibole $M(4)$ and pyroxene $M2$ regarding the partitioning of ferrous iron, manganese and magnesium are not known, but at least the latter apparently participate in the ex-

change. The complex fractionation model is reflected in a value of n departing markedly from unity, 1.5. Because of the relative low compliance of the sodic pyroxene $M1$ site, manganese apparently is too large to be accommodated in major amounts, hence as previously mentioned, it is located chiefly in the Na-pyroxene $M2$ position.

Aluminum and ferric iron evidently are ordered chiefly in $M(2)$ in the sodic amphibole, and mainly in the sodic pyroxene $M(1)$ site according to the investigations of Whittaker (1949), Colville and Gibbs (1965) personal communication, 1969), Prewitt and Burnham (1966), Clark and Papike (1968) and Papike and Clark (1968), summarized in Table 5. The value of n , 0.9, is sufficiently close to unity to presume an ion-for-ion type of equilibrium; as suspected for this case, only a single set of positions for each participating phase seems to be involved in the exchange. Pronounced fractionation of Al , Fe^{3+} and Ti between the Na-amphibole $M(2)$ and Na-pyroxene $M1$ sites is not evident, as illustrated in Figure 4. This is reflected in a K_D value close to unity, 1.2. For coexisting aluminous pairs, ferric iron (and titanium) are relatively enriched in the sodic amphibole, whereas in the two riebeckite + aegirine pairs, the sodic amphiboles are more Al -rich than the associated sodic pyroxenes. Compliance to accommodate a large cation apparently is more marked in aegirine $M1$ than in riebeckite $M(2)$, whereas compliance of the appropriate glaucophane site evidently exceeds that of the corresponding jadeite position.

The partitionings of TiO_2 and MnO between sodic amphibole and sodic pyroxene are shown on Nernst (infinite dilution) plots in Figure 5. Although the distributions are fairly regular, some scattering is apparent. These minor elements are not strongly fractionated, probably because of roughly compensating effects among the contrasting structural sites involved.

In conclusion, it is evident that $(\text{Fe}^{2+} + \text{Mn})/\text{Mg}$ and $(\text{Fe}^{3+} + \text{Ti})/\text{Al}$ distributions are systematic between coexisting sodic amphiboles and sodic pyroxenes. In the first case $n \neq 1$ because of the complexity of the fractionation (a three- or four-site versus a two-site model), whereas in the second case $n \approx 1$, and the partitioning is virtually ion-for-ion (one-site versus one-site model). Characteristically, the bigger iron cations are concentrated in the amphibole structural positions—which therefore exhibit large metal-oxygen bond distances—compared to the coexisting $\text{Mg} + \text{Al}$ -rich pyroxenes. As pointed out by Burns (1968), increased octahedral distortion produces a greater crystal-field stabilization energy for Fe^{2+} , hence a distinct site preference for this ion; judging from the ferrous iron distribution observed in the present study, the sodic amphibole $M(1)$ and $M(3)$ (and $M(2)?$) sites might be expected to depart more from symmetrical configurations than the $M1$ (and $M2?$) positions of coexisting sodic pyroxenes.

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REFERENCES

- AGRELL, S. O., M. G. BOWN, AND D. MCKIE (1965) Deerite, howieite, and zussmanite, three new minerals from the Franciscan of the Laytonville district, Mendocino County, California (abstr.). *Amer. Mineral.*, **50**, 278.
- BAILEY, D. K. (1969) The stability of acmite in the presence of H₂O. *Amer. J. Sci.* **267A**, 1-16.
- BAILEY, E. H., W. P. IRWIN, AND D. L. JONES (1964) Franciscan and related rocks, and their significance in the geology of western California. *Calif. Div. Mines Geol. Bull.* **183**, 171 p.
- BANNO, S. (1959) Notes on rock-forming minerals (10) glaucophanes and garnet from the Kôtu District, Shikoku. *J. Geol. Soc. Jap.*, **65**, 658-663.
- BARNES, V. E. (1930) Changes in hornblende at about 800°C. *Amer. Mineral.*, **15**, 393-417.
- BELL, P. M., AND B. T. C. DAVIS (1965) Temperature-composition section for jadeite-diopside. *Carnegie Inst. Wash. Year Book*, **64**, 120-123.
- , AND ——— (1967) Investigation of a solvus in the system jadeite-diopside. *Carnegie Inst. Wash. Year Book* **65**, 239-241.
- BORG, I. Y. (1967) Optical properties and cell parameters in the glaucophane-riebeckite series. *Contrib. Mineral. Petrology*, **15**, 67-92.
- BURNS, R. G. (1968) Crystal-field phenomena and iron enrichments in pyroxenes and amphiboles. *Pap. Proc. Int. Mineral. Ass. Meet.* Mineralogical Society, London, p. 170-183.
- , AND F. J. PRENTICE (1968) Distribution of iron cations in the crocidolite structure. *Amer. Mineral.*, **53**, 770-776.
- CHESTERMAN, C. W. (1966) Mineralogy of the Laytonville quarry, Mendocino County, California. *Calif. Div. Mines Geol. Bull.*, **190**, 503-508.
- CLARK, J. R., AND J. J. PAPIKE (1968) Crystal-chemical characterization of omphacites. *Amer. Mineral.*, **53**, 840-868.
- COLEMAN, R. G., AND D. E. LEE (1963) Glaucophane-bearing metamorphic rock types of the Cazadero area, California. *J. Petrology*, **4**, 260-301.
- , AND J. R. CLARK (1968) Pyroxenes in the blueschist facies of California. *Amer. J. Sci.*, **266**, 43-59.
- , AND J. J. PAPIKE (1968) Alkali amphiboles from the blueschists of Cazadero, California. *J. Petrology*, **9**, 105-122.
- COLVILLE, A. A., AND GIBBS, G. V. (1965) Refinement of the crystal structure of riebeckite (abstr.). *Geol. Soc. Amer. Spec. Pap.*, **82**, 31.
- COLVILLE, P., W. G. ERNST, AND M. C. GILBERT (1966) Relationships between cell parameters and chemical compositions of monoclinic amphiboles. *Amer. Mineral.*, **51**, 1727-1754.
- DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1963) *Rock-forming Minerals. Vol. 2, Chain Silicates.* John Wiley and Sons, Inc., New York, 379.
- DOBRETSOV, N. L. (1962) Miscibility limits and average composition of the jadeite pyroxenes. *Akad. Nauk S.S.S.R. Doklady*, **146**, 676-679 [Transl. *Acad. Sci. U.S.S.R. Doklady, Earth Sci. Sec.*, **146**, 118-120 (1964)].
- ERNST, W. G. (1960) The stability relations of magnesioriebeckite. *Geochim. Cosmochim. Acta*, **19**, 10-40.
- (1962) Synthesis, stability relations, and occurrence of riebeckite and riebeckite-arfvedsonite solid solutions. *J. Geol.*, **70**, 689-736.
- (1963) Polymorphism in alkali amphiboles. *Amer. Mineral.*, **48**, 241-260.
- (1964) Petrochemical study of coexisting minerals from low-grade schists, Eastern Shikoku, Japan. *Geochim. Cosmochim. Acta*, **28**, 1631-1668.
- (1965) Mineral parageneses in Franciscan metamorphic rocks, Panoche Pass, California. *Geol. Soc. Amer. Bull.*, **76**, 879-914.
- , Y. SEKI, H. ONUKI, AND M. C. GILBERT (in press) Comparative study of low-grade metamorphism in the California Coast Ranges and the Outer Metamorphic Belt of Japan. *Geol. Soc. Amer. Mem.*, **124**.
- ESSENE, E. J., AND W. S. FYFE (1967) Omphacite in Californian rocks. *Contrib. Mineral. Petrology*, **15**, 1-23.
- FISCHER, K. F. (1966) A further refinement of the crystal structure of cummingtonite, (Mg,Fe)₇(Si₄O₁₁)₂(OH)₂. *Amer. Mineral.* **51**, 814-818.
- GHOSE, S. (1961) The crystal structure of a cummingtonite. *Acta Crystallogr.* **14**, 622-627.
- AND E. HELLNER (1959) The crystal structure of grunerite and observations on the Mg-Fe distribution. *J. Geol.*, **67**, 691-701.
- GILBERT, M. C. (1967) Acmite. *Carnegie Inst. Wash. Year Book*, **65**, 241-244.
- GROVER, J. E., AND P. M. ORVILLE (1969) The partitioning of cations between coexisting single- and multi-site phases with application to the assemblages: orthopyroxene-clinopyroxene and orthopyroxene-olivine. *Geochim. Cosmochim. Acta*, **33**, 205-226.
- IWASAKI, M. (1960) Colorless glaucophane and associated minerals in quartzose schist from eastern Sikoku, Japan. *J. Geol. Soc. Jap.*, **66**, 566-574.
- (1963) Metamorphic rocks of the Kôtu-Bizan area, eastern Sikoku. *J. Fac. Sci., Univ. Tokyo, Sec. II*, **15**, 1-90.
- KLEIN, C., JR. (1964) Cummingtonite-grunerite series: a chemical, optical and x-ray study. *Amer. Mineral.*, **49**, 963-982.
- KUSHIRO, I. (1965) Clinopyroxene solid solutions at high pressures. *Carnegie Inst. Wash. Year Book* **64**, 112-117.
- MATSUI, Y., AND S. BANNO (1965) Intracrystalline exchange equilibria in silicate solid solutions. *Pro. Jap. Acad.*, **41**, 461-466.
- MIYASHIRO, A. (1957) The chemistry, optics, and genesis of the alkali-amphiboles. *J. Fac. Sci. Univ. Tokyo, Sec. II*, **11**, pt. 1, 57-83.
- (1967) Chemical compositions of rocks in relation to metamorphic facies. *Jap. J. Geol. Geogr.*, **38**, 149-157.
- , AND M. IWASAKI (1957) Magnesioriebeckite in crystalline schists of Bizan in Sikoku, Japan. *J. Geol. Soc. Jap.*, **63**, 698-703.
- MUELLER, R. F. (1962) Energetics of certain silicate solid solutions. *Geochim. Cosmochim. Acta*, **26**, 581-598.
- PAPIKE, J. J., AND J. R. CLARK (1968) The crystal structure and cation distribution of glaucophane. *Amer. Mineral.*, **53**, 1156-1173.
- PREWITT, C. T., AND C. W. BURNHAM (1966) The crystal structure of jadeite, NaAlSi₃O₆. *Amer. Mineral.*, **51**, 956-975.
- ROSS, M., J. J. PAPIKE AND P. W. WEIBLEN (1968) Exsolution in clinopyroxenes. *Science*, **159**, 1099-1102.
- SEKI, Y., AND H. ONUKI (1967) Variation of unit-cell dimensions in natural jadeite-diopside mineral series. *J. Japan. Ass. Mineral., Petrology, Econ. Geol.*, **58**, 233-237.
- SHANNON, R. D., AND C. T. PREWITT (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.*, **B25**, 925-946.
- SMITH, D., AND A. L. ALBEE (1967) Petrology of a piemontite-bearing gneiss, San Geronio Pass, California. *Contrib. Mineral. Petrology*, **16**, 189-203.
- THOMPSON, J. B., JR. (1969) Chemical reactions in crystals. *Amer. Mineral.*, **54**, 341-375.
- WHITTAKER, E. J. W. (1949) The structure of Bolivian crocidolite. *Acta Crystallogr.*, **2**, 312-317.
- YAGI, K. (1966) The system acmite-diopside and its bearing on the stability relations of natural pyroxenes of the acmite-hedenbergite-diopside series. *Amer. Mineral.*, **51**, 976-1000.
- ZUSSMAN, J. (1955) The crystal structure of an actinolite. *Acta Crystallogr.*, **8**, 301-308.