Mineral. Soc. Amer. Spec. Pap. **2**, 137–148 (1969).

MÖSSBAUER AND ABSORPTION SPECTRAL STUDY OF ALKALI AMPHIBOLES

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ABSTRACT

Mössbauer, visible and infrared spectral measurements have been made of alkali amphiboles of the glaucophane-crossite-riebeckite and magnesioriebeckite-riebeckite series. From the computer calculated areas in the Mössbauer spectra, estimates have been made of the Fe^{2+} site populations of the $M(1)$, $M(2)$ and $M(3)$ structural positions, together with the proportions of Fe^{2+} and Fe^{3+} ions in each mineral. These results agree well with X-ray structure and chemical analysis.

The site population estimates from Mössbauer spectroscopy, together with infrared measurements of the O-H stretching frequencies, provide the cation distribution in each mineral. In crocidolites and glaucophanes of low temperature-high pressure origins, cations are highly ordered with the majority of Fe^{3+} and Al^{3+} ions occurring in $M(2)$ positions. The Fe^{2+} and Mg^{2+} ions are concentrated in $M(1)$ and $M(3)$ positions, and relative enrichments of the divalent cations in these positions are reversed along the glaucophane-riebeckite composition line. The cations in pegmatitic alkali amphiboles of high temperature origins are more randomly distributed in the crystal structures.

The characteristic colorless-violet-blue pleochroism of alkali amphiboles may be explained by the cation distribution. The intense charge transfer bands in the visible region originate from electron transfer between neighboring Fe^{2+} and Fe^{3+} ions in the structures.

INTRODUCTION

Minerals of the alkali amphibole group are of interest not only because they are representative of wide ranges of composition as well as temperatures and pressures of crystallization, but also because they display unusual physical properties such as characteristic colour and pleochroic schemes. These properties relate to the arrangements of cations, including Na^{+}, Mg^{2+}, Fe^{2+}, Al^{3+} and Fe^{3+}, in the amphibole crystal structure. The positions of these cations in alkali amphiboles have been deduced from X-ray diffraction measurements (Whittaker, 1949; Colville and Gibbs, 1964; Papike and Clark, 1968).

However, it is very difficult to distinguish between ferrous and ferric ions in a crystal structure from an X-ray analysis. Distributions of Fe^{2+} and Fe^{3+} ions have been deduced from additional considerations involving ion size, charge and electronegativity criteria (Whittaker, 1960; Ghose, 1965). Thus, in a recent refinement of the glaucophane structure (Papike and Clark, (1968) these criteria formed the basis for assigning the oxidation states of iron cations in specific crystallographic positions.

Using spectroscopic techniques involving the Mössbauer effect in iron and the fundamental hydroxyl stretching frequency in the infrared, it has been possible not only to distinguish between Fe^{2+} and Fe^{3+} ions in a structure, but also to estimate Fe^{2+} site populations in several alkali amphiboles of the magnesio-riebeckite-riebeckite series, $Na_2(Mg,Fe^{2+})_3Fe^{3+}{}_2Si_8O_{22}(OH)_2$ (Burns and Prentice, 1968; Bancroft, Burns and Stone, 1968). In the present paper these techniques are extended to the aluminous alkali amphiboles of the glaucophane-crossite-riebeckite series, $Na_2(Mg,Fe^{2+})_3(Al,Fe^{3+})_2Si_8O_{22}(OH)_2$.

SPECIMENS AND EXPERIMENTAL TECHNIQUES

Specimens. The compositions and sources of the specimens used in this study are listed in Table 1. The diagram in Figure 1 shows the Fe^{2+} and Fe^{3+} ion contents of the specimens in terms of the end-member compositions of the alkali amphibole series. The aluminous varieties were selected from specimens whose compositions lie close to the glaucophane-crossite-riebeckite composition line, and all are derived from rocks of the Californian Franciscan formation. The riebeckite (specimen 5) and one of the magnesio-riebeckites (specimen 6) are asbestiform crocidolites, and the other magnesioriebeckite (specimen 7) is a prismatic variety from pegmatite.

Infrared spectroscopy. The infrared technique for measuring site populations in amphiboles has been described previously (Burns and Strens, 1966; Burns and Prentice, 1968). It is based on the stretching frequencies of the O-H band of hydroxyl ions coordinated to cations in specific positions of the amphibole structure. Measurements were made in the region 3800–3500 cm^{-1} with a Perkin-Elmer model 221 recording spectrophotometer on powdered amphibole specimens in pressed KBr discs. Approximately 2 mg of the mineral was ground under acetone and blended with 200 mg of KBr. The mixture was placed in a dye cylinder either preheated to 110°C for periods of up to 15 minutes or no heat was applied. The disc was pressed under a vacuum at 14 tons and the spectrum measured immediately in a humidity-controlled, air-conditioned room. Eight to ten separate spectra were run on different samples of each amphibole specimen. It was found that the relative intensities of peaks and inflections in the spectra were remarkably uniform despite the wide variation of preparative procedures.

Mössbauer spectroscopy. The Mössbauer spectrometer and technique for measuring the spectra of silicates have been described previously (Bancroft, Maddock and Ward, 1965; Bancroft, Burns and Maddock, 1967a). Most absorbers were prepared by simply sandwiching the finely ground mineral between cellotape. A uniform layer of mineral was obtained having a total iron concentration of 10 mg/cm^2, but for specimen 1 the concentration was only 3 mg/cm^2. This mode of preparation gave slightly orientated samples for some absorbers. A random sample of specimen 1 was made by mixing the finely ground mineral with powdered Perspex. The Perspex treatment led to line broadening in some of the spectra of the other specimens and was abandoned. At least two, and in most cases three, spectra were taken at room temperature for each mineral. Specimens 1 and 7 were also run at liquid nitrogen temperature.

TABLE 1. CHEMICAL ANALYSES DESCRIPTIONS OF THE SPECIMENS

	1	2	3	4	5	6	7
SiO_2	58.04	56.38	55.38	52.16	51.19	56.10	53.5
TiO_2	0.66	0.11	0.36	0.04	0.03	tr	0.25
Al_2O_3	10.31	8.45	5.29	4.51	0.17	0.66	1.3
Fe_2O_3	2.89	4.98	9.74	10.53	16.55	15.60	14.5[a]
FeO	6.12	9.40	13.07	18.19	21.27	4.06	6.99[a]
MnO	0.07	0.19	0.18	0.51	0.32	0	0.13
MgO	11.71	9.89	6.31	3.93	1.30	14.5	12.5
CaO	1.37	1.29	1.10	1.19	0.83	0.11	2.25
Na_2O	6.97	6.77	6.40	6.27	6.14	5.45	6.42
K_2O	0.02	0.08	0.05	0.09	0.05	0.71	0.08
H_2O+	1.98	1.86	1.99	2.25	2.26	n.d.	2.57
H_2O-	0.00	0.04	0.09	0.05	0.00	n.d.	n.d.
others	0.03	0.02	0.03	0.10	0.00	0.00	0.00
total	100.17	99.46	99.99	99.82	100.11	—	100.49
Si	7.92	7.94	8.00	7.84	7.94	7.94	7.71
Ti	0.06	0.01	0.04	0.01	0	0	0.03
Al	1.66	1.40	0.90	0.90	0.03	0.11	0.22
Fe^{3+}	0.30	0.53	1.06	1.20	1.93	1.66	1.57
Fe^{2+}	0.70	1.11	1.58	2.29	2.76	0.48	0.84
Mn	0.01	0.02	0.02	0.07	0.04	0	0.02
Mg	2.38	2.08	1.36	0.88	0.30	3.06	2.68
Na	1.84	1.85	1.79	1.83	1.85	1.38	1.79
Ca	0.20	0.20	0.17	0.19	0.14	0.17	0.35
K	0	0.01	0.01	0.01	0.01	0.13	0.02
OH	1.80	1.75	1.92	2.20	2.25	—	2.47
F	0	0	0.01	0.05	0	0	0

[a] Redetermined values: Fe_2O_3, 9.91; FeO, 7.07.

1. Glaucophane, glaucophane schist inclusion in serpentinite, Tiburon Peninsula, Marin County, California (Ernst, personal comm.; Papike and Clark, 1968). Anal. S. Imai.
2. Glaucophane, glaucophane-chlorite rock, Healdsburg Quad., California (Borg, 1967). Anal. C.O. Ingamells. Collection No.: U.C., Berkeley 331-M-19B (Borg, 1967, no. 5).
3. Crossite, quartz-crossite schist, Healdsburg Quad., California. (Borg, 1967). Anal. C. O. Ingamells. Collection No. U.C., Berkeley 331-M-56 (Borg, 1967, no. 7).
4. Crossite, iron formation, Laytonville, Mendicino County, California (Agrell, personal comm.; Agrell, Bown and McKie, 1965). Anal. J. H. Scoon. Collection No: Cambridge 93995.
5. Riebeckite (crocidolite), iron formation, Laytonville, Mendicino County, California (Agrell, pers. comm.; Agrell, Bown and McKie, 1965). Anal. J. H. Scoon. Collection No: Cambridge 93720.
6. Magnesioriebeckite (crocidolite), metasomatized dolomite, Cochabamba, Bolivia (Ahlfeld, 1943, Whittaker, 1949). Anal. R. D. Swinburn.
7. Magnesioriebeckite, pegmatite, Sheep Creek, Montana (Ernst, 1963). Anal. E. Szentvari; J. H. Scoon.

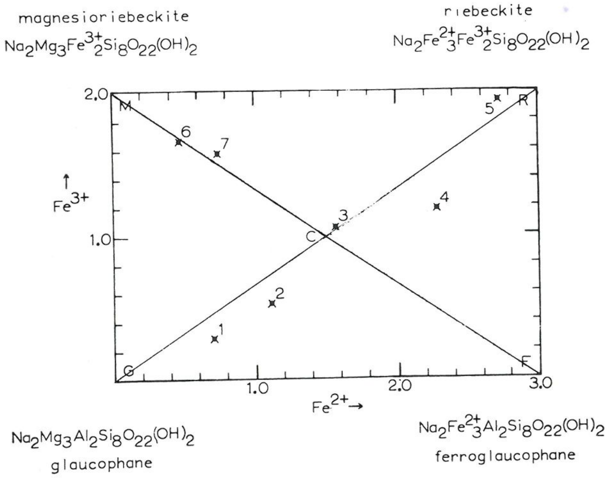

FIG. 1. Composition diagram of the alkali amphiboles series. The numbers refer to the specimen numbers in table 1. G, F, M and R represent end-member compositions of glaucophane, ferroglaucophane, magnesioriebeckite and riebeckite, respectively; C represents the composition of crossite.

The spectra were fitted by computer to Lorentzian line shapes using a program described by Stone (1967) and methods described in the earlier paper (Bancroft, Burns and Stone, 1968). All spectra were fitted initially to three doublets. With specimen 7, however, it was possible to fit four doublets, and the fitting procedure is described in the appendix. Either the half-widths (for slightly orientated samples) or the intensities (for random samples) of the component peaks of the doublets were constrained to be equal. Although the intensity constraint has been found to be satisfactory previously for random absorbers, it is no longer justified for orientated absorbers. The half-width constraints is justified by the fact that with very few exceptions, the component peaks of a doublet in the Mössbauer spectra of silicates have the same half-width (Bancroft, Burns and Maddock, 1967b; Bancroft, Burns and Stone, 1968).

THE ALKALI AMPHIBOLE CRYSTAL STRUCTURE

The amphibole structure illustrated in Figure 2 consists of bands of cations cross-linked by double chains of linked SiO_4 tetrahedra running parallel to the *c* axis. There are three distinct positions of six-fold coordination, designated $M(1)$, $M(2)$ and $M(3)$, and one of six to eight coordination which is designated $M(4)$. Cations in the two $M(1)$ and one $M(3)$ positions per half unit cell are each coordinated to four oxygen and two hydroxyl ions, and six oxygen ions surround the cations in each of the two $M(2)$ positions. Cations in the two $M(4)$ positions are surrounded by four oxygen ions each linked to one silicon atom, and two to four oxygen atoms which are each shared by two silicon atoms.

In the crystal structures of crocidolite (Whittaker, 1949) and glaucophane (Papike and Clark, 1968), Na^+ ions occupy the $M(4)$ positions and Mg^{2+}, Fe^{2+}, Fe^{3+} and Al^{3+} ions are distributed over the $M(1)$, $M(2)$ and $M(3)$ positions. The coordination polyhedra about the $M(1)$ and $M(3)$ positions approximate octahedral symmetry, and the metal-oxygen distances in the two sites are approximately 2.09 Å. The $M(2)$ coordination site is distorted from octahedral symmetry and metal-oxygen distances in glaucophane are 1.85 Å (2), 1.94 Å (2) and 2.04 Å (2). The average metal-oxygen distance of the $M(2)$ site increases from 1.94 Å in glaucophane to 2.07 Å in crocidolite,

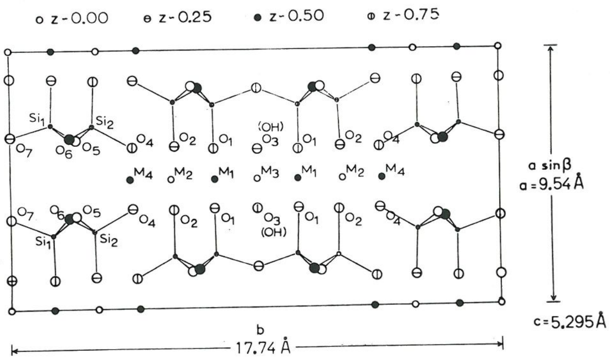

FIG. 2. The amphibole crystal structure. Cell parameters for glaucophane from Papike and Clark (1968). Atomic coordinates not to scale.

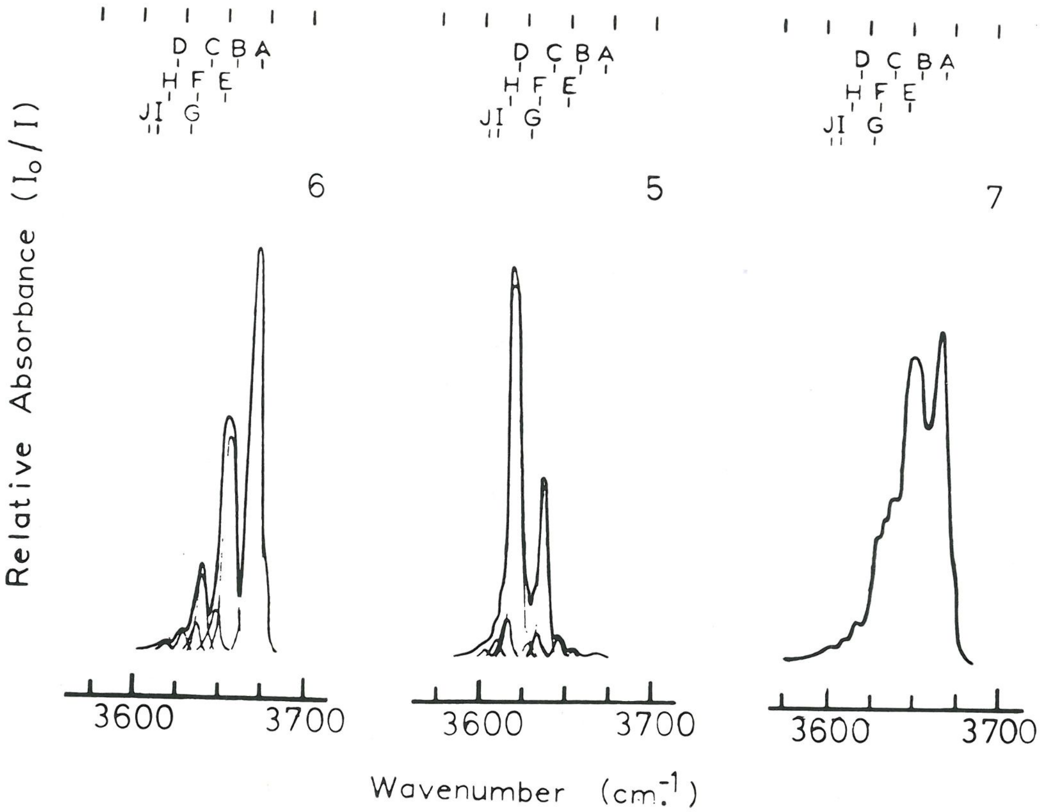

FIG. 3. Infrared spectra of Mg-Fe^{2+}-Fe^{3+} alkali amphiboles in the region of the hydroxyl stretching frequency: magnesian crocidolite (specimen 6), ferrous crocidolite (specimen 5), magnesioriebeckite (specimen 7).

whereas the mean distances in the *M*(1) and *M*(3) sites remain approximately the same between the two structures. Whittaker (1949) suggested from charge balance criteria that trivalent Fe^{3+} ions occupy *M*(2) positions when the *M*(4) positions are occupied by Na^+ ions, and that Mg^{2+} and Fe^{2+} ions are randomly distributed over the *M*(1) and *M*(3) positions. Infrared spectroscopy (Burns and Prentice, 1968) has largely confirmed these assignments. However, some Fe^{3+} ions occur in *M*(1) and *M*(3) positions, and Fe^{2+} ions show relative enrichment in *M*(1) positions. In the refinement of the glaucophane structure (Papike and Clark, 1968), Al was assigned to the *M*(2) position on the basis of the shorter metal-oxygen distances in the *M*(2) site, and Mg was distributed among the *M*(1) and *M*(3) positions. A site occupancy program was used to obtain Fe-Mg distributions in the *M*(1) and *M*(3) positions, which indicated a relative enrichment of Fe in the *M*(3) position.

RESULTS: INFRARED SPECTROSCOPY

The infrared spectra of the crocidolites and magnesioriebeckites are shown in Figure 3. Over the Mg^{2+}-Fe^{2+} range measured, four prominent major peaks A, B, C and D occur in the crocidolite spectra at 3669, 3655, 3639 and 3619 cm^{-1}, together with several inflections which lead to broadening of some of the major peaks. In the earlier study (Burns and Prentice, 1968) it was possible to resolve these inflections into an additional six peaks E, F, G, H, I and J, from measurements on oxidized samples and synthetic specimens and from peak periodicities (Prentice, 1967). The ten peaks, A . . . J, represent all possible distributions of the Mg^{2+}, Fe^{2+} and Fe^{3+} ions in the two *M*(1) and one *M*(3) positions of the amphibole structure. The peak assignments are listed in Table 2. Note that peaks attributed to Fe^{3+} ions lie on the low wavenumber sides of the major peaks due to Mg^{2+} and Fe^{2+} ions only. From the normalized intensities (peak heights) it is possible to estimate the distributions of cations in the *M*(1) *M*(3) *M*(1) positions. There are two approaches for obtaining these estimated site populations. First, approximate amounts of Mg^{2+} and Fe^{2+} ions only in the *M*(1) *M*(3) *M*(1) positions may be estimated from peaks A, B, C and D only. The values obtained by this method (for example, Strens, 1966 and personal communication) usually exceed the amounts of Mg^{2+} or Fe^{2+} ions present in the mineral according to the chemical analysis, indicating that some Fe^{3+} ions are also present in the *M*(1) *M*(3) *M*(1) positions. Second, the inflections on the major Mg^{2+} -Fe^{2+} peaks may be resolved into a series of overlapping minor peaks due to Fe^{3+} ions, leading to an estimate of the amounts of Mg^{2+},

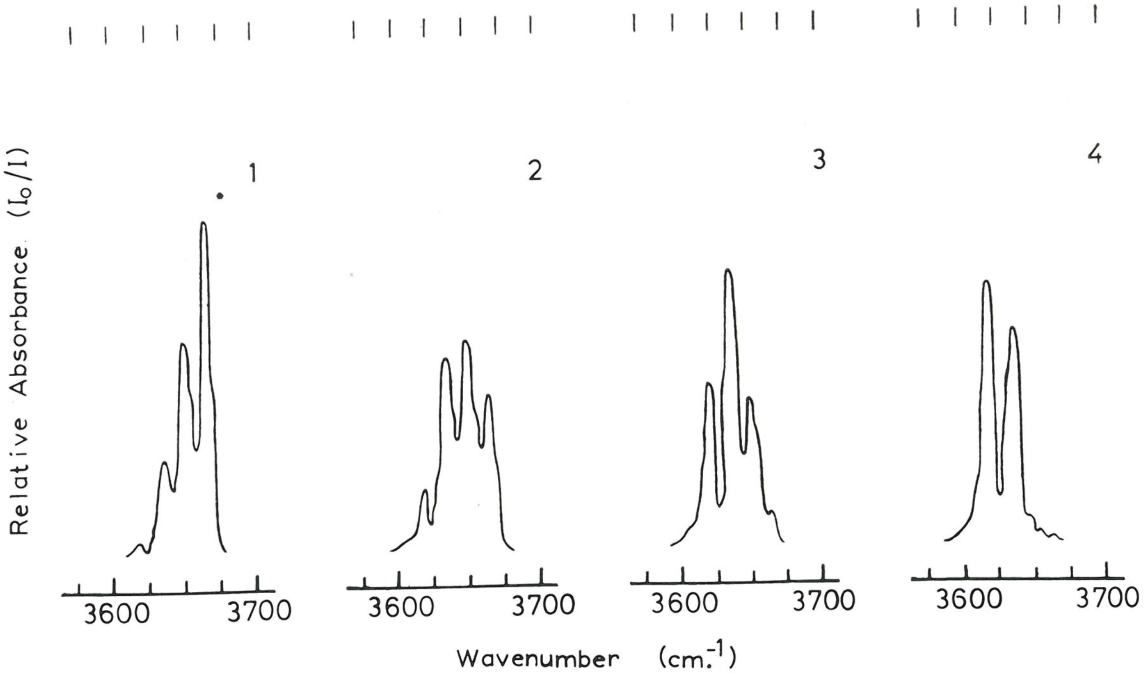

FIG. 4. Infrared spectra of Mg-Al-Fe^{2+}-Fe^{3+} alkali amphiboles in the region of the hydroxyl stretching frequency: glaucophane (specimen 1), glaucophane (specimen 2), crossite (specimen 3), crossite (specimen 4).

Fe^{2+} and Fe^{3+} ions in the $M(1)$ $M(3)$ $M(1)$ positions. Site populations for the $M(2)$ positions may then be obtained by difference from the chemical formula. Further details of the crocidolite spectra are given in the earlier paper (Burns and Prentice, 1968).

The infrared spectrum of the pegmatitic magnesioriebeckite (specimen 7) proved to be too complex for accurate resolution into component peaks. Furthermore, the spectrum showed evidence of oxidation of the sample during KBr disc preparation. Nevertheless, the spectrum indicates that there is a substantial amount of Fe^{3+} ions in the $M(1)$ $M(3)$ $M(1)$ positions of this specimen from pegmatite.

The infrared spectra of the aluminous alkali amphiboles are shown in Figure 4. Again, there is evidence of broadening and inflections on both the high and low wavenumber sides of the major peaks. In addition to the ten possible distributions of Mg^{2+}, Fe^{2+} and Fe^{3+} ions in the $M(1)$ $M(3)$ $M(1)$ positions, there are ten others involving the Al^{3+} ion. These are included in table 2. It has not been possible to resolve the infrared spectra into components of the twenty overlapping peaks. However, the additional inflections indicate that a small proportion of Al^{3+} ions, together with some Fe^{3+} ions, occur in the $M(1)$ $M(3)$ $M(1)$ positions of the glaucophane structure. It should be noted that site population estimates based only on the normalized intensities of the major peaks lead to Mg^{2+} or Fe^{2+} ion contents in excess of the amounts expressed by the chemical formulae. This further supports the belief that small amounts of trivalent ions occupy the $M(1)$ $M(3)$ $M(1)$ positions and contribute to absorption in the infrared spectra of aluminous alkali amphiboles.

RESULTS: MÖSSBAUER SPECTROSCOPY

Spectra. The computer-plotted spectra of the crocidolites and magnesioriebeckite are illustrated in Figure 5. Figure 6 shows the spectra of the aluminous alkali amphiboles. Table 3 summarizes the average values of the chemical shift (C.S.), quadrupole splitting (Q.S.), half-width (H.W.) and percent of the total area for each doublet in the spectrum of each mineral, together with representative χ^2 values. The parameters in all spectra, except specimen 6, are reproducible to within ± 0.02 mm/sec.

Each spectrum (except Fig. 5d.) consists of three doublets, two of which arise from absorption by Fe^{2+} ions (peaks A and A′, and peaks C and C′) and one from Fe^{3+} ions (peaks B and B′). As in the previous study (Bancroft, Burns and Maddock, 1968), the peaks may be assigned as follows:

outer peaks A and A′, to Fe^{2+} in $M(1)$ positions
inner peaks C and C′, to Fe^{2+} in the $M(3)$ and $M(2)$ positions
peaks B and B′, to Fe^{3+} in the $M(1)$, $M(2)$ and $M(3)$ positions.

Apart from specimen 7, the C.S. and Q.S. parameters for the three quadrupole doublets are remarkably uniform with changes in Mg^{2+}-Fe^{2+} composition, in contrast to the Mössbauer spectra of other ferromagnesian silicates which generally show a decrease of Q.S. with rising Fe^{2+} ion content (Bancroft, Burns and Maddock, 1967b). However, with specimen 7 it was possible to resolve a third doublet due to Fe^{2+} ions by using only half-width constraints and the χ^2 value decreased from 445 for the six-peak spectrum to 400 for the eight-peak spectrum (Appendix 1). This spectrum is illustrated in Figure 5d. The three doublets have quadrupole splittings of 2.79 2.40 and 2.00 mm/sec, and these may be assigned to Fe^{2+} ions in the $M(1)$, $M(3)$ and $M(2)$ positions, respectively. The parameters for the $M(1)$ and $M(3)$ positions are now in good agreement with those for the other spectra. In the eight-peak spectrum (Fig. 5d) the peak area due to Fe^{2+} ions in the $M(1)$ positions is almost identical to that in the spectrum fitted to six peaks (Fig. 5c).

The data in Table 3 show that the widths of the inner peaks C and C′ are usually larger than those of the outer peaks A and A′. This broadening arises from Fe^{2+} ions in $M(2)$ positions, which do not give parameters identical to Fe^{2+} ions in $M(3)$ positions. In specimen 7 there is enough Fe^{2+} in $M(2)$ positions and the parameters are appreciably different from Fe^{2+} in $M(1)$ and $M(3)$ positions, so that resolution into three component doublets is possible and reproducible results can be obtained. For the other specimens it was not possible to resolve peaks due to Fe^{2+} ions in $M(2)$ positions without constraints such as peak position, which we believe to be unjustifiable. This lack of resolution indicates that either there is little Fe^{2+} present in $M(2)$ positions (less than 10% of the total iron) and/or the parameters for the $M(2)$ positions are only slightly different from those of the $M(3)$ positions in the glaucophane-riebeckite series. The latter possibility applies to specimen 5, for example, for which the half-widths of the peaks C and C′ are small (Table 3) and an appreciable amount of Fe^{2+} ions occur in $M(2)$ positions (Table 4). It must be emphasized that if appreciable amounts of Fe^{2+} ions were present in $M(2)$ positions of aluminous alkali amphiboles and the doublet from Fe^{2+} ions in this position lay somewhere between peaks A and A′ and peaks C and C′, then accurate areas could not be determined.

TABLE 2. PEAK ASSIGNMENTS IN THE INFRARED SPECTRA OF ALKALI AMPHIBOLES

Peak	Coordinating Group to OH in the $M(1)$ $M(3)$ $M(1)$ positions	Approximate Position (cm.$^{-1}$)	
		magnesioriebeckite -riebeckite	glaucophane -crossite
A	MgMgMg	3669	3665–68
B	MgMgFe^{2+}, MgFe^{2+}Mg, Fe^{2+}MgMg	3655	3648–51
C	MgFe^{2+}Fe^{2+}, Fe^{2+}MgFe^{2+}, Fe^{2+}Fe^{2+}Mg	3639	3635–38
D	Fe^{2+}Fe^{2+}Fe^{2+}	3619	3616–18
E	MgMgFe^{3+}, MgFe^{3+}Mg, Fe^{3+}MgMg	3648	a
F	MgFe^{2+}Fe^{3+}, MgFe^{3+}Fe^{2+}, Fe^{2+}MgFe^{3+}, Fe^{2+}Fe^{3+}Mg, Fe^{3+}MgFe^{2+}, Fe^{3+}Fe^{2+}Mg	3632	3632^{b}
G	MgFe^{3+}Fe^{3+}, Fe^{3+}MgFe^{3+}, Fe^{3+}Fe^{3+}Mg	3628	a
H	Fe^{2+}Fe^{2+}Fe^{3+}, Fe^{2+}Fe^{3+}Fe^{2+}, Fe^{3+}Fe^{2+}Fe^{2+}	3614	3614
I	Fe^{2+}Fe^{3+}Fe^{3+}, Fe^{3+}Fe^{2+}Fe^{3+}, Fe^{3+}Fe^{3+}Fe^{2+}	3609	a
J	Fe^{3+}Fe^{3+}Fe^{3+}	3604	a
K	MgMgAl, MgAlMg, AlMgMg		3654
L	MgFe^{2+}Al, MgAlFe^{2+}, AlMgFe^{2+}, AlFe^{2+}Mg, Fe^{2+}MgAl, Fe^{2+}AlMg		3641
M	Fe^{2+}Fe^{2+}Al, Fe^{2+}AlFe^{2+}, AlFe^{2+}Fe^{2+}		3625
N	MgAlAl, AlMgAl, AlAlMg		a
O	Fe^{2+}AlAl, AlFe^{2+}Al, AlAlFe^{2+}		a
P	MgFe^{3+}Al, MgAlFe^{3+}, AlMgFe^{3+}, AlFe^{3+}Mg, Fe^{3+}MgAl, Fe^{3+}AlMg		a
Q	Fe^{2+}Fe^{3+}Al, Fe^{2+}AlFe^{3+}, Fe^{3+}Fe^{2+}Al, Fe^{3+}AlFe^{2+}, AlFe^{2+}Fe^{3+}, AlFe^{3+}Fe^{2+}		a
R	Fe^{3+}Fe^{3+}Al, Fe^{3+}AlFe^{3+}, AlFe^{3+}Fe^{3+}		a
S	Fe^{3+}AlAl, AlFe^{3+}Al, AlAlFe^{3+}		a
T	AlAlAl		a

^{a} position of peak unknown.
^{b} position of peak assumed.

The spectra of specimens 1 and 7 taken at liquid nitrogen temperature indicated that the separation between peaks A and A′ and peaks C and C′ decreased slightly compared to the room-temperature spectra, which is in contrast to the increased peak separation observed in the Mössbauer spectra of orthopyroxenes between room temperature and 80°K. However, in specimen 7 the resolution between the third Fe^{2+} doublet (peaks D and D′) and the other two doublets (peaks A and A′ and peaks C and C′) increased in the spectra obtained at 80°K. The area ratios in the room temperature and liquid nitrogen temperature spectra, however, are in good agreement.

Most of the χ^2 values quoted in Table 3 are slightly above the statistically acceptable limit of 430. Causes of poor χ^2 values were discussed in a previous paper (Bancroft, Burns and Stone, 1968). In the present study the most important cause of poor χ^2 is the unresolved overlap of peaks from Fe^{2+} ions in $M(3)$ and $M(2)$ positions. The results for specimen 7 show that the χ^2 values decrease appreciably when the spectra are fitted to eight peaks instead of six (Appendix 1.).

The spectrum of specimen 1 presented a special computing problem. Peak B′ is much more intense than it should be. Although random samples were run and the peak area of A equals A′ and area C equals C′ as expected, the area of peak B′ was still almost twice that of peak B. The cause of this anomaly is not known, but one possible explanation is the presence of low-spin iron which normally gives rise to peaks in this region.

Area data. The proportion of each iron species giving rise to absorption may be estimated directly from the ratios of the computer-calculated areas in the Mössbauer spectra, using the relationship

$$A_2/A_1 = C \cdot n_2/n_1$$

and assuming that $C = 1$. (Bancroft, Burns and Stone, 1968; Bancroft, 1967). In Table 4 the amounts of Fe^{2+} ions in the $M(1)$ and $M(3)$ ($+$ $M(2)$) positions are summarized, together with the percentages of Fe^{3+} ions to total iron obtained from the Mössbauer spectra. Agreement with available X-ray site population and chemical analytical data is reasonably good.

For example, in glaucophane (specimen 1) Papike and

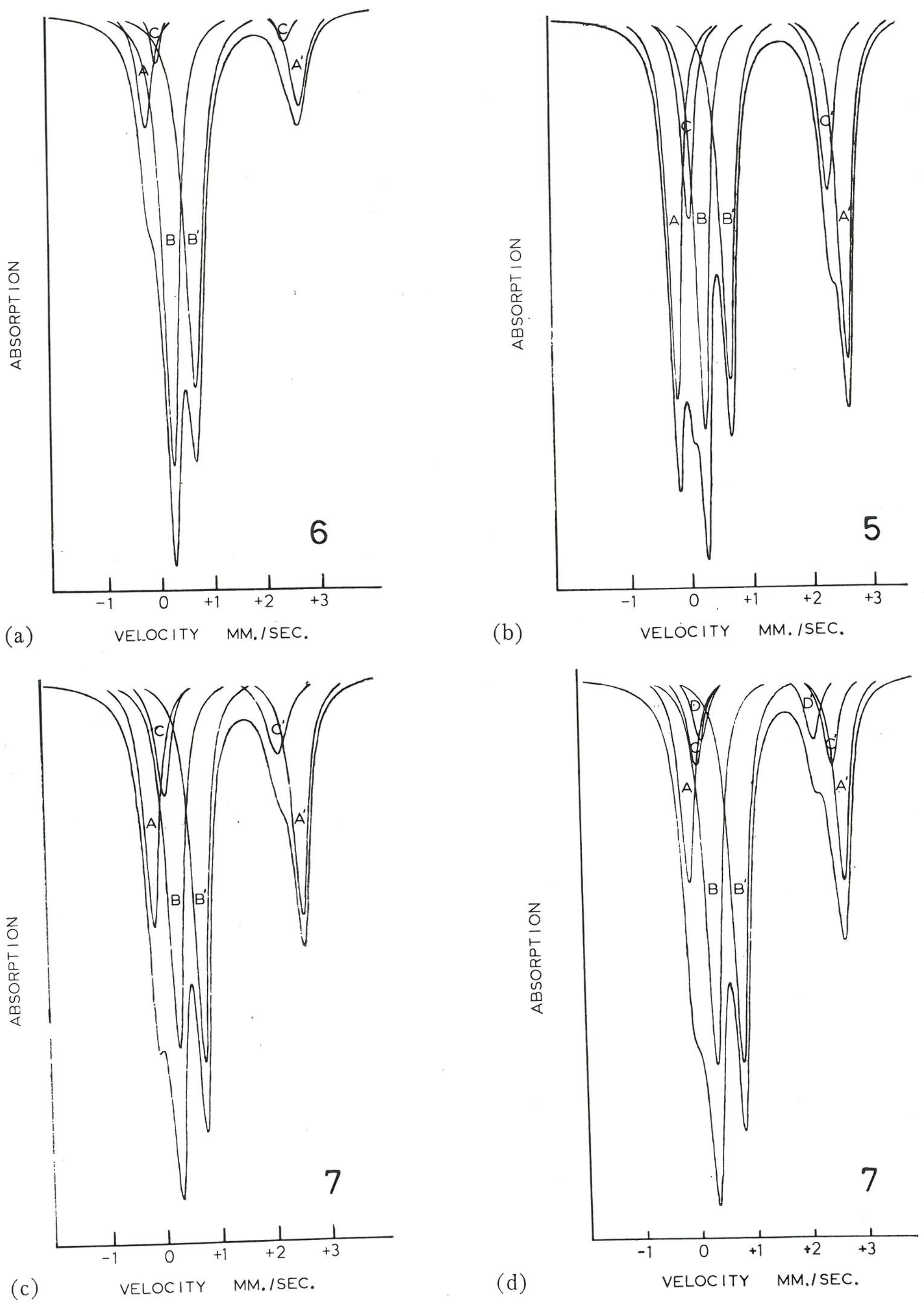

FIG. 5. Computer plots of the Mössbauer spectra of crocidolites and magnesioriebeckite. (a) magnesian crocidolite (specimen 6). (b) ferrous crocidolite (specimen 5). (c) magnesioriebeckite, six-peak spectrum (specimen 7). (d) magnesioriebeckite, eight-peak spectrum (specimen 7).

Clark (1968) estimated that 0.16 Fe^{2+} ions per formula unit occupy each $M(1)$ position, whereas each $M(3)$ position contains 0.29 Fe^{2+}. The Mössbauer data (Table 4) give: $M(1)$ position, 0.19 Fe^{2+}; $M(3)$ position, 0.32 Fe^{2+}. Although there are differences in absolute amounts between the estimates of the two methods arising from the choice of total ferrous iron concentration in the mineral, there is excellent agreement between the *proportions* of Fe^{2+} ions distributed over the two sites. Apart from specimens 1 and 7 the estimates of Fe^{3+} ion percentages in the total iron obtained from the peak areas in the Mössbauer spectra are in reasonable agreement with the chemically determined

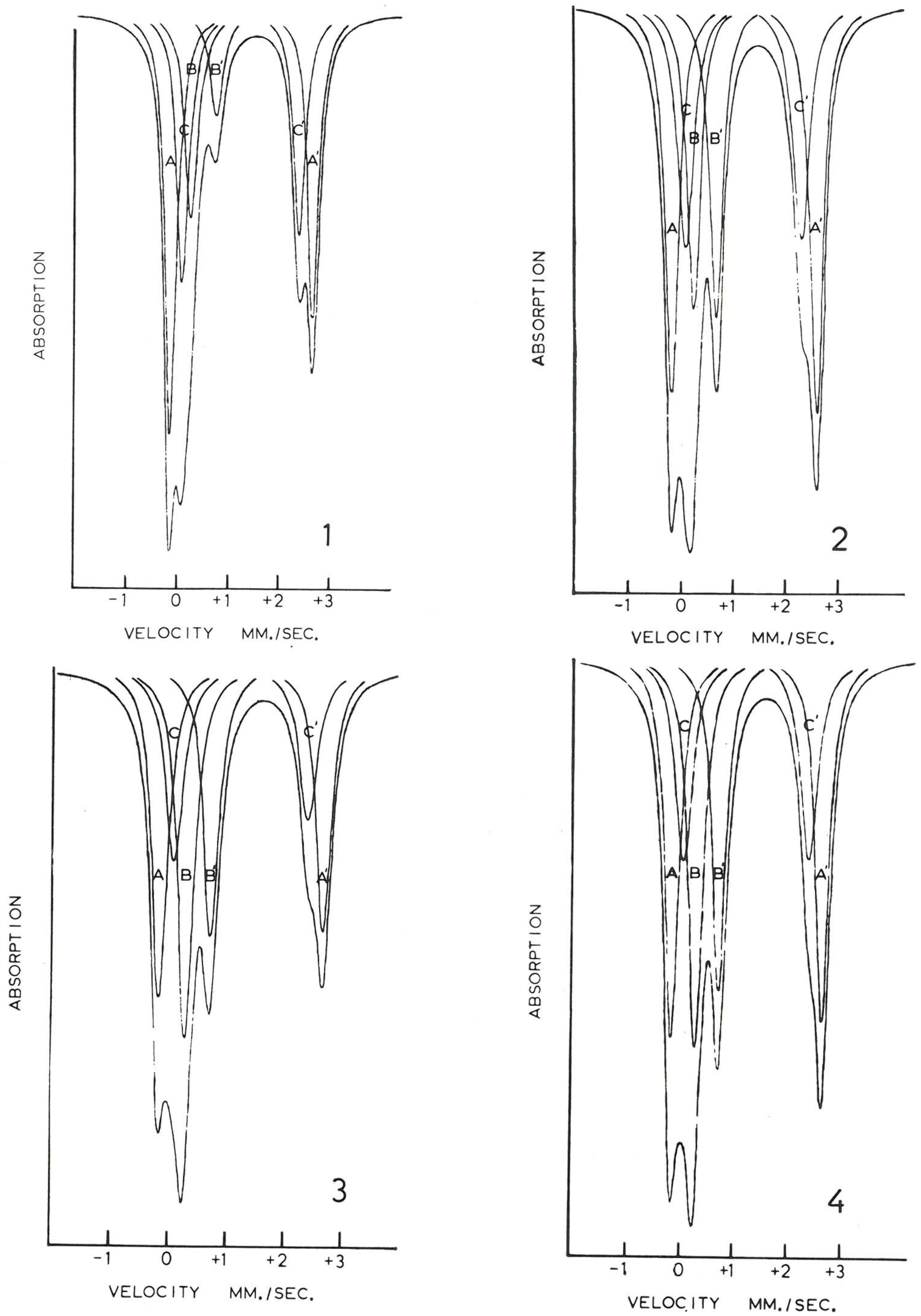

FIG. 6. Computer plots of the Mössbauer spectra of glaucophanes and crossites; glaucophane (specimen 1), glaucophane (specimen 2), crossite (specimen 3), crossite (specimen 4).

proportions of Fe^{3+} and Fe^{2+} ions. The large discrepancy for specimen 7 between the chemical analysis (65.1% Fe^{3+}) and Mössbauer (52.6% Fe^{3+}) results led to a redetermination of the FeO and Fe_2O_3 contents of this amphibole by Mr. J. H. Scoon at Cambridge. The new partial analysis for specimen 7 (see footnote, Table 1) shows that the new chemically determined Fe^{3+} ion percentage (55.8% Fe^{3+}) is now in good agreement with the Mössbauer result (52.6% Fe^{3+}). The Mössbauer data for specimen 1, together with the Fe^{3+} ion content calculated from the quali-

TABLE 3. MÖSSBAUER PARAMETERS FOR THE ALKALI AMPHIBOLES

Speci-men	Absorption by Fe^{2+} Ions								Absorption by Fe^{3+} Ions				χ^2
	Peaks A and A′				Peaks C and C′				Peaks B and B′				
	C.S. mm/sec	Q.S. mm/sec	H.W. mm/sec	Area (%)	C.S. mm/sec	Q.S. mm/sec	H.W. mm/sec	Area (%)	C.S. mm/sec	Q.S. mm/sec	H.W. mm/sec	Area (%)	
1	1.22	2.82	0.30	43.2	1.20	2.33	0.33	35.1	0.45	0.48	0.33	21.7	430
2	1.23	2.82	.36	39.4	1.22	2.27	.40	32.6	.47	.42	.35	28.4	487
3	1.23	2.82	.31	38.7	1.23	2.32	.38	24.1	.47	.42	.30	37.2	436
4	1.23	2.85	.31	38.1	1.21	2.36	.41	25.1	.48	.47	.34	36.8	530
5	1.23	2.83	.29	38.2	1.20	2.32	.29	21.2	.47	.43	.29	40.6	462
6	1.25	2.82	.38	16.6	1.25	2.39	.31	7.2	.46	.41	.44	76.2	530
7a	1.22	2.75	.32	31.8	1.14	2.15	.42	15.6	.49	.49	.34	52.5	445
7b	1.23	2.79	.31	28.9	1.20	2.41	.34	10.5	.49	.48	.34	52.5	400

Note: spectrum for specimen 7 b was fitted to four quadrupole doublets. A third doublet, peak D and D′ (Fig. 5d.), arising from absorption by Fe^{2+} ions has parameters: C.S., 1.12 mm/sec; Q.S., 2.00 mm/sec; H.W., 0.34 mm/sec; % area, 8.2; and χ^2, 400. The errors in the C.S., Q.S. and H.W. are 0.02 mm/sec, except for specimens 6 and 7 b where the errors for peaks A and A′ and peaks C and C′ are ±0.05 mm/sec. All centre shifts are quoted relative to the value zero for stainless steel; add 0.16 mm/sec to convert the values relative to sodium nitroprusside.

tative site population estimate by Papike and Clark (1968) suggest that the chemical analysis of this glaucophane may also be in error.

It should be noted that the Mössbauer data have not been corrected for saturation effects which may be significant but will be small for thin absorbers (Bancroft, 1968). If, as in specimen 1 (Fig. 6 a), the peak heights and widths are similar, such corrections may be small or non-existent. In other specimens, however, such as specimen 6 (Fig. 5 a), areas under the more intense peaks (B and B′) might be larger by four or five percent relative to those under the smaller peaks A and A′ and C and C′. Further work on saturation corrections is now in progress.

On the basis of the reproducibility of the results and the good agreement with independent measurements by X-ray diffraction and chemical analytical methods, we believe that the Mössbauer data in Table 4 are accurate to within ± 10 percent of the amounts stated for the Fe^{2+} ion site population estimates and somewhat better than this for the Fe^{3+} ion percentages.

DISCUSSION

Cation distributions in the alkali amphibole structure. The results of this and earlier studies (Burns and Prentice, 1968; Bancroft, Burns and Stone, 1968) prove that in crocidolites of the magnesioriebeckite-riebeckite series, it is the Fe^{3+} ions which predominate in the $M(2)$ positions and Fe^{2+} ions that are concentrated in the $M(1)$ and $M(3)$ positions, with relative enrichment in $M(1)$ positions. These results conform with Whittaker's (1949) deductions from charge balance criteria. However, Whittaker (1949) and Ghose (1965) also suggested that Fe^{2+} ions are randomly

TABLE 4. SITE POPULATIONS IN ALKALI AMPHIBOLES FROM MÖSSBAUER AND INFRARED SPECTROSCOPY

Speci-men	Composition		Fe^{2+} in $M(3)+M(2)$ (Möss.)	Fe^{2+} in $M(2)$ (*ir* or Möss.)	Fe^{2+} in $M(3)$ (Möss. and *ir*)	Fe^{2+} in $M(1)$ total (Möss.)	Fe^{2+} in $M(1)$ per site (Möss.)	Relative Enrichment Fe^{2+} in $M(1)$ & $M(3)$	Percentage Fe^{3+}/total iron	
	Fe^{2+}	Fe^{3+}							Möss.	Anal.
1	0.70	0.30	0.32	n.d.	0.32	0.38	0.19	M(3)>M(1)	21.7	30.0
2	1.11	0.53	.50	n.d.	.50	0.61	.31	M(3)>M(1)	28.4	32.3
3	1.57	1.05	.62	n.d.	.57	0.95	.48	M(3)>M(1)	37.2	40.0
4	2.29	1.19	.96	0.15[a]	.81	1.33	.67	M(3)≥M(1)	36.8	34.2
5	2.76	1.93	.98	0.23[a]	.75	1.78	.89	M(3)<M(1)	40.6	41.2
6	0.48	1.66	.14	0.05[a]	.09	0.34	.17	M(3)<M(1)	76.2	77.6
7a	0.84	1.57	.28	n.d.	.28	0.56	.28	M(3)<M(1)	52.6	65.1[b]
7b	0.84	1.57	.33	0.15	.18	0.51	.26	M(3)<M(1)	52.6	65.1[b]

[a] Data from Prentice (1967) and Burns and Prentice (1968), in which error estimates are also given.

[b] The new partial chemical analysis (table 1) gives: Fe^{3+}/total iron = 55.8%.

Note: for specimen 7, a refers to the spectrum fitted to six peaks (figure 5c), and b refers to the spectrum fitted to eight peaks (figure 5d).

distributed over the $M(1)$ and $M(3)$ positions of crocidolites, and this is not substantiated by the infrared or Mössbauer measurements. The Mössbauer spectra of glaucophanes show that Fe^{2+} ions are again concentrated in the $M(1)$ and $M(3)$ positions with relative enrichment in the $M(3)$ positions, which is in accord with results from the structure refinement (Papike and Clark, 1968). Thus, in the glaucophane-crossite-riebeckite series there is a change of relative enrichment of the Fe^{2+} ion from $M(3)$ position to $M(1)$ position with increasing Fe^{3+} ion content of the alkali amphibole.

The infrared spectra indicate that the majority of the Al^{3+} and Fe^{3+} ions occupy $M(2)$ positions in glaucophanes and crossites, although the additional inflections in the spectra suggest that small amounts of these trivalent ions are also present in the $M(1)$ and $M(3)$ positions. The vacancies in the $M(2)$ positions caused by small amounts of Al^{3+} and Fe^{3+} ions entering $M(1)$ and $M(3)$ positions are probably filled mainly by Mg^{2+} ions (0.65 Å) in glaucophane and Fe^{2+} ions (0.76 Å) in riebeckites. Indeed, broadening of the inner Fe^{2+} doublet (peaks C and C′) in the Mössbauer spectra of glaucophanes and crossites suggest that small amounts of Fe^{2+} ions are present in $M(2)$ positions. The increased site occupancy of $M(2)$ positions by Fe^{2+} ions along the glaucophane-riebeckite series may be correlated with the increased metal-oxygen distances in the $M(2)$ site between glaucophane (Papike and Clark, 1968) and crocidolite (Whittaker, 1949) resulting from the replacement of Al^{3+} ions by larger Fe^{3+} ions. It may be noted thaat similar enrichments of Mg^{2+} ions over Fe^{2+} ions in $M(2)$ positions are found in most magnesian amphiboles of the anthophyllite (Bancroft, Burns, Maddock and Strens, 1966), cummingtonite (Ghose, 1961; Bancroft, Burns and Maddock, 1967a) and actinolite (Bancroft and Burns, unpublished work) series, which may be correlated with the slightly smaller average dimensions of this site in each structure.

Therefore, Mössbauer spectroscopy, together with inferences from the infrared spectra, enables the compositional variations of site populations in the alkali amphibole structure to be delineated rapidly and accurately on a suite of specimens.

Influence of pressures and temperatures of mineral formation on site populations. The Mössbauer spectrum of magnesioriebeckite (Fig. 5d)., together with the infrared spectrum of this (Fig. 3c) and other riebeckites from pegmatites (Prentice, 1967), indicate that cations are more randomly distributed in the structures of these phases than in crocidolites and glaucophanes. Crocidolites form at low temperatures (150–200°C; Trendall, personal communication), and glaucophanes from the Californian Franciscan formation crystallized under conditions of relatively low temperatures and high pressures (150–300°C and 5–10 kbars respectively; Essene, Fyfe and Turner, 1965). Pegmatitic riebeckites, however, crystallized from magma at much higher temperatures (600–800°C; Turner and Verhoogen, 1960, p. 428). Thus, site populations in alkali amphibole structures appear to be influenced by temperatures and, perhaps, pressures of mineral formation.

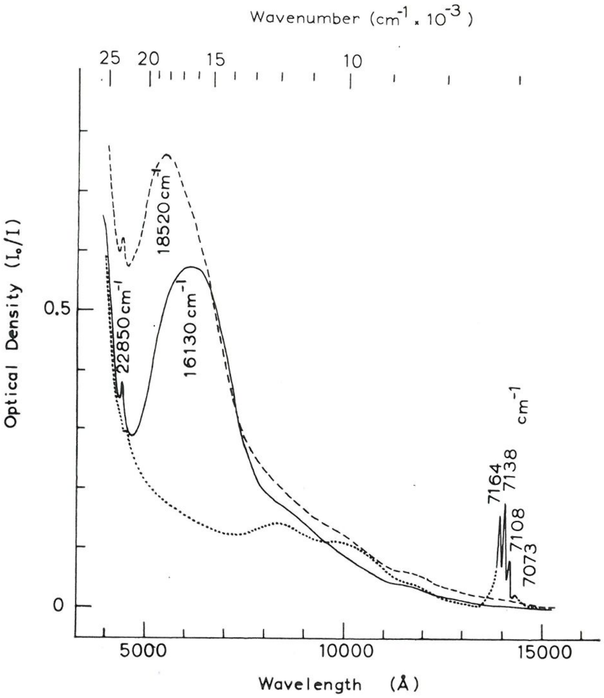

FIG. 7. Polarized absorption spectra of glaucophane (specimen 2). · · · α spectrum; – – – β spectrum; —— γ spectrum. (optic orientation: α:a = 10°; β =b; γ:c = 4°).

Color and pleochroism of alkali amphiboles. Alkali amphiboles of the glaucophane-crossite-riebeckite series are characterized by their distinctive colorless-violet-blue pleochroism in transmitted polarized light. In general, the intensities of the colors increase with increasing Fe^{2+} and Fe^{3+} ion contents of the alkali amphibole, and pegmatitic varieties are more intensely colored than crocidolites and glaucophanes derived from schist and metamorphosed iron formations.

The colors originate from absorption of light in the visible region of the electromagnetic spectrum (4000 Å to 7000 Å). The different positions and intensities of absorption determine the nature of the color in polarized light. For example, the polarized absorption spectra of a glaucophane (specimen 2) having the pleochroic scheme: α colorless, β light violet, γ light blue[1] are illustrated in Figure 7. Light polarized along the α indicatrix axis (α:a=10°) shows little differential absorption in the visible region,

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[1] Note that the optic orientation, and hence pleochroic scheme, depends on the composition and paragenesis of alkali amphiboles (Borg, 1967).

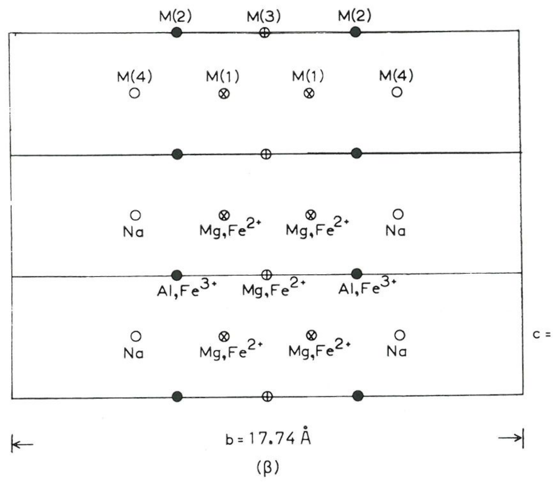

FIG. 8. Portion of the glaucophane structure projected onto (100). The cation positions are indicated in the top unit cell. The middle unit cell shows the cation distribution in the glaucophane structure.

and the sharp peaks in the short-wave infrared at about 1400 Å represent the first overtone of the O-H stretching frequency of the OH group in the amphibole structure (Burns and Strens, 1966). However, light polarized parallel to *b* (*β* spectrum) shows an intense absorption band at 5400 Å and a region of minimum absorption around 4500 Å, which produce violet transmitted light. When light is polarized along the *c* axis (*γ* spectrum), a slightly less intense absorption band occurs at 6200 Å with minimum absorption at 4650 Å, giving rise to blue polarized light. Absorption spectra of other alkali amphiboles (Chesnokov, 1961; Littler and Williams, 1965; Manning and Nickel. 1969; Burns, unpublished work) show that intensities of absorption bands increase with rising Fe^{2+} and Fe^{3+} ion contents, and intensities are higher for riebeckites from pegmatites.

The absorption maxima in the region 5400–6200 Å are charge transfer bands arising from electron transfer between neighboring Fe^{2+} and Fe^{3+} ions in the crystal structure (Littler and Williams, 1965; Faye, Manning and Nickel, 1968; Burns, 1969). The cation distribution in glaucophane is summarized in Figure 8. This (100) projection of the structure shows an infinite band of cations extending along the *c* axis. Sodium ions fill *M*(4) positions, Fe^{2+} and Mg^{2+} ions are concentrated in *M*(1) and *M*(3) positions, and Fe^{3+} and Al^{3+} ions predominate in the *M*(2) positions. Electron transfer between adjacent Fe^{2+} and Fe^{3+} ions takes place across favorably oriented overlapping 3*d* orbitals of the iron cations lying in the (100) plane. This occurs when light is polarized across (parallel to *b*) and along (parallel to *c*) the band of cations. Since adjacent Fe^{3+}-Fe^{2+} cation pairs in *M*(2) and *M*(3) positions, respectively, lie along the *b* axis, whereas Fe^{3+}-Fe^{2+} pairs in *M*(2) and *M*(1) positions, respectively, are inclined to the *c* axis, interaction is greater with light polarized along the *b* axis relative to the *c* axis. Thus, the intensity of absorption is higher in the *β* spectrum than the *γ* spectrum.

A higher flux of adjacent Fe^{3+}-Fe^{2+} cation pairs leads to increased probability of charge transfer between neighboring iron cations, and hence greater absorption of light or intensity of color. This accounts for the increased color intensity generally observed in the glaucophane-crossite-riebeckite series and magnesioriebeckite-riebeckite series. Furthermore, there is a statistical increase of adjacent Fe^{3+}-Fe^{2+} pairs when cations are randomly distributed in the crystal structure, which may be induced by high temperatures of crystallization. The high absorption of light and intensity of color or opacity shown by most pegmatitic riebeckites is due to electron transfer between the large number of adjacent Fe^{3+} and Fe^{2+} ions in the crystal structures.

Ferrous-to-ferric ratios from Mössbauer spectroscopy. The percentages of the peak areas assigned to absorption by Fe^{3+} ions in the Mössbauer spectra are generally in good agreement with the proportions of ferric iron obtained from chemical analyses of the alkali amphiboles. In cases where there was poor agreement between the two methods, such as the magnesioriebeckite (specimen 7), it was the chemical analysis that was found to be in error. These results conform with findings in the earlier study of complex iron silicates (Bancroft, Burns and Stone, 1968). In wet chemical analysis of silicates, particularly those resistant to chemical decomposition such as staurolite, sapphirine and tourmaline, there is an element of uncertainty regarding the changes of oxidation state of iron during dissolution, particularly when other transition metals such as titanium and manganese are present. However, Mössbauer spectroscopy can provide an accurate, unambiguous and nondestructive method for obtaining ferrous-to-ferric iron ratios in silicate minerals.

CONCLUSIONS

This paper describes the Mössbauer and infrared absorption spectra of several alkali amphiboles of the glaucophane-crossite-riebeckite and magnesioriebeckite-riebeckite series. It illustrates the way that these spectroscopic techniques may be used to elucidate the crystal chemistry and optical properties of complex Fe^{2+}-Fe^{3+} silicates. The spectral data in each Mössbauer spectrum have been resolved by computer analysis into three or four component quadrupole doublets representing absorption by the Fe^{3+} ions and by Fe^{2+} ions in each structural position. Computer calculated areas of each doublet have yielded Fe^{2+} site populations and the proportions of ferrous and ferric iron in each mineral.

The Mössbauer spectra show that Fe^{2+} ions are concentrated in *M*(1) and *M*(3) positions. In glaucophanes and crossites there is relative enrichment of these ions in *M*(3) positions as pointed out by Papike and Clark (1968), whereas the Fe^{2+} ions are enriched in *M*(1) positions of crocidolites. The infrared spectra indicate that the majority of the Fe^{3+} and Al^{3+} ions occur in $M(2)$ positions, although small amounts of these trivalent ions do occur in the $M(1)$ and $M(3)$ positions. These results are in general agreement with X-ray diffraction data for one glaucophane and one crocidolite. Thus, cation distributions in suites of alkali amphiboles may be obtained rapidly and accurately by Mössbauer and infrared spectroscopy.

The cation distributions are temperature and, possibly, pressure dependent. The Mössbauer spectrum of a pegmatitic magnesioriebeckite indicates that significant amounts of Fe^{2+} ions occur in $M(2)$ positions, and the infrared spectra of this and other riebeckites from pegmatites show that the Fe^{3+} ion contents of $M(1)$ and $M(3)$ positions are appreciable. Thus, cations are more randomly distributed in riebeckites of high temperature origins than in glaucophanes and crocidolites that crystallized at relatively low temperatures and high pressures.

The characteristic colorless-violet-blue pleochroism of alkali amphiboles is related to the cation distribution and originates from charge transfer transitions between neighboring Fe^{2+} and Fe^{3+} ions in the crystal structures. The electron transfer takes place when light is polarized in the plane of the bands of cations that extend along the *c* axis. The intensity of color is related to the number of adjacent Fe^{3+}-Fe^{2+} cation pairs. This is a maximum when cations are randomly distributed in the crystal structures, and increases with rising Fe^{2+} and Fe^{3+} ion concentrations in the amphibole. This accounts for the intense colors or opacity of pegmatitic riebeckites and the increased color intensity along the glaucophane-crossite-riebeckite series.

The proportions of ferrous and ferric ions in the alkali amphibole estimated from the area data in a Mössbauer spectrum are in good agreement with the values obtained by chemical analysis. Indeed, the Mössbauer results have pointed to errors in some chemical analysis values. Thus, Mössbauer spectroscopy provides a rapid, non-destructive method for evaluating ferrous-to-ferric ratios in a mineral.

ACKNOWLEDGEMENTS

We wish to thank most sincerely the following people who made available analysed minerals from which specimens for this and subsequent studies were chosen: Drs. S. O. Agrell, K. Aoki, G. Borley, R. O. Chalmers, R. G. Coleman, D. W. P. Corbett, W. G. Ernst, H. Heritsch, M. Iwasaki, C. Klein, C. Milton, A. Miyashiro, A. Nicolas, J. J. Papike, P. A. Sabine, D. M. Seaman, G. Switzer, K. Sutherland, A. H. Trendall, A. J. R. White and E. J. W. Whittaker. We thank Mr. J. H. Scoon for partially reanalysing specimen 7, and Dr. S. O. Agrell for permission to use unpublished analyses for specimens 4 and 5. This work was supported by a Natural Environment Research Council grant. R. G. B. gratefully acknowledges financial support from the Royal Society and the Lockey Bequest.

APPENDIX

Computer analysis of eight-peak Mössbauer spectra. The fitting procedures for four- and six-peak spectra have been described in previous papers (Bancroft, Burns and Maddock, 1967b; Bancroft, Burns and Stone, 1968). In the present study there was the possibility of the spectral data being resolved into eight peaks: one doublet arising from absorption by Fe^{3+} ions, and three others from Fe^{2+} ions in the M (1), $M(2)$ and $M(3)$ positions of the alkali amphibole structure. Only in specimen 7, however, was the cation distribution sufficiently random for appreciable amounts of Fe^{2+} ions to occur in all three positions. Furthermore, the parameters for Fe^{2+} ions in the three positions of this amphibole proved to be sufficiently different to make resolution of each doublet possible.

The fitting procedure was as follows. A typical six-peak fit (fit 1) gavel a χ^2 value of 445. In the second fit, peak D′ was added by constraining its intensity, I, to be equal to that of peak C′, and by constraining peaks A, C, B and B′ to have the same parameters (position, half-width and intensity) as in fit 1. This fit converged to give a χ^2 value of 420. The intensity constraint $I_{C'} = I_{D'}$ was then removed in fit 3 giving the value 419 for χ^2. This fit gave accurate values for the parameters of peaks A′, C′ and D′. In fit 4 an eighth peak, peak D, was added such that peaks D and D′ had a C.S. similar to that of peaks A and A′ and peaks C and C′. Thus, in this fit eleven constraints were imposed: three for the peak positions of peaks A′, C′ and D′ (as in fit 3); four for each of the half-widths of component peaks in the doublets to be equal; and four for the intensities to be equal. This fit converged, resulting in a χ^2 value of 410. Finally, in fit 5 the intensity and position constraints were removed and the fit converged with $\chi^2 = 400$.

Attempts to fit eight peaks to the spectral data of the other specimens used in this study were unsuccessful. As stated in the text this indicates one or both of two possiblities: first, the Fe^{2+} ion contents of the $M(2)$ positions are very small (less than about 10% of the total ferrous iron); second, the Mössbauer parameters of Fe^{2+} ions in $M(2)$ positions are very similar to those for the $M(3)$ positions. In particular, the peak separation must exceed the half-width and half height, which is about 0.15 mm/sec for a Co^{57} on palladium source.

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