MÖSSBAUER, INFRARED, X-RAY AND OPTICAL STUDY OF CATION ORDERING AND DEHYDROGENATION IN NATURAL AND HEAT-TREATED SODIC AMPHIBOLES

W. G. ERNST AND C. M. WAI[1] *Department of Geology and Institute of Geophysics and Planetary Physics, University of California Los Angeles, California 90024.*

ABSTRACT

Investigation of 12 natural sodic amphiboles, all but one of which crystallized under low-grade metamorphic conditions, confirms the conclusions of earlier workers that refringence and unit cell dimensions increase with increasing iron content. The present study further demonstrates that Fe^{3+} is concentrated in the $M(2)$ structural position whereas Fe^{2+} is ordered in $M(1)$ and $M(3)$. Aluminous sodic amphiboles characteristically display a Fe^{2+}/Mg fractionation where $M(3)$ is enriched in ferrous iron relative to $M(1)$; the converse relationship seems to hold for iron-rich analogues.

Heat treatment of iron-bearing sodic amphiboles in air at $705 \pm 2°C$ results in rapid loss of hydrogen and concomitant increase in ferric:ferrous ratio. To the extent that Fe^{2+} ions are available in $M(1)$ and $M(3)$ sites, electrons are transferred to adjacent bonded hydroxyls, allowing neutralization and expulsion of hydrogen. Dehydrogenation takes place over a period on the order of an hour under the experimental conditions. Subsequent to loss of all hydrogen, continued oxidation takes place by a much slower process, possibly involving electron and/or ion diffusion. In addition, significant disordering of cations occurs on experiments of four days' duration. Sodic oxyamphiboles possess shorter a, b and c axis repeats, higher indices of refraction and birefringence compared to natural starting materials.

Natural iron-bearing glaucophane hydrothermally heated for 15,667 hours at $513 \pm 10°C$, P_{fluid} of 2000 bars and f_{O_2} of about 10^{-22} bars, was partially oxidized, completely lost its hydrogen (as H_2O?), and now displays both unusually large a and b axis dimensions and elevated refringence. It is tentatively concluded that the octahedrally coordinated cations are virtually completely disordered in this oxyglaucophane anhydride.

INTRODUCTION

Based on single-crystal X-ray studies, the differential occupancy by cations of clinoamphibole octahedrally and eight-fold coordinated sites was proposed by Whittaker (1949), and further documented by Ghose (1961). Ernst (1963) suggested that observed polymorphism in synthetic members of the glaucophane-riebeckite series formed under controlled physical conditions might reflect such order-disorder relations. More recent three-dimensional crystal structure refinements (Colville and Gibbs, 1965, and personal communication, 1969; Fischer, 1966; Papike and Clark, 1968; Papike, Ross and Clark, 1969; Finger, 1969) combined

---

[1] Present address. Department of Chemistry, University of Idaho, Moscow, Idaho 83843.

with Mössbauer and infrared spectral studies (Whitfield and Freeman, 1967; Bancroft, Burns and Maddock, 1967; Bancroft, Maddock and Burns, 1967; Bancroft, Burns and Stone, 1968; Burns and Prentice, 1968; and Bancroft and Burns, 1969) have substantially demonstrated the variations in cation distributions for a variety of naturally occurring double-chain silicates.

For the natural specimens studied thus far, it is clear that the eight-fold coordinated $M(4)$ structural position accommodates Ca and Na in the calcic and sodic series, whereas $M(4)$ preferentially accepts Fe^{2+} and Mn^{2+} over Mg in the iron-magnesium amphiboles. (For descriptions of clinoamphibole crystal structures, site nomenclature and chemical variations, see Whittaker, 1949, 1960; Ghose, 1965; and Ernst, 1968.) Although a few exceptions have been noted, the $M(1)$ and $M(3)$ octahedral positions contain similar cation populations; the occupants of these sites characteristically possess smaller ionic radii than those residing in $M(4)$. In general, the even smaller six-fold coordinated Fe^{3+} and Al are concentrated in $M(2)$. Where trivalent cations are absent from these octahedral sites, fractionation among $M(1)$, $M(2)$ and $M(3)$ positions is not pronounced (*e.g.*, see Fischer, 1966; Burns, 1968). Site occupancy strongly influences unit cell dimensions, but evidently scarcely affects optical properties, as pointed out by Colville, Ernst and Gilbert (1966).

Up to the present time, completely disordered natural Na-amphiboles have not been reported. Because of the possible petrologic significance with respect to the origin of rocks of the blueschist and related metamorphic facies, and alkalic, felsic igneous rocks as well, heating experiments were undertaken in the present study in an attempt to disorder natural sodic amphiboles under specified laboratory conditions. However, although some cation rearrangement took place, oxyamphiboles were produced. Accordingly, the experimental-analytical emphasis shifted toward investigation of the nature and process of sodic amphibole cation disordering accompanying dehydrogenation and the mechanism of hydrogen loss itself. With a few exceptions (*e.g.*, Barnes, 1930; Hodgson, Freeman and Taylor, 1965; Addison and White, 1968) devolatilized natural and synthetic amphiboles have not received much attention. Those which have been studied are principally the commercially important crocidolites[1] (*e.g.*, see Addison, Neal and Sharp, 1962; Addison *et al.*, 1962; Patterson, 1965; Patterson and O'Connor, 1966; Clark and Freeman, 1967).

The compositions of the twelve sodic amphiboles studied are shown in Figure 1. One of the magnesioriebeckites, specimen no. S.C., from Sheep

---

[1] Fibrous members of the riebeckite-magnesioriebeckite series.
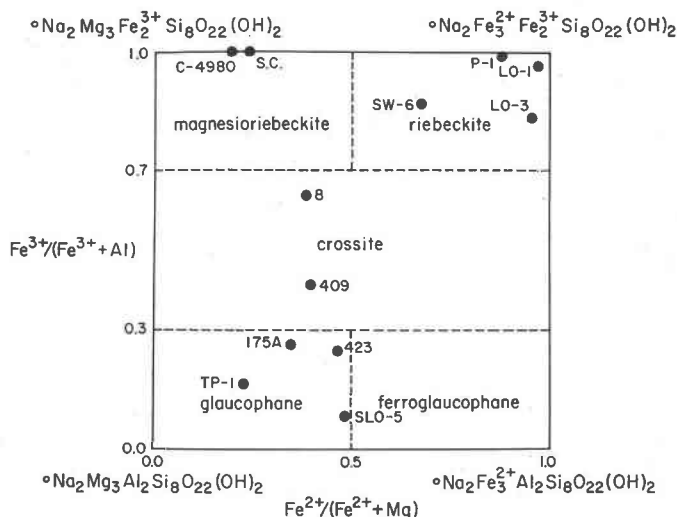
FIG. 1. Compositional variation in terms of six-fold coordinated major cations for members of the glaucophane-riebeckite-magnesioriebeckite series studied in this work. Chemical analyses and source references are presented in Table 1. The terminalogical classification employed is modified slightly from that proposed by Miyashiro (1957).

Creek, Montana, occurs in a hypothermal rare-earth vein transecting hornblendic gneiss, amphibolite and marble (see Heinrich and Levinson, 1961, p. 1437–1438). The pair of investigated crocidolites, nos. P-1 and C-4980, are from feebly recrystallized South African and Bolivian ironstones, respectively (e.g., see Hall, 1930; Ahlfeld, 1943). The remaining nine samples come from the low-grade blueschists of western California and Shikoku, Japan.

Conventional gravimetric analyses for these sodic amphiboles are presented in Table 1. Corresponding cation proportions listed in Table 2 were computed on the basis of 23 oxygens and assuming one H_2O per formula unit, as advocated by Miyashiro (1957); such a scheme recognizes the unreliability of water analyses for double-chain silicates. However, as pointed out by Borg (1967a), the sums for four-, six- and eightfold coordinated cations generally approach normal stoichiometric proportions in amphiboles simply because of compensating and compounded errors of opposite sign inherent in this method. Manganese has been assigned to octahedral positions of the sodic amphiboles listed in Table 2. Judging from the individual sums of six-fold versus eight-fold coordinated cations, this assumption appears to be valid, even for a Mn^{2+}-rich riebeckite (no. LO-3), except for a single sample: the manganiferous crossite, specimen no. SW-6, evidently contains approximately equal

TABLE 1. CHEMICAL ANALYSES FOR INVESTIGATED SODIC AMPHIBOLES

Sample no. / Oxide	TP-1	175A	SLO-5	423	409	8	C-4980	S.C	SW-6	P-I	LO-3	LO-1
SiO_2	58.04	55.19	55.36	54.88	54.56	55.10	55.44	53.5	49.95	51.94	51.97	52.05
TiO_2	0.66	0.11	0.45	0.87	0.23	0.68	0.04	0.25	0.11	—	0.19	0.44
Al_2O_3	10.31	9.94	12.16	9.86	8.29	4.27	0.22	1.3	4.23	0.20	2.01	0.40
Fe_2O_3	2.89	4.63	1.56	4.35	7.94	10.61	16.77	14.5	16.93	18.64	14.14	16.57
FeO	6.12	9.21	12.11	12.02	10.31	9.78	5.23	6.99	13.05	19.39	19.59	21.77
MnO	0.07	0.16	0.16	0.14	0.13	0.48	0.09	0.13	4.95	—	3.00	0.13
MgO	11.71	9.75	7.23	7.69	8.74	8.86	12.30	12.5	3.52	1.37	0.48	0.36
CaO	1.37	1.69	1.02	1.95	0.81	1.43	2.17	2.25	0.39	0.19	0.75	0.15
Na_2O	6.97	6.57	6.75	5.62	6.71	6.38	6.76	6.42	4.94	6.07	5.83	6.29
K_2O	0.02	0.19	0.15	0.09	0.14	0.09	0.15	0.08	0.32	0.04	0.34	0.20
H_2O+	1.98	2.19	2.34	2.22	2.18	1.96	0.55	2.57	0.87	2.58	1.78	1.49
H_2O-	0.00	0.32	0.29	0.13	0.07	0.06	0.05	—	—	0.31	0.20	0.04
Other	0.03	0.04	0.32	0.00	0.01	0.05	0.26	—	0.00	—	—	—
Total	100.17	99.99	99.90	99.82	100.12	99.75	100.03	100.49	99.26	100.73	100.28	99.89
Analyst	H. B. Wiik	S. Imai	H. Haramura		D. Thaemlitz		H. B. Wiik	E. Szentvari	F. A. Gonyer	H. E. Vassar	H. Onuki	

TP-1. Ernst (in press, Table 3), glaucophane from Tiburon Peninsula, California.
175A. Ernst (in press, Table 6), glaucophane from Little Panoche Pass, California.
SLO-5. Ernst (in press, Table 7), glaucophane from San Luis Obispo, California.
423. Banno (1959, Table 1, no. 2), glaucophane from Kotu Mine, eastern Shikoku.
409. Banno (1959, Table 1, no. 1), crossite from Kotu Mine, eastern Shikoku.
8. Borg (1967b, Table 1, no. 8), crossite from Berkeley Hills, California.
C-4980 Ernst (1960, Table 12), magnesioriebeckite from Cochabamba, Bolivia.
S.C. Ernst (1963, Table 9), magnesioriebeckite from Sheep Creek, Montana; Fe_2O_3 and FeO redetermined by J. H. Scoon as 9.91 and 7.07 respectively (Bancroft and Burns, 1969, Table 1).
SW-6 Switzer (1951, Table 3, no. 6), riebeckite from Mill Creek, California.
P-I. Peacock (1928, Table V, no. I), riebeckite from Kliphuis, South Africa.
LO-3 Onuki and Ernst (1969, Table 3), riebeckite from Laytonville, California.
LO-1. Onuki and Ernst (1969, Table 3), riebeckite from Laytonville, California.

W. G. ERNST AND C. M. WAI

TABLE 2. CATION PROPORTIONS FOR INVESTIGATED SODIC AMPHIBOLES

Cation		Sample no. TP-1	175A	SLO-5	423	409	8	C-4980	S.C.	SW-6	P-I	LO-3	LO-1
IV	Si	7.880	7.741	7.792	7.762	7.752	7.925	7.903	7.71	7.539	7.985	7.966	8.020
	Al	0.120	0.259	0.208	0.238	0.248	0.075	0.034	0.22	0.461	0.015	0.034	0.000
VI	Al	1.529	1.384	1.809	1.405	1.139	0.648	0.000	0.00	0.291	0.022	0.329	0.072
	Ti	0.068	0.012	0.047	0.093	0.025	0.073	0.009	0.03	0.013	—	0.022	0.051
	Fe^{3+}	0.295	0.489	0.165	0.462	0.800	1.147	1.796[a]	1.57	1.922	2.149	1.631	1.915
	Fe^{2+}	0.695	1.080	1.425	1.421	1.225	1.176	0.624	0.84	1.646	2.492	2.511	2.796
	Mg	2.368	2.037	1.516	1.620	1.850	1.898	2.609	2.68	0.790	0.315	0.110	0.083
	Mn	0.008	0.019	0.019	0.017	0.015	0.059	0.009	0.02	0.633[b]	—	0.390	0.017
Total VI		4.963	5.021	4.981	5.018	5.054	5.001	5.047	5.14	5.295	4.978	4.993	4.934
VIII	Ca	0.199	0.254	0.154	0.296	0.123	0.220	0.336	0.35	0.063	0.037	0.123	0.025
	Na	1.833	1.785	1.841	1.541	1.847	1.779	1.865	1.79	1.444	1.816	1.733	1.877
	K	0.003	0.034	0.027	0.017	0.024	0.016	0.026	0.02	0.062	0.000	0.067	0.039
Total VIII		2.035	2.073	2.022	1.837	1.994	2.015	2.227	2.16	1.569	1.853	1.923	1.941

[a] Approximately 0.073 atoms of the Fe^{3+} probably in 4-fold coordination
[b] Nearly half of the Mn probably in 8-fold coordination.

amounts of Mn^{2+} in six- and eight-fold sites. Other clinoamphiboles—such as members of the cummingtonite-grunerite series (*e.g.*, see Klein, 1964, p. 969; Bancroft, Burns and Maddock, 1967, p. 1024; Papike, Ross and Clark, 1969)—evidently contain manganese chiefly in the eight-fold coordinated $M(4)$ site.

<div align="center">EXPERIMENTAL AND ANALYTICAL TECHNIQUES</div>

X-ray diffraction and Mössbauer investigations were performed for all twelve naturally-occurring Na-amphiboles listed in Tables 1 and 2. Optical properties were determined or are available from the literature for these samples; for a few, infrared spectra were measured. Unit cell dimensions have been calculated from the diffraction data; in addition, utilizing both Mössbauer and infrared spectra it was possible to compute the cation site occupation for these natural phases. Four samples, glaucophane no. TP-1, magnesiorie-beckite no. C-4980, and riebeckites no. P-1 and no. LO-1, were heat-treated in the laboratory and their properties reinvestigated by the techniques mentioned above.

Three of these phases, nos. P-I, C-4980 and TP-1 will be discussed in some detail. The riebeckite, no. P-I, is similar compositionally to the material for which Colville and Gibbs (1965) presented a crystal structure analysis. The magnesioriebeckite, no. C-4980, is from the exact locality whence came the crocidolite Whittaker (1949) employed for his crystal structure analysis. The glaucophane, no. TP-1, is the sample for which Papike and Clark (1968) performed their three-dimensional refinement.

Hydrothermal and One-Atmosphere Heating Runs. Two types of experiments were conducted. (1) The glaucophane, no. TP-1, was heated in a sealed gold capsule at $513 \pm 10°C$ and 2000 bars fluid pressure for 15,667 hours (more than 652 days) employing conventional hydrothermal methods and equipment (*e.g.*, see Ernst, 1960). A 2.5 molal NaOH charge solution was used to promote recrystallization. Because of the gradual diffusion of hydrogen through the capsule wall, oxygen fugacity was more or less maintained at a value appropriate for the $NiO-Ni+\frac{1}{2}O_2$ equilibrium—about 10^{-22} bars (Eugster and Wones, 1962, Table 2)—by equilibration of the charge+fluid with H_2O pressure medium+bomb wall (Haynes alloy 25) system. The glaucophane starting material was introduced as a fine powder and was not noticeably coarsened during the experiment. Its color changed from an initial medium intensity blue to blue-green. (2) The crocidolites, no. C-4980 and no. P-I, were heated in unsealed gold capsules at $705 \pm 2°C$ and one atmosphere total pressure in air ($f_{O_2} = 10^{-0.3}$ bars) for periods of 1, 6, 29 and 94 hours. The starting material consisted of bundles of fibres; individual strands were considerably less than 0.1 mm thick. The run products consisted of golden brown (no. C-4980) or dark brown (no. P-I) fibres which in other respects megascopically resembled the light or dark blue starting materials. The glaucophane, no. TP-1, was heated to $706 \pm 2°C$ in air for one and 95 hours; the color changed from medium intensity blue to tan. In a final experiment, riebeckite, no. LO-1, was oxidized in air at 707°C for 95 hours; its color changed from dark blue to brownish black. The grain sizes (0.1–0.2 mm) of the starting materials (nos. TP-1 and LO-1) in these latter two heating experiments were considerably coarser than in the case of the heat-treated crocidolites.

X-ray and Optical Measurements. Unit cell dimensions and optical properties for all the untreated and several heat-treated sodic amphiboles are presented in Table 3. X-ray diffraction techniques have been described previously (Ernst, 1963). The maximum standard errors of the axial lengths, the β angles and unit cell volumes determined by a

TABLE 3. UNIT CELL DIMENSIONS AND OPTICAL PROPERTIES FOR UNTREATED
AND SEVERAL HEAT-TREATED SODIC AMPHIBOLES

| Sample No. | Unit cell dimensions | | | | | Optical Properties | | Experimental conditions | | |
	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$\beta(°)$	vol (Å^3)	α	γ	P (bars)	T (°C)	duration (hrs)
TP-1	9.554	17.738	5.298	103.72	872.3	1.615	1.635	—	—	—
TP-1A	9.550	17.758	5.293	103.69	872.1	1.617	1.638	1	705	1
TP-1B	9.524	17.716	5.269	103.64	863.9	1.645	1.654	1	707	95
TP-4XR	9.827	17.903	5.294	103.75	904.6	1.643	1.652	2000	513	15,667
175A	9.591	17.814	5.306	103.69	880.7	1.621	1.646	—	—	—
SLO-5	9.551	17.781	5.310	103.61	876.5	1.625	1.649	—	—	—
423	9.592	17.834	5.308	103.70	882.2	1.633	1.654	—	—	—
409	9.617	17.862	5.312	103.69	886.6	1.643	1.662	—	—	—
8	9.673	17.923	5.316	103.68	894.4	1.663	1.669	—	—	—
C-4980	9.727	17.958	5.306	103.75	900.2	1.666	1.675	—	—	—
C-4980C	9.683	17.912	5.287	103.62	891.2	1.679	1.703	1	706	94
C-4980D	9.680	17.913	5.292	103.64	891.7	1.679	1.704	1	704	1
S.C.	9.742	17.955	5.287	103.96	897.5	1.653	1.663	—	—	—
SW-6	9.720	18.018	5.326	103.60	906.6	1.680	1.685	—	—	—
P-I	9.760	18.070	5.339	103.66	914.9	1.698	1.706	—	—	—
P-IC	9.619	17.946	5.295	103.24	889.8	1.710	1.749	1	706	94
P-ID	9.635	17.953	5.286	103.30	889.9	1.709	1.750	1	704	1
LO-3	9.719	18.014	5.328	103.62	906.5	1.693	1.703	—	—	—
LO-1	9.740	18.045	5.336	103.42	912.5	1.699	1.706	—	—	—
LO-1A	9.618	17.902	5.286	103.40	885.3	1.723	1.766	1	707	95

least squares fit of the X-ray data are ±0.008 Å(a), ±0.019 Å(b) ±0.007 Å(c), $\pm0.11°$ (β) and ±1.7 Å^3 (vol.) Measurements of most samples yield associated errors less than one-half or one-third of the values quoted. Indices of refraction were determined employing a flat stage petrographic microscope, immersion oils of 0.002 interval for refringences below 1.700, 0.010 interval above (mixed to 0.005 intervals) and white light; accuracy is estimated in all cases as better than ±0.003 below 1.700 and ±0.006 above.

Infrared Spectra Measurements. A Perkin-Elmer model 421 spectrometer was used for infrared spectra measurements. The frequency region studied was that containing the fundamental bands of O–H stretching at approximately 3600–3700 cm^{-1}. The ordinate and abscissa of the spectrometer were expanded to obtain high resolution for the spectra. The abscissa was expanded to 10 times the normal scale in order that the frequency reading could be measured accurately to ±1 cm^{-1}. Usually spectra were recorded in the region from 3800 cm^{-1} to 3500 cm^{-1}. The instrument was calibrated against H_2O and CO_2.

Sample minerals were ground to fine powders. Each sample consisted of 3–4 mg of weighed material mixed with about 150 mg of KBr and pressed into a disc. The spectrometer laboratory was not air dried, hence the control of adsorbed water in the KBr disc was difficult. In most cases, a broad water peak contributed to the background in the frequency region studied; however, this by no means affects qualitative discussions of the obtained spectra.

Mössbauer Spectra and Computer Analysis. The Mössbauer spectrometer consisted of a conventional loudspeaker drive with data stored in the time mode of a 400 channel analyzer. A detailed schematic of this Mössbauer spectrometer has been described elsewhere (Kündig *et al.*, 1966). A source of 5 mC-Co^{57} in palladium was used for all the spectra measurements.

The minimum line width of the palladium source was 0.20 mm/sec. The spectrometer was calibrated against metallic iron. All chemical shifts quoted in this work are relative to zero mm/sec for metallic iron.

Sample materials were ground to fine powders and evenly distributed in a thin-wall plastic container. The size of the container varied in order to maintain iron concentration in the sample at about 5–10 mg/cm.[2] All spectra were taken at room temperature and at least 10^6 counts per channel were recorded for each measurement.

Computer processing was essentially in order to resolve the individual lines in the spectra and to determine parameters for all peaks. A general least-squares program (Kündig, unpublished) was employed to fit the spectrometer output to an assumed Lorentzian shape. The program was written in Fortran IV and used with an IBM 360–75 computer, University of California, Los Angeles, Computing Facility. This program also produced plots of the fitted spectra and of the residual deviations. The spectrum was finally adopted that had the lowest χ^2 (the sum of the squared deviations from the best fit divided by the variance at a single channel and divided by the total number of channels). Curve fitting involved the constraints that: individual peak heights were identical for a specific doublet; and all line widths at half height were equal. Unique solutions, in general, are difficult to obtain for such complex, multisite minerals without imposing these constraints. Actually, the intensities of paired quadrupole lines for powdered random absorbers are usually almost equal, whereas half-widths of Fe^{2+} and Fe^{3+} vary. (For measurement of the unconstrained variance in somewhat analogous minerals, the orthopyroxenes, see Virgo and Hafner, 1970, p. 204 and Table 2.) The best-fits obtained in the present investigation from computer analysis based on these constraints agree very well with the actual spectra in most cases. Inasmuch as the assumptions of equality of line width and paired peak intensities are not strictly valid, it should be emphasized that the calculated site populations are only semi-quantitative in nature. Nevertheless, further corrections to line width and peak height are unlikely to change the conclusions drawn in this paper. Improved Mössbauer analysis which requires high-resolution spectroscopy is of course desirable and is being considered in further studies of this subject.

INTERPRETATION OF SPECTRA

Infrared Spectra of the Sodic Amphiboles. The ir spectra of natural and heat-treated riebeckite, no. P-I, magnesioriebeckite, no. C-4980, and glaucophane, no. TP-1, in the frequency region between 3700 cm^{-1} and 3600 cm^{-1} are shown in Figures 2–4 respectively.

For different cations coordinated to hydroxyl, the strength of the O–H bond should be slightly different; this in turn will shift the frequency of the O–H absorption band. Moreover, in the case of amphiboles, each OH located in the anion O(3) site, is coordinated to three cations, two of which reside in the $M(1)$ site and one of which is located in $M(3)$. If two or more metal species are distributed among these sites, they will give rise to different combinations of cations coordinated to the OH group in O(3), and hence result in slightly different absorption band frequencies. With a high resolution infrared spectrometer, the fundamental band of O–H stretching can be resolved into several absorption peaks, corresponding to the different nearest neighbor cation combinations. In general, replacement of Mg by Fe tends to shift the O–H band

TABLE 4. INFRARED ANALYSES OF NATURAL AND HEAT-TREATED SODIC AMPHIBOLES,
NOS. P-I, C-4980 AND TP-1

Sample no.	Observed Absorption of O–H stretching frequency (cm^{-1}) and assigned cation combinations					
	[Mg, Mg, Mg]	minor peak	[Mg, Mg, Fe^{2+}]	[Mg, Fe^{2+}, Fe^{2+}]	minor peak	[Fe^{2+}, Fe^{2+}, Fe^{2+}]
P-I	—		—	3633	(?)	3617
P-ID	—		—	—		—
P-IC	—		—	—		—
C-4980	3664	(3654)[a]	3647	3632	(3625)[b]	3616
C-4980D	3663	(3654)	—	—	(3624)	—
C-4980C	3662	(3654)	—	—	(3624)	—
TP-1	3660	(?)	3644	3630	—	3614
TP-1A	3659	(3654)	3644	3630	—	3614
TP-1B	3661	(3654)	—	(?)	—	—
TP-4XR	—	—	—	—	—	—

[a] Possible [Mg, Mg, Fe^{3+}].

[b] Uncertain cation combinations, possibly [Mg, Fe^{3+}, Fe^{3+}]

toward lower frequencies (Burns and Strens, 1966). The assignments of cation combinations for the O–H fundamental bands observed in these ir spectra are presented in Table 4. Although there are small differences in peak positions, the assignments are similar to those given for sodic amphiboles by Burns and Prentice (1968) and by Bancroft and Burns (1969). Infrared studies yielding comparable results regarding hydroxyl cation neighbors and O–H stretching frequencies in micas have been published by Vedder (1964, p. 755–762) and by Vedder and Wilkins (1969, Table 1).

Let us consider the fundamental bands observed in natural riebeckite, no. P-I, shown in Figure 2. As seen from Table 2, the computed cation proportions among the five octahedrally-coordinated positions—$2M(1)$, $2M(2)$ and $1M(3)$ sites—are Fe^{2+} (2.492), Fe^{3+} (2.149) and Mg (0.315). Ferric iron is ordered in the $M(2)$ site as will be demonstrated in the next section which deals with Mössbauer study of the sodic amphiboles. The possible combinations of Fe^{2+} and Mg in the two $M(1)$ and one $M(3)$ sites coordinated to an OH group are [Fe^{2+}, Fe^{2+}, Fe^{2+}], [Fe^{2+}, Fe^{2+}, Mg], [Fe^{2+}, Mg, Mg], and [Mg, Mg, Mg]. Here it has been assumed that the $M(1)$ and $M(3)$ are equivalent sites, in other words, that combinations such as [Fe$^{2+}_{M(1)}$, Fe$^{2+}_{M(1)}$, Mg$_{M(3)}$]OH and [Fe$^{2+}_{M(1)}$, Mg$_{M(1)}$, Fe$^{2+}_{M(3)}$]OH
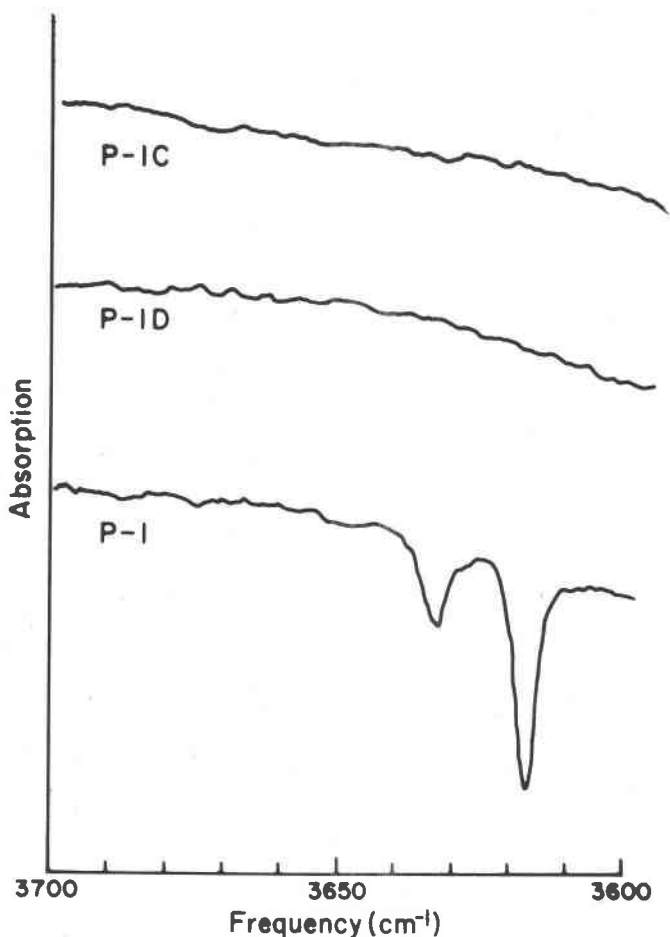
FIG. 2. Infrared spectra of natural and heat-treated riebeckite in the frequency region 3700-3600 cm^{-1}. The spectra were taken at room temperature employing a Perkin-Elmer Model 421 spectrophotometer. Sample no. P-I is the natural material, whereas nos. P-ID and P-IC have been heat treated at one atmosphere, $f_{O_2} = 10^{-0.3}$, $T = 705 \pm 2°$C for one and 94 hours respectively.

have such a small difference in energy that separate ir peaks cannot be distinguished. The ir spectrum of natural riebeckite has a weaker absorption peak at 3617 cm^{-1} and a stronger peak at 3633 cm^{-1}. These peaks are most probably combinations of [Fe^{2+}, Fe^{2+}, Fe^{2+}]OH for the 3617 cm^{-1} peak and [Fe^{2+}, Fe^{2+}, Mg]OH for the 3633 cm^{-1} peak as suggested by Burns and Prentice (1968); random site occupations calculated for the ferrous iron and magnesium proportions listed in Table 2 would yield

about 70 percent [Fe^{2+}, Fe^{2+}, Fe^{2+}], nearly 27 percent [Fe^{2+}, Fe^{2+}, Mg]. According to the "wet" chemistry, sample no. P-I contains a sum total of only 2.807 ferrous iron and magnesium ions per formula unit, whereas it carries about 2.149 Fe^{3+} (see Table 2). If the analysis is correct—and there is no reason to question it, as demonstrated by the Mössbauer results to be presented in the next section—then at least 0.149 ferric ions must reside in $M(1)$ and $M(3)$ positions. The inflection on the low energy side of the 3633 cm^{-1} peak could represent the $MgFe^{3+}Fe^{3+}$ configuration; however, as seen from Figure 2, the intensity is too low to warrant a definitive statement. Absorption peaks representing hydroxyl coordinated to combinations of two and three Mg ions were not observed, apparently due to their low probabilities, hence intensities (random site occupations would be approximately three and zero percents respectively). No O–H absorption bands were observed in riebeckite, no. P-ID and no. P-IC, heat-treated in the atmosphere for one and 94 hours respectively. The loss of hydrogen obviously was completed in less than one hour of heating in air at about 705°C. The dehydrogenation mechanism will be shown later to be related to the oxidation of Fe^{2+} coordinated to the OH group.

The ir spectrum of the natural magnesioriebeckite, no. C-4980, illustrated in Figure 3, contains four major absorption peaks at 3616, 3632, 3647 and 3664 cm^{-1}. The spectrum displays the same characteristics as one presented for Bolivian crocidolite by Burns and Prentice (1968, Fig. 1a). The 3616 cm^{-1} and 3632 cm^{-1} peaks were assigned to [Fe^{2+}, Fe^{2+}, Fe^{2+}]OH and [Fe^{2+}, Fe^{2+}, Mg]OH respectively, by analogy with those observed in natural riebeckite. The intensity of the 3616 cm^{-1} peak in this case is much less than that of the 3632 cm^{-1} peak, due to the high Mg population (2.609) relative to Fe^{2+} (0.624) in $M(1)$ and $M(3)$ of the magnesioriebeckite (Table 2). The other two more intense absorption peaks at 3647 cm^{-1} and 3664 cm^{-1} have been assigned to [Fe,$^{2+}$ Mg, Mg]OH and [Mg, Mg, Mg]OH respectively. Comparable to sample no. P–I, the increase in O–H stretching frequency for each Mg replacing an Fe^{2+} coordinated to OH is about 16 cm^{-1}. Assuming random, or totally disordered, magnesium and ferrous iron occupation of $M(1)$ and $M(3)$ sites, the relative proportions of [Fe^{2+}, Fe^{2+}, Fe^{2+}], [Fe^{2+}, Fe^{2+}, Mg], [Fe^{2+}, Mg, Mg] and [Mg, Mg, Mg] are computed as nearly one, about 9, 38 and 52 percent respectively, based on compositional data presented in Table 2. Two other very minor peaks may be discerned at 3625 cm^{-1} and 3654 cm^{-1}; these peaks may possibly result from OH groups coordinated to small amounts of ferric iron in $M(1)$ and $M(3)$ sites. The samples of magnesioriebeckite heat-treated in air for one hour, no. C-4980D, and for 94 hours, no. C-4980C, gave only one and the same major absorption
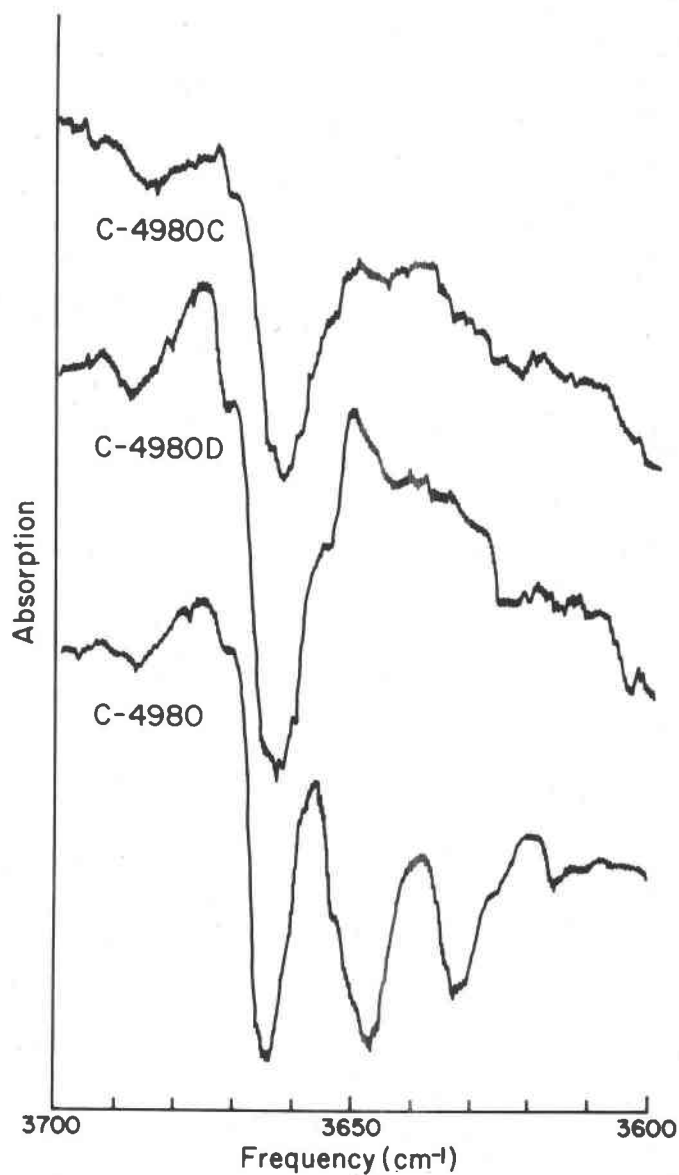
FIG. 3. Infrared spectra of natural and heat-treated magnesioriebeckite in the frequency region 3700-3600 cm^{-1}. Analytical conditions identical to those of Fig. 2. Sample no. C-4980 is the natural material, whereas nos. C-4980D and C-4980C have been heat treated at one atmosphere, $f_{O_2} = 10^{-0.3}$, $T = 705 \pm 2°C$ for one and 94 hours respectively.

peak at 3663 cm^{-1}, which has been assigned to [Mg, Mg, Mg]OH bonding analogous to peak assignments for the natural material. All other prominent peaks representing O–H stretching frequencies, hence hydroxyls coordinated to Fe^{2+}, were lost after one hour of heating in the atmosphere at about 705°C. The two minor peaks at 3625 cm^{-1} and 3654 cm^{-1} are still observable in the heat-treated magnesioriebeckite, suggesting that the OH groups responsible for these bands are coordinated not to Fe^{2+} but to Fe^{3+}. Just as in the case of riebeckite, the dehydrogenation mechanism is rapid and appears to be related to the oxidation of iron residing in $M(1)$ and $M(3)$ sites.

The infrared spectrum of natural glaucophane, no. TP-1, shown in Figure 4, is similar to the ir spectrum of natural magnesioriebeckite, no. C-4980. The four major peaks at 3614, 3630, 3644 and 3660 cm^{-1} correspond to the combinations [Fe^{2+}, Fe^{2+}, Fe^{2+}]OH, [Fe^{2+}, Fe^{2+}Mg]OH, [Fe^{2+}, Mg, Mg]OH and [Mg, Mg, Mg]OH respectively. Again assuming random occupation of $M(1)$ and $M(3)$ cation positions by magnesium and ferrous iron, and using the chemical data of Table 2, the relative proportions of [Fe^{2+}, Fe^{2+}, Fe^{2+}], [Fe^{2+}, Fe^{2+}, Mg], [Fe^{2+}, Mg, Mg], and [Mg, Mg, Mg] are calculated to be 1, 12, 41 and 46 percent respectively, in general agreement with peak intensities illustrated in Figure 4. The frequencies of these fundamental bands are about 4 cm^{-1} lower than the corresponding peaks in magnesioriebeckite, and also the two analogous absorption peaks in riebeckite, presumably due to the effect of the high Al content in glaucophane (Table 2; see also Bancroft and Burns, 1969, Fig. 4). The dehydrogenation of sample no. TP-1 at about 705°C in air did not proceed as rapidly as that of magnesioriebeckite. The glaucophane heated for one hour at this condition still showed an O–H absorption band reflecting coordination to Fe^{2+}, although of a lower intensity than that of the untreated material. Hydroxyl stretching vibrations assigned to OH-cation coordinations involving Fe^{2+} ions were not observed in the sample heated for 94 hours (Fig. 4); in this longer experiment, the only O–H stretching frequency remaining was the [Mg, Mg, Mg]OH band at approximately 3660 cm^{-1}. However, in the 15,667 hour hydrothermal run, sample no. TP-4XR, ($P_{fluid} = 2000$ bars, $T = 513°C$ and $f_{O_2} = 10^{-22}$ bars) all of the O–H band disappeared including the [Mg, Mg, Mg]OH peak, suggesting that hydrogen escape can take place through more than one mechanism.

The information obtained from these infrared studies of natural and heat-treated sodic amphiboles can be summarized as follows: (1) Dehydrogenation occurs rapidly—on the order of an hour or two—at about 705°C and atmospheric pressure ($f_{O_2} = 10^{-0.3}$ bars). The ir spectra indicate that all OH groups coordinated to Fe^{2+} are lost through the heat treat-
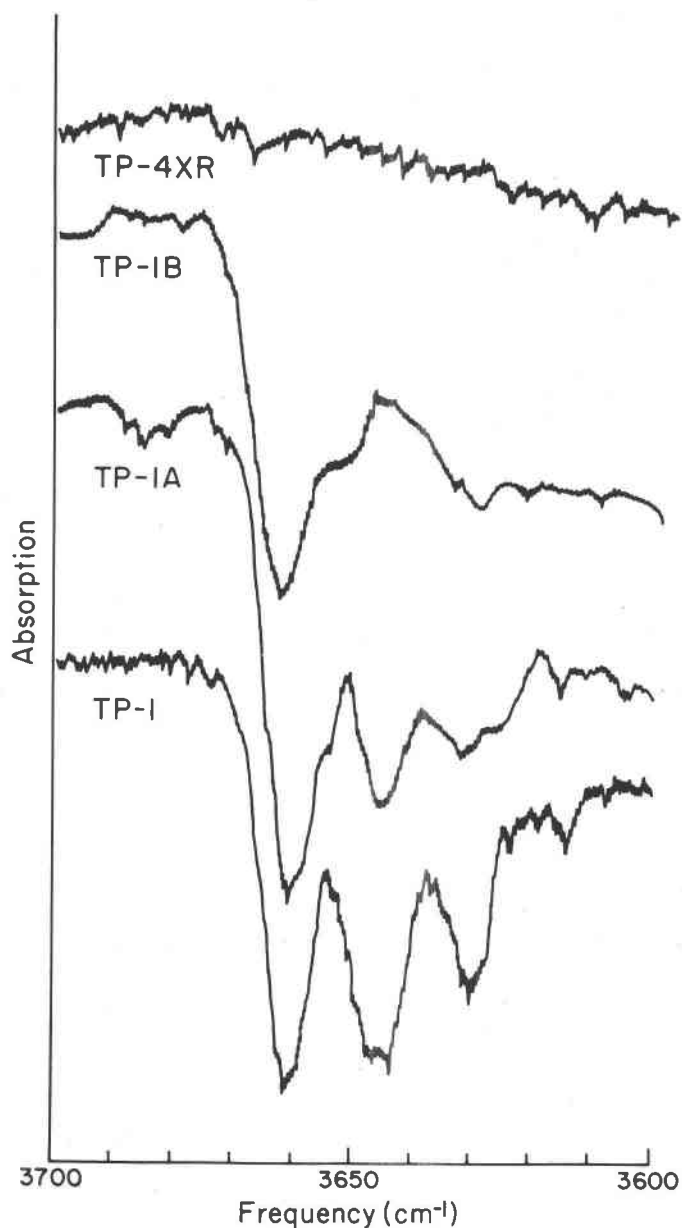
FIG. 4. Infrared spectra of natural and heat-treated glaucophane in the frequency region 3700-3600 cm^{-1}. Analytical conditions identical to those of Fig. 2. Sample no. TP-1 is the natural material, whereas nos. TP-1A and TP-1B have been heat treated at one atmosphere, $f_{O_2} = 10^{-0.3}$, $T = 706 \pm 2°C$, for one and 95 hours respectively; TP-4XR was subjected to hydrothermal treatment at 2000 bars P_{fluid}, $f_{O_2} \approx 10^{-22}$, $T = 513 \pm 10°C$ for 15,667 hours.

ment. Only the [Mg, Mg, Mg]OH group definitely is unaffected by 94 hours of heating under the experimental conditions; however, small peaks of uncertain assignment, but most probably representing magnesium-ferric iron combinations, also appear to persist. The dehydrogenation mechanism apparently is related to the removal of electrons from ferrous iron ions residing in the $M(1)$ and $M(3)$ sites and bonded to hydroxyl. The transfer of electrons to the ligand allows the neutralization and expulsion of H_2, $e.g.$,

$$Fe^{2+}-O-H \rightarrow Fe^{3+}-O + \tfrac{1}{2}H_2 \uparrow .$$

Mössbauer studies of these sodic amphiboles, to be discussed in the next section, give further support to this mechanism. (2) Dehydrogenation of glaucophane is also observed in the hydrothermal experiment performed at 513°C, 2 kbar fluid pressure and $f_{O_2} \approx 10^{-22}$ bars, and over a period of 15,667 hours. All of the O–H stretching frequencies including that attributable to the [Mg, Mg, Mg]OH configuration are absent from the ir spectrum. This dehydrogenation must be due to another mechanism which is probably a very slow process involving the diffusion of hydrogen (as H_2O?) out of the silicate structure.

Rather similar conclusions were arrived at by Vedder and Wilkins (1969) in their investigation of natural and heat-treated biotites, and by Hodgson, Freeman and Taylor (1965) and Clark and Freeman (1967) for synthetically dehydrated crocidolites.

Mössbauer Spectra of the Sodic Amphiboles. Examples of Mössbauer spectra for natural and heat-treated riebeckite, no. P-I, magnesioriebeckite, no. C-4980, and glaucophane, no. TP-1, are shown in Figures 5, 6, and 7. The parameters which can be measured from the Mössbauer spectrum of a paramagnetic compound are the electric quadrupole splitting, $Q.S.$, the chemical isomer shift, $I.S.$, and, of course, the intensities or relative absorbances. The characteristic paired line pattern of quadrupole splitting for Fe^{57} results from the interactoin of the nuclear electric quadrupole moment with the electric field gradient tensor. The two major contributions to the electric field gradient tensor at an atomic site are that arising from non-spherically symmetric electron shells and that resulting from charges on the ligand atoms. The isomer shift arises mainly from the coulombic interaction between the nucleus and the overlapping electron orbitals. Discussions of the principles and applications of Mössbauer spectroscopy are readily available in the literature ($e.g.$, see Wertheim, 1964; Herber, 1967). The two Mössbauer parameters, $Q.S.$, and $I.S.$, are sensitive to the oxidation state, electronic configuration, coordination number and site symmetry of the iron atom (Bancroft, Maddock and
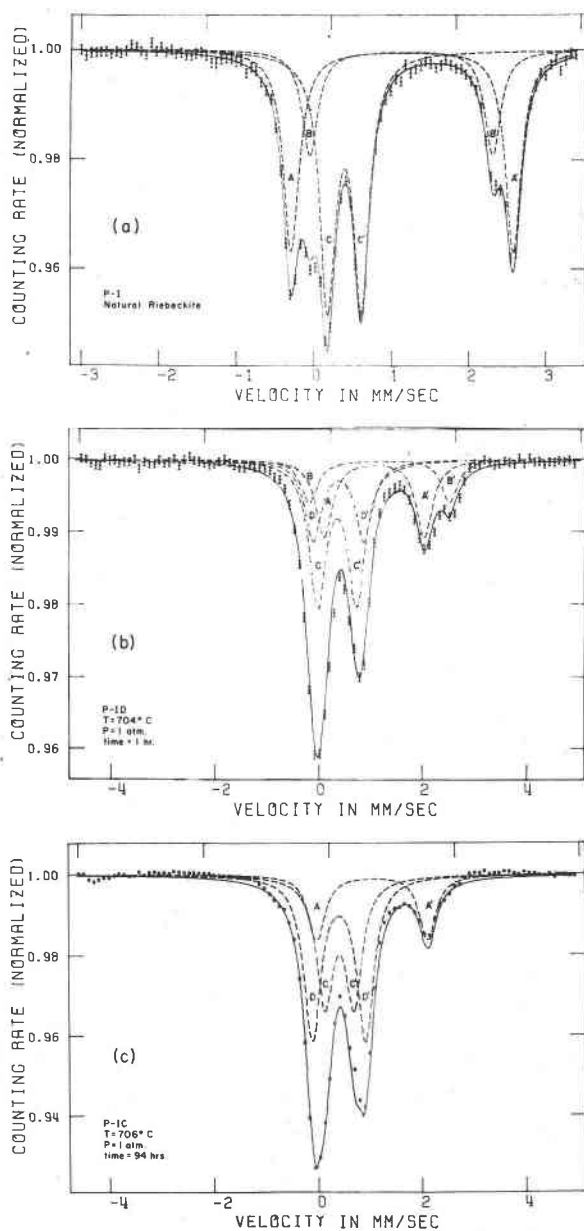
FIG. 5. Computer plotted Mössbauer spectra of natural and heat-treated riebeckite taken at room temperature. The velocities are relative to zero mm/sec for metallic iron. The source was Co[57] in palladium.
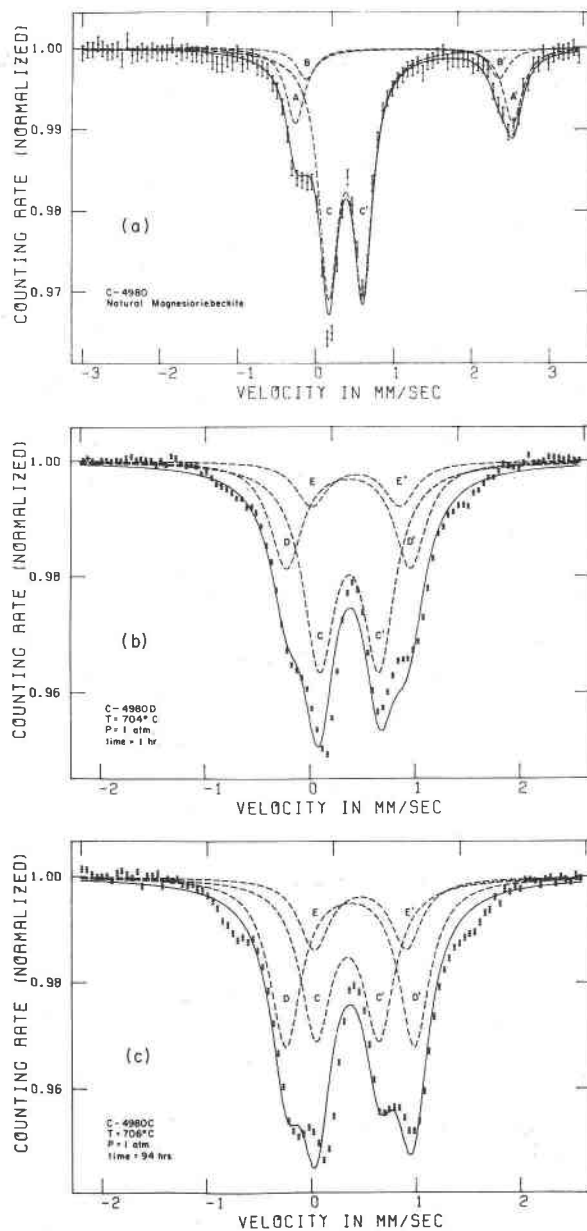
FIG. 6. Computer plotted Mössbauer spectra of natural and heat-treated magnesiorie-beckite taken at room temperature. Analytical conditions identical to those of Fig. 5.
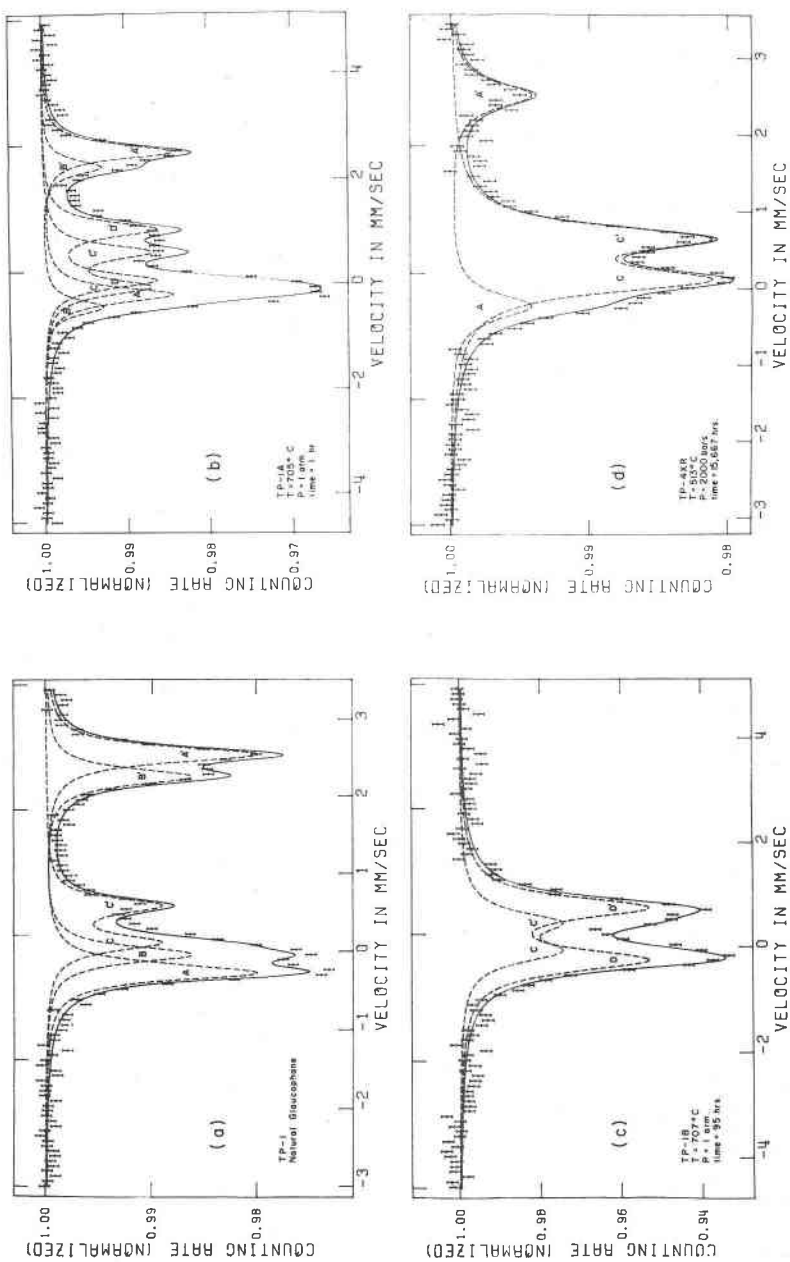
Fig. 7. Computer plotted Mössbauer spectra of natural and heat-treated glaucophane taken at room temperature. Analytical conditions identical to those of Fig. 5.

TABLE 5. MÖSSBAUER ANALYSES OF Fe^{2+} AND Fe^{3+} IN DIFFERENT OCTAHEDRAL SITES
OF NATURAL SODIC AMPHIBOLES

Sample no.	Fe^{2+} in $M(1)$			Fe^{2+} in $M(3)$			Fe^{3+} in $M(2)$		
	$I.S.$[a]	$Q.S.$[a]	percent[b]	$I.S.$	$Q.S.$	percent	$I.S.$	$Q.S.$	percent
TP-1	1.13	2.81	45.3	1.10	2.30	31.5	0.34	0.48	23.2
175A	1.13	2.79	45.6	1.12	2.24	25.1	0.38	0.46	29.3
SLO-5	1.13	2.82	50.9	1.11	2.22	32.5	0.36	0.47	16.6
423	1.14	2.82	48.4	1.11	2.23	24.3	0.38	0.47	27.3
409	1.14	2.82	41.3	1.12	2.25	19.0	0.37	0.46	39.7
8	1.14	2.82	37.7	1.07	2.27	13.3	0.37	0.47	49.1
C-4980	1.14	2.79	22.4	1.12	2.48	9.2	0.39	0.44	68.4
S.C.	1.14	2.75	34.7	1.04	2.01	11.1	0.40	0.50	54.2
SW-6	1.14	2.83	33.3	1.07	2.33	15.8	0.37	0.45	50.9
P-I	1.14	2.87	36.4	1.12	2.36	19.0	0.40	0.44	44.6
LO-3	1.14	2.86	36.1	1.09	2.38	18.8	0.37	0.44	45.1
LO-1	1.14	2.88	36.7	1.11	2.33	18.9	0.37	0.42	44.4

[a] Isomer shift ($I.S$) and Quadrupole splitting ($Q.S.$) expressed in mm/sec, relative to zero mm/sec for metallic iron.

[b] Total Fe ($Fe^{2+}+Fe^{3+}$) taken as 100 percent; absorption or intensity = cation proportion.

Burns, 1967; Bancroft, Burns and Stone, 1968); in silicates containing high-spin iron, Fe^{2+} generally has both larger quadrupole splitting and isomer shift than that associated with Fe^{3+}. In addition, the areas under peaks in the Mössbauer spectra (absorption or intensity) are proportional to the number of iron nuclei. Assuming that the recoil-free fractions are about the same for Fe^{2+} and Fe^{3+} in different sites, the area measurement enables quantitative estimation of the relative site populations of iron in Fe-bearing minerals.

Results of the Mössbauer analyses for twelve chemically analyzed natural sodic amphiboles are presented in Table 5. The parameters are similar to those obtained by Whitfield and Freeman (1967, Table 1), and by Bancroft, Burns and Stone (1968, Table 2) and Bancroft and Burns (1969, Table 3). Differences in values of $I.S.$ result from the choice of different reference standards (zero mm/sec)—cobalt in a Pd source, or stainless steel, versus metallic iron in the present study.

The Mössbauer spectra of all twelve natural sodic amphiboles show patterns that can be fitted to three individual sets of quadrupole doublets. These include two Fe^{2+} doublets, one with a range of $I.S.$ between 1.13 and 1.14 mm/sec and $Q.S. = 2.75 - 2.88$ mm/sec, and the other pair with a range of $I.S.$ between 1.04 and 1.12 mm/sec and $Q.S. = 2.01 - 2.48$ mm/sec—and a single ferric pair with a range of $I.S.$ between 0.34 and 0.40 mm/sec and $Q.S. = 0.42$–0.50 mm/sec. The values of isomer

shift and quadrupole splitting for similar peak pairs are quite consistent among the eleven low-temperature samples. However, the pematitic magnesioriebeckite, no. S.C., has relatively lower values of *I.S.* and *Q.S.* for peaks assigned to absorbance by Fe^{2+}, and higher *I.S.* and *Q.S.* associated with ferric iron absorbance. Bancroft and Burns (1969, Table 4 and p. 145) have suggested that this high-temperature phase exhibits a lesser degree of order among octahedral cations than do analogues from low-grade metamorphic rocks.

Inasmuch as only one Fe^{3+} quadrupole doublet has been resolved in natural sodic amphiboles, and as the ranges of isomer shift and quadrupole splitting are reasonably narrow, it appears that ferric iron is restricted to a single cation site. Judging from the relatively small ionic radius of ferric iron in octahedral coordination (0.645 Å, versus 0.720 Å for Mg, 0.770 Å for Fe^{2+} and 0.820 Å for Mn^{2+} according to Shannon and Prewitt, 1969, Table 1) it seems plausible that Fe^{3+} should be ordered in $M(2)$, a structural position of small compliance (Onuki and Ernst, 1969). A similar conclusion was arrived at by Whittaker (1949, 1960), and by Ghose (1965), based on charge balance considerations. Moreover, infrared studies of riebeckite, magnesioriebeckite and glaucophane previously discussed (see also Burns and Prentice, 1968; Bancroft and Burns, 1969) have demonstrated that Fe^{2+} is bonded to hydroxyl and resides chiefly in $M(1)$ and $M(3)$, hence because Na is virtually confined to $M(4)$ as proven by crystal structure analyses (Whittaker, 1949; Colville and Gibbs, 1965; Papike and Clark, 1968), the only remaining octahedral cation site available to accommodate ferric iron is $M(2)$. Mössbauer spectra obtained for all 12 natural sodic amphiboles investigated in this study (Table 5) seem to show that Fe^{3+} is principally concentrated in this single structural position, $M(2)$. Some of the observed peak broadening and the range in *I.S.* parameters may be related to minor amounts of ferric iron residing in $M(1)$ and $M(3)$; however, as will be shown in the discussion of heat-treated samples, the run products display characteristic Mössbauer spectra including new peaks assigned to Fe^{3+} in $M(1)$ and $M(3)$ which contrast with the ferric iron $M(2)$ peak present in both natural and oxidized sodic amphiboles.

In each spectrum, the intensity ratio of the two quadrupole doublets attributable to Fe^{2+} is roughly constant at 2:1. The more intense pair invariably shows the larger *I.S.* and *Q.S.* values, as seen from Table 5 and Figs. 5a, 6a and 7a. Because amphiboles contain two $M(1)$ sites and only one $M(3)$ site, the relative populations of Fe^{2+} in $M(1)$ and $M(3)$ should reflect this ratio, except for the situation where strong positional ordering of ferrous iron occurs. The validity of this argument is clearest for ferrous iron-rich sodic amphiboles such as no. LO-1; here the more intense doublet assignable to Fe^{2+} represents 1.85 atoms (36.7 percent of
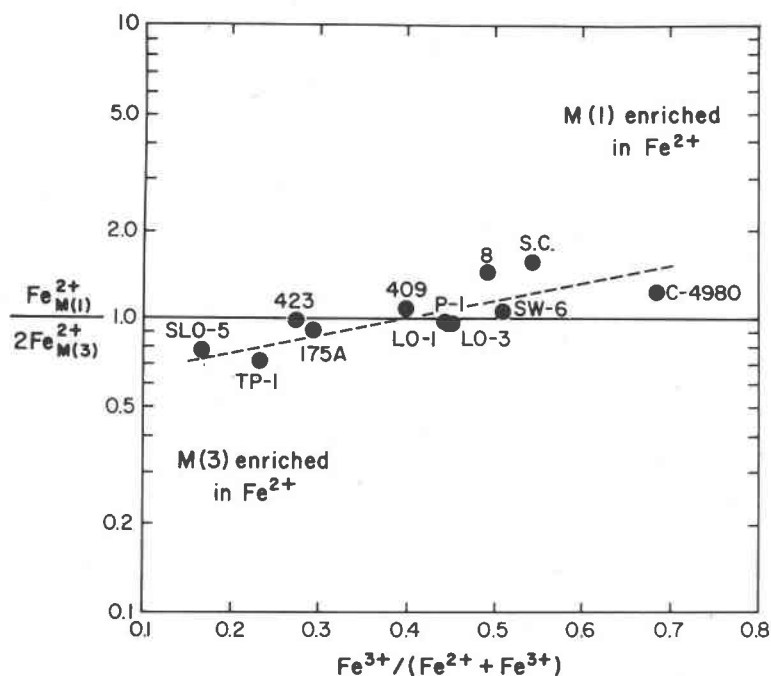
FIG. 8. Relationship of ferrous iron site preference in $M(1)$ or $M(3)$ of natural sodic amphiboles as a function of oxidation state.

the total Fe), whereas the weaker stands for 0.95 atoms (18.9 percent of the total Fe). Thus reasonable assignments for the two observed Fe^{2+} quadrupole doublets are that the one with larger values of *I.S.*, *Q.S.*, and intensity be associated with the two $M(1)$ sites, whereas the other pair with smaller values of *I.S.*, *Q.S.*, and intensity be related to the single $M(3)$ position. The lower values of *I.S.* and *Q.S.* for Fe^{2+} in $M(3)$ suggest that this site is more distorted from octahedral symmetry than the $M(1)$ site (Bancroft, Burns and Stone, 1968, p. 549). The intensity ratio of the two Fe^{2+} quadrupole doublets assigned to $M(1)$ and $M(3)$ actually deviates from exactly 2, with values, hence cation population ratios, either higher or lower than 2 for different members of the sodic amphibole series investigated. Evidently there is a slight preference by Fe^{2+} for differential occupancy of either $M(1)$ and $M(3)$ sites with respect to magnesium in these sodic amphiboles (see also Bancroft and Burns, 1969). As illustrated in Figure 8, a rough correlation exists between ferrous iron fractionation in these positions and the Fe^{3+} content: with increasing oxidation ratio, the ferrous iron becomes slightly more enriched in $M(1)$.

The proportions of Fe^{2+} and Fe^{3+} in sodic amphiboles determined from Mössbauer spectra in general are consistent with the results obtained from chemical analyses (see Tables 1 and 5). However, the Mössbauer data may be more accurate than the gravimetric analyses inasmuch as chemical processes such as dissolution and oxidation or reduction are not involved in the Mössbauer measurements. Bancroft and Burns (1969, Tables 1 and 4, samples nos. 1 and 7) present Mössbauer spectra for two of our samples, nos. TP-1 and S.C. We report 23.2 and 54.2 atomic percent ferric iron in these specimens respectively (Table 5), in good agreement with their corresponding values of 21.7 and 52.6; our analytical results for similar materials to those investigated by them from Laytonville, California, and from Cochabamba, Bolivia, also agree with their

TABLE 6. MÖSSBAUER ANALYSES OF NATURAL AND HEAT-TREATED RIEBECKITE, NO. P-I

Sample no.	Duration of run (hrs)	Absorption by Fe^{2+}						Absorption by Fe^{3+}					
		I.S.	Q.S.	per-cent	I.S.	Q.S.	per-cent	I.S.	Q.S.	per-cent	I.S.	Q.S.	per-cent
P-I[b]	0	1.14[a]	2.87[a] $M(1)$	36.4[a]	1.12	2.36 $M(3)$	19.0	—	—	—	0.40	0.44 $M(2)$	44.6
P-ID[b]	1	0.95	2.08 $M(1)$	21.3	1.10	2.70 $M(3)$	11.5	0.32	0.98 $M(1)+M(3)$	24.6	0.36	0.61 $M(2)$	42.6
P-IC[b]	94	1.05	2.13 $M(1)+M(2)+M(3)$	18.6	—	—	—	0.41	1.02 $M(1)+M(3)$	46.7	0.42	0.58 $M(2)$	34.7

[a] I.S. and Q.S. expressed in mm/sec, relative to zero mm/sec for metallic iron; total Fe ($Fe^{2+}+Fe^{3+}$) taken as 100 percent (absorption or intensity = cation proportion).

[b] Line width for P-I = 0.26 mm/sec; for P-ID and P-IC = 0.39 mm/sec.

data. As pointed out by Bancroft and Burns, the gravimetric analysis by E. Szentvari of sample no. S.C. (Ernst, 1963, Table 9) yields a $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ proportion exceeding 65 percent, in only fair agreement with both independently determined Mössbauer analyses; a new partial "wet" analysis by J. H. Scoon gives a more compatible ferric iron proportion, 55.8 percent, but the revised total iron content is so low that the oxide total would be slightly under 96 percent. For this reason the original value is reported in Table 1, but the problem is unresolved.

Computer analyses of the Mössbauer spectra for natural and heat-treated riebeckite (nos. P-I, P-ID and P-IC) are presented in Table 6. In terms of total Fe, the percentage site populations of iron in natural riebeckite determined from the areas under the peaks labeled in Figure 5a as AA', BB' and CC' are 36.4 percent Fe^{2+} in $M(1)$, 19.0 percent Fe^{2+} in $M(3)$, and 44.6 percent Fe^{3+} in $M(2)$, respectively. The cation proportions in these octahedral positions calculated from the gravimetric analysis (Table 2) are 2.492 Fe^{2+} and 2.149 Fe^{3+}, or 54 percent Fe^{2+} and

46 percent Fe^{3+}. The ferrous:ferric ratios determined by Mössbauer and "wet" chemical methods are in excellent agreement in this case.

The Mössbauer spectrum of the riebeckite heated in air for one hour (no. P-ID) could be decomposed to four quadrupole doublets, two Fe^{2+} pairs and two Fe^{3+} pairs (Fig. 5b). The line widths of the resolved peaks are about 30 percent larger than those observed in the natural riebeckite spectrum, probably because of irresolvable complex overlapping. The intensities of the two Fe^{2+} doublets are 21.3 percent (AA′) and 11.5 percent (BB′). Based on their relative intensities, the former pair was assigned to Fe^{2+} in $M(1)$, and the latter to Fe^{2+} in $M(3)$. The important observation here is the decrease in total Fe^{2+} population from 55.4 percent in natural riebeckite to 32.8 percent in the material heated in air for one hour. This net decrease of ferrous iron by 22.6 percent out of a total of 4.64 iron atoms per formula unit (see Table 2) is equivalent to oxidizing 1.05 Fe^{2+} to Fe^{3+} among these $2M(1)+1M(3)$ octahedral positions. Inasmuch as amphiboles ideally carry two hydroxyls per three cation occupants of $M(1)$ and $M(3)$, the electrons stripped from the Fe^{2+} of sample no. P-ID clearly would be insufficient to neutralize all the protons in OH groups and hence account for complete dehydrogenation of an originally fully hydrated amphibole. The ir spectrum of P-ID (Fig. 2) indicates that the O–H stretching bands were indeed all lost after a single hour of heating. Inasmuch as conventional gravimetric and Mössbauer analyses give comparable ferrous:ferric ratios, either the total iron content exceeds that quoted by Peacock (1928, Table V, no. I)—thought to be unlikely, especially inasmuch as the oxide total is suspiciously high anyway, 100.73—or the H_2O+ analysis by gravimetric methods is actually less than reported. This latter possibility seems more likely, as reflected by the high oxide total, and the general lack of reliability for older water analyses; a smaller amount of H_2O in the "wet" analysis would permit complete dehydrogenation of the riebeckite at an electron stripping value considerably less than 2. Whatever the case, the combination of ir and Mössbauer spectra provide evidence that the dehydrogenation mechanism is associated with electron transfer from the ferrous iron to the proton in the OH group. This process must be rapid because dehydrogenation is complete within one hour of heating in air at 705°C.

The overlapping Fe^{3+} peaks in P-ID could be resolved into two doublets (Fig. 5b). The intensity of the first Fe^{3+} doublet (CC′) accounts for 42.6 percent of the iron absorbance, that of the second (DD′) for 24.6 percent. The CC′ doublet has Mössbauer parameters and an intensity close to that inferred to represent Fe^{3+} in the $M(2)$ site of the natural riebeckite (Fig. 5a, doublet CC′) and thus was similarly assigned. The other doublet (peaks DD′) has Mössbauer parameters which clearly

indicate absorption by ferric iron; because the $M(2)$ assignment is already accounted for, and a 22.6 percent reduction in octahedral Fe^{2+} is dictated by the area under paired peaks AA′ and BB′, this last doublet must be assigned to Fe^{3+} in $M(1)$ and $M(3)$. Inasmuch as the population of Fe^{3+} in $M(1)$ and $M(3)$ sites (24.6 percent) of the oxidized sample, no. P-ID, agrees well with the decrease of Fe^{2+} (22.6 percent) in $M(1)$ and $M(3)$ sites compared to the starting material, riebeckite no. P–I, no appreciable migration of cations between different sites needs to have taken place during one hour of heating at 705°C in air.

The Mössbauer spectrum of the 94 hour heat-treated riebeckite (no. P-IC) was fitted by one Fe^{2+} and two Fe^{3+} doublets (Fig. 5c). The two Fe^{3+} doublets were identified as Fe^{3+} in the $M(2)$ site (peaks CC′) and Fe^{3+} in the $M(1)$ and $M(3)$ sites (peaks DD′) based on Mössbauer parameters similar to the spectrum of specimen no. P-ID (compare Figs. 5b and 5c). Intensities of the two Fe^{3+} doublets in the sample heated for the longer time period indicate 34.7 percent of the total iron in Fe^{3+} in $M(2)$ and 46.7 percent is Fe^{3+} in $M(1)$ and $M(3)$ positions. The intensity ratio of the two doublets is fairly close to 2 : 3 indicating almost equal preference for Fe^{3+} to occupy two $M(2)$ and three $M(1)+M(3)$ sites in this sodic oxyamphibole. This phenomenon could result in part from electron transfer. However, unless minor quantities of Fe^{2+} now reside in $M(2)$, some net loss of iron from this site is indicated; in any case, significant disordering of Fe^{3+} occurred during 94 hours of oxidation at 705°C under atmospheric pressure. The continued decrease in total Fe^{2+} population from 32.8 percent after one hour heating to 18.6 percent after 94 hours heating should be noticed. Inasmuch as dehydrogenation is complete after one hour of heating, the further oxidation must proceed by another mechanism unrelated to the dehydrogenation process.

The results of Mössbauer analyses of the natural and heat-treated magnesioriebeckite, no. C-4980, C-4980D and C-4980C, are given in Table 7. The spectra are reproduced in Figure 6. Peak assignments were made by analogy with riebeckite. The populations of iron in the different octahedral positions of natural magnesioriebeckite, no. C-4980, are calculated to be 22.4 percent Fe^{2+} in the $M(1)$ site, 9.2 percent Fe^{2+} in $M(3)$ and 68.4 percent Fe^{3+} in $M(2)$, peaks AA′, BB′ and CC′, respectively of Figure 6a. The cation proportions in these six-fold coordinated positions calculated from the "wet" analysis (Table 2) are 0.624 Fe^{2+} and 1.733 Fe^{3+}, or more than 26 percent ferrous iron, nearly 74 percent ferric, in reasonably good agreement with proportions derived from the Mössbauer analysis. The cation proportions of Table 2 demonstrate that the ratio of Fe^{2+} to OH should be considerably less than unity, provided the sample possesses the normal hydroxyl content characteristic of

TABLE 7. MÖSSBAUER ANALYSES OF NATURAL AND HEAT-TREATED MAGNESIORIEBECKITE, NO. C-4980

Sample no.	Duration of run (hrs)	Absorption by Fe²⁺						Absorption by Fe³⁺								
		I.S.	Q.S.	percent	I.S.	Q.S.	percent	I.S.	Q.S.	percent	I.S.	Q.S.	percent	I.S.	Q.S.	percent
C-4980[b]	0	1.14ᵃ	2.79ᵃ M (1)	22.4ᵃ	1.12	2.48 M (3)	9.2	—	—	—	—	—	—	0.39	0.44 M (2)	68.4
C-4980D	1	—	—	—	—	—	—	0.38	1.18 M (1)	30	0.45	0.84 M (3)	13	0.38	0.57 M (2)	57
C-4980C	94	—	—	—	—	—	—	0.37	1.23 M (1)	41	0.47	0.87 M (3)	19	0.35	0.60 M (2)	40

ᵃ I.S. and Q.S. expressed in mm/sec, relative to zero mm/sec for metallic iron; total Fe (Fe²⁺+Fe³⁺) taken as 100 percent (absorption or intensity=cation proportion).

ᵇ Line width for C-4980=0.29 mm/sec; for C-4980D and C-4980C=0.38 mm/sec.

amphiboles. However, as seen from the gravimetric analysis in Table 1, magnesioriebeckite, no. C-4980, apparently carries an exceptionally small amount of hydroxyl. The Mössbauer spectrum of the one hour heat-treated magnesioriebeckite, no. C-4980D, shows no Fe^{2+} absorption. This complete oxidation of all the ferrous iron is associated with the loss of the O–H band characteristic of the stretching of hydroxyls initially coordinated to Fe^{2+} as shown in the ir spectrum (Fig. 3). The overlapping Fe^{3+} peaks in the heat-treated magnesioriebeckite, nos. C-4980D and C-4980C, could be resolved into three quadrupole doublets (Fig. 6b, 6c). The Mössbauer parameters and intensities of these doublets in the C-4890D spectrum are 57 percent Fe^{3+} in the $M(2)$ site, 30 percent Fe^{3+} in $M(1)$ and 13 percent Fe^{3+} in $M(3)$, peaks CC′, DD′, and EE′ respectively of Figure 6b. The assignment of these doublets is based on their intensities and Mössbauer parameters compared with the natural magnesioriebeckite (Fig. 6a). The slight decrease in Fe^{3+} in the $M(2)$ site (from 68.4 percent to 57 percent) after one hour of heating suggests that migration of Fe^{3+} may have taken place to a slight but observable degree in magnesioriebeckite over this time period. The Mössbauer spectrum of the material heat treated for 94 hours, no. C-4980C, indicates 40 percent Fe^{3+} in $M(2)$, 41 percent Fe^{3+} in $M(1)$ and 19 percent Fe^{3+} in $M(3)$ (Fig. 6c). The ferric iron populations in octahedral positions thus exhibit virtually complete disordering for the magnesioriebeckite heated in air for nearly four days. As evident in Table 7, the $Q.S.$ for Fe^{3+} in $M(2)$ increases due to the heat treatment, whereas the $I.S.$ decreases; such changes suggest an increase in distortion of the site from octahedral symmetry (Bancroft, Burns and Stone, 1968, p. 549).

It may be mentioned in passing that a small unassigned marginal doublet evidently representing absorption by ferric iron is visible in the spectra of Figure 6b and 6c for heat-treated magnesioriebeckite. The peaks exhibit a smaller isomer shift but larger quadrupole splitting compared to that associated with six-fold coordinated Fe^{3+}. Similar to conclusions reached by Bancroft, Burns and Stone for yellow sapphirine (1968, Table 2 and p. 556), this doublet is tentatively referred to tetrahedral ferric iron. Alternatively, this doublet, could reflect the presence of optically undetected spinel or some other dehydration product. These small peaks are evidently swamped out in the spectrum of the untreated material, but are probably present judging from the Si+Al deficiency exhibited by the cation proportions computed from the chemical analysis (Table 2).

The Mössbauer analyses of natural and heat-treated glaucophane are presented in Table 8. Peaks were assigned by analogy with riebeckite and magnesioriebeckite. The spectrum of the natural material, no. TP-1,

shown in Fig. 7a, reflects 45.3 percent Fe^{2+} in the $M(1)$ site (peaks AA'), 31.5 percent Fe^{2+} in the $M(3)$ site (peaks BB') and 23.2 percent Fe^{3+} in the $M(2)$ site (peaks CC'). The cation proportions in these octahedral positions computed from the gravimetric analysis (Table 2) are $0.695 Fe^{2+}$ and $0.295\ Fe^{3+}$, or slightly more than 70 percent ferrous iron, almost 30 percent ferric; these proportions agree moderately well with those obtained by the Mössbauer study. Natural glaucophane is one of the sodic amphiboles investigated with a rather low oxidation ratio and shows a high preference of Fe^{2+} in $M(3)$ over $M(1)$. Heating glaucophane for one hour at 705°C in air only oxidized part of the Fe^{2+} (29.9 percent of

TABLE 8. MÖSSBAUER ANALYSES OF NATURAL AND HEAT-TREATED
GLAUCOPHANE, NO. TP-1

Sample no.	Duration of run (hrs)	Absorption by Fe^{2+}						Absorption by Fe^{3+}					
		I.S	Q.S.	per-cent	I.S.	Q.S.	per-cent	I.S.	Q.S.	per-cent	I.S.	Q.S.	per-cent
TP-1	0	1.13	2.81 M(1)	45.3	1.10	2.30 M(3)	31.5	—	—	—	0.34	0.48 M(2)	23.2
TP-1A	1	1.11	2.82 M(1)	31.6	1.13	2.14 M(3)	15.3	0.43	1.22 M(1)+M(3)	26.9	0.31	0.59 M(2)	26.2
TP-1B	95	—	—	—	—	—	—	0.39	1.30 M(1)+M(3)	67.1	0.31	0.71 M(2)	32.9
TP-4XR	15667	1.15 M(1), or M(1) +M(2)+M(3)	2.74	25.6	—	—	—	—	—	—	0.39 M(2), or M(1) +M(2)+M(3)	0.54	74.4

[a] *I.S.* and *Q.S.* expressed in mm/sec, relative to zero mm/sec for metallic iron; total $Fe(Fe^{2+}+Fe^{3+})$ taken as 100 percent (absorption or intensity =cation proportion).

[b] Line width for TP-1 =0.25 mm/sec; for TP-1A =0.34 mm/sec; for TP-1B =0.60 mm/sec; for TP-4XR =0.40 mm/sec.

the total iron, instead of the 76.8 percent Fe^{2+} available) as shown in the spectrum TP–1A (Fig. 7b). This persistence of ferrous iron is also apparent from the ir spectrum (Fig. 4) in which the O–H stretching frequencies representing hydroxyl coordinated to Fe^{2+} are still observable in the one hour heat-treated sample. It is evident from Fig. 7a and 7b that the decrease of Fe^{2+} in $M(1)$ and $M(3)$ sites (peaks AA' and BB') is associated with the appearance of a new doublet (peaks DD') with *Q.S.* and *I.S.* values appropriate to ferric iron. This pair has been assigned to Fe^{3+} in the same $M(1)$ and $M(3)$ structural positions based on differences compared to the doublet representing Fe^{3+} in $M(2)$, CC'; peaks DD' possess a relative absorbance (hence reflect an atomic population) of 26.9 percent. The Mössbauer spectrum of no. TP-1B, glaucophane heated in air for 95 hours, showed no Fe^{2+} absorption (Fig. 7c). Its ir spectrum (Fig. 4) also shows a loss of all OH coordinated to Fe^{2+}. The

populations of Fe^{3+} in the $M(2)$ site and in the $M(1)+M(3)$ sites (peaks CC' and DD'; see also Table 8) roughly approach a 2:3 ratio and suggest disordering of Fe^{3+} (or at least the oxidation of small amounts of undetected ferrous iron residing in $M(2)$ initially) under the experimental conditions.

The Mössbauer spectrum of TP-4XR, natural glaucophane hydrothermally heated for 15,667 hours at 513°C, 2 kbar fluid pressure and at an f_{O_2} of about 10^{-22} bars, gave two observable quadrupole doublets, one for Fe^{2+} and one for Fe^{3+} (peaks AA' and CC' of Fig. 7d). The Mössbauer parameters are similar to those representing peaks for Fe^{2+} in $M(1)$ and Fe^{3+} in $M(2)$ exhibited by the natural glaucophane. The line width of the peaks for the hydrothermally-treated sample presented in Figure 7d is 0.40 mm/sec compared with 0.26/mm/sec for the natural glaucophane. These peaks may actually consist of overlapping doublets possessing very similar Mössbauer parameters because it is possible that after such a long period of heating, all of the six-fold coordinated sites approach similar octahedral geometries. However, if as they appear, they are not composite doublets, then a high degree of ordering would seem to be required to explain the concentration of Fe^{2+} in $M(1)$ and Fe^{3+} in $M(2)$—such a phenomenon could not account for the observed line broadening, however. The populations of Fe^{2+} and Fe^{3+} are 25.6 and 74.4 percents respectively, which is probably the equilibrium oxidation ratio for glaucophane of the specific bulk composition at this f_{O_2}. Considerable oxidation of the initial material evidently took place during the hydrothermal experiment inasmuch as the percentages of ferrous and ferric iron in no. TP-1 are about 70 and 30 percent respectively. The proportion of Fe^{2+} to OH in the natural glaucophane is considerably less than unit value according to the chemical analysis (Tables 1 and 2). However, the ir spectrum of TP-4XR (Fig. 4) shows a complete absence of the O–H absorption band in the region 3700 to 3600 cm^{-1}, even though Fe^{2+} is still present as deduced from the corresponding Mössbauer spectrum. The proposed rapid one-atmosphere dehydrogenation mechanism related to the oxidation of Fe^{2+} is not in complete agreement with this observation, hence another, perhaps slower, mechanism for the expulsion of hydrogen—possibly as molecular H_2O—must have been involved in addition. Differences in devolatilization mechanisms are plausible in the light of contrasting experimental conditions (i.e., one atmosphere, short run duration, oxidizing environment, $705 \pm 2°C$ versus 2000 bars aqueous fluid pressure, long run length, more nearly neutral redox environment, $613 \pm 10°C$).

The information obtained from the Mössbauer studies of the natural and heat-treated sodic amphiboles can be summarized as follows: (1)

In natural specimens, ferric iron is ordered in the $M(2)$ site and Fe^{2+} is distributed among $M(1)$ and $M(3)$. There is a slight tendency for Fe^{2+} to occupy preferentially the $M(3)$ position in glaucophane of low oxidation state (e.g., see also Papike and Clark, 1968, Table 2); in contrast, crossites and magnesioriebeckites of high ferric:ferrous ratio tend to concentrate Fe^{2+} in $M(1)$ (e.g., see Burns and Prentice, 1968, p. 775). (2) Oxidation of Fe^{2+} to Fe^{3+} occurs rapidly, on the order of an hour or two, when sodic amphibole is heated in air at 705°C. The stripping of electrons from Fe^{2+} is related to the dehydrogenation process, as deduced through Mössbauer and infrared observations. However, continued heating beyond completion of the dehydrogenation results in further oxidation but at a much slower rate—and by an unknown mechanism, possibly diffusion linked. (3) The one-atmosphere disordering of Fe^{3+} among octahedral positions $M(1)$ and $M(3)$ sites was observed after a relatively long period of heating ($\sim$90 hrs) at 705°C and one atmosphere total pressure; some of the Fe^{3+} disordering undoubtedly reflects simple electron transfer among iron atoms in edge-shared octahedra, but on the longer runs, atomic proportions roughly approach the ideal disordered values. Except for the sample of magnesioriebeckite, inappreciable migration of cations was observed in one hour of heating at this condition.

DISCUSSION

Judging from the previous sections dealing with infrared and Mössbauer spectra of natural and experimentally treated sodic amphiboles, several processes take place simultaneously, but at different rates, in material heated in air.

Most rapid is the dehydrogenation process whereby electrons are stripped from ferrous irons residing in $M(1)$ and $M(3)$ sites, allowing the evolution of hydrogen from neighboring hydroxyls. Probably it can be safely assumed that the rate of diffusion of neutral H_2 out of the sample is quite rapid compared to the length of the experiment. The increase in $Fe^{3+}:Fe^{2+}$ ratio and loss of O–H bonds results in elevated birefringence and indices of refraction of the run products proportional to the amount of oxidation (see Table 3). Oxidation also causes a concomitant decrease in unit cell volume (on the order of one percent for ferrous iron-poor sodic amphiboles such as nos. TP-1 and C-4890, more than two percent for Fe^{2+}-rich riebeckites such as nos. LO-1 and P-I), reflecting contraction along all crystallographic axes but scarcely affecting β. The decreased c repeat signifies an increased degree of kinking along the tetrahedral double chains, whereas contraction of a and $a \sin \beta$ indicates compression across octahedral and/or tetrahedral strips (chains). The

smaller b axis repeat results from a closer approach of adjacent tetrahedral double chains parallel to the b direction produced by distortion of the octahedral sites—as suggested also by interpretation of the Mössbauer spectra; the phenomenon occurs in spite of a tendency for octahedral cation disordering, which Colville, Ernst and Gilbert (1966) showed, tends to lengthen the b repeat.

Once the hydrogen has been expelled from the structure, or at least removed from the $O(3)$ site, further oxidation of iron apparently proceeds by a much slower reaction. Although the process has not been elucidated by the present study, results are compatible with the mechanism of electron switching or diffusion proposed by Addison and White (1968). Here electrons derived from initially Fe^{2+} ions are thought to migrate toward the surface of individual crystals, and are transferred through marginal iron cations to external attracted oxygens, which are thereby bound as an anionic surface layer. Presumably the extent to which this mechanism could operate would be a function of grain size, but the present investigation did not test this effect.

The hydrothermal experiment of nearly two years' duration on glaucophane, no. TP-4XR, yielded perplexing and conflicting results. Judging from its optical and X-ray properties, the run product is still a sodic clinoamphibole—albeit an anhydrous one. Although all O–H stretching frequencies were lost, the dehydrogenation was accompanied by only partial oxidation, even though initially the Fe^{2+} to OH ratio was less than unity. It is conceivable that molecular H_2O was released during the course of the hydrothermal experiment, resulting in an amphibole anhydride (see Hodgson, Freeman and Taylor, 1965); here local charge balance might be maintained by random omission of oxygens. Furthermore, as compatible with the Mössbauer analysis, the Fe^{2+} and Fe^{3+} could have been markedly ordered in $M(1)$ and $M(2)$ positions respectively by the heat treatment (but this would fail to explain the rather high line widths observed, 0.40 mm/sec). The unit cell volume increased by more than three percent, reflecting large increments in a and b axis lengths. This effect is understandable in light of the hypothesized random anion defects, which would tend to cause inflation of the structure due to cation—[omission]—cation repulsions. Nonetheless, regardless of the enlarged cell volume, refringence increased considerably. Evidently indices of refraction in this sodic amphibole are more nearly a function of hydroxyl content and $Fe^{3+}:Fe^{2+}$ ratio than of volume. The expanded amphibole cell may be explicable in terms of rather thorough disordering among octahedral cations and possibly random anion defects; therefore, it is tentatively concluded that the Mössbauer spectrum for no. TP-4XR (Fig. 7d) should be interpreted as nearly completely disordered ferric

and ferrous iron occupancy of six-fold coordinated positions of closely similar structural configurations (Table 8). This conclusion is supported not only by the line broadening observed in the Mössbauer spectrum of Figure 7d for the hydrothermally treated glaucophane, but is perhaps also reflected by the lowered birefringence of the run products (Table 3); such a decrease in $N_\gamma - N_\alpha$ (from 0.020 in no. TP-1, to 0.009 in no. TP-4XR) is compatible with lesser distortions and closer similarities among all octahedral sites.

Somewhat analogous to results presented by Bancroft and Burns (1969), this investigation demonstrates that natural sodic amphiboles exhibit a marked tendency for ferric iron to be ordered in $M(2)$, ferrous iron in $M(1)$ and $M(3)$. Aluminous members of the series tend to have Fe^{2+} concentrated in $M(3)$ relative to $M(1)$; the latter site is thereby relatively enriched in Mg and possibly other non-ferrous cations. In contrast, the converse situation applies for ferric iron-rich sodic amphiboles.

Finally, optical and X-ray measurements presented in Table 3 are in accord with the results of previous workers (*e.g.*, Miyashiro, 1957; Deer, Howie and Zussman, 1963, Fig. 82; Colville, Ernst and Gilbert, 1966; Borg, 1967b; Coleman and Papike, 1968) which have documented systematic increments in refractive indices and unit cell dimensions of natural sodic amphiboles with increasing iron content.

References Cited

Addison, C. C., W. E. Addison, G. H. Neal, and J. H. Sharp (1962) Amphiboles. Part I. The oxidation of crocidolite. *J. Chem. Soc.* **1962,** 1468–1471.

Addison, W. E., G. H. Neal, and J. H. Sharp (1962) Amphiboles. Part II. The kinetics of the oxidation of crocidolite. *J. Chem. Soc.* 1472–1475.

———, and A. D. White (1968) The oxidation of Bolivian crocidolite. *Mineral. Mag.* **36,** 791–796.

Ahlfeld, F. (1943) Los yacimientos de crocidolita en las yungas de Cochabamba. *Notas Museo La Plate* **8** (*Geol. No. 27*), 355–371.

Bancroft, G. M., and R. G. Burns (1969) Mössbauer and absorption spectral study of alkali amphiboles. *Mineral. Soc. Amer. Special Pap.* **2,** 137–148.

———, R. G. Burns, and A. G. Maddock (1967) Determination of cation distribution in

the cummingtonite-grunerite series by Mössbauer spectra. *Amer. Mineral.* **52,** 1009–1026.

————, A. G. MADDOCK, AND R. G. BURNS (1967) Applications of the Mössbauer effect to silicate mineralogy—I. Iron silicates of known crystal structure. *Geochim. Cosmochim. Acta* **31,** 2219–2246.

————, R. G. BURNS, AND A. J. STONE (1968) Applications of the Mössbauer effect to silicate mineralogy—II. Iron silicates of unknown and complex crystal structures. *Geochim. Cosmochim. Acta* **32,** 547–559.

BANNO, S. (1959) Notes on rock-forming minerals (1) glaucophanes and garnet from the Kotu District, Shikoku. *J. Geol. Soc.* **65,** 658–663.

BARNES, V. E. (1930) Changes in hornblende at about 800°C. *Amer. Mineral.* **15,** 393–417.

BORG, I. Y. (1967a) On conventional calculations of amphibole formulae from chemical analyses with inaccurate H₂O(+) and F determinations. *Mineral. Mag.* **36,** 583–590.

———— (1967b) Optical properties and cell parameters in the glaucophane-riebeckite series: *Contrib. Mineral. Petrology,* **15,** 67–92.

BURNS, R. G., AND R. G. J. STRENS (1966) Infrared study of the hydroxyl bands in clino-amphiboles. *Science,* **153,** 890–892.

———— (1968) Enrichments of transition-metal ions in silicate crystal structures. *In* L. H. Ahrens (ed.), *Origin and Distribution of the Elements.* Pergamon, Oxford, 1151–1164.

————, AND F. J. PRENTICE (1968) Distribution of iron cations in the crocidolite structure. *Amer. Mineral.* **53,** 770–776.

CLARK, M. W., AND A. G. FREEMAN (1967) Kinetics and mechanism of dehydration of crocidolite. *Trans. Faraday Soc.* **63,** 2051–2056.

COLEMAN, R. G. AND J. J. PAPIKE (1968) Alkali amphiboles from the blueschists of Cazadero, California. *J. Petrology* **9,** 105–122.

COLVILLE, A. A., AND G. V. GIBBS (1965) Refinement of the crystal structure of riebeckite (abstr.). *Geol. Soc. America 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 p.

ERNST, W. G. (1960), The stability relations of magnesioriebeckite. *Geochim. Cosmochim. Acta,* **19,** 10–40.

———— (1963) Polymorphism in alkali amphiboles. *Amer. Mineral.* **48,** 241–260.

———— (1968) Amphiboles, crystal chemistry, phase relations and occurrences. Springer-Verlag, Inc., New York, 125 p.

———— (in press) Element partitioning in blueschist tectonic inclusions from serpentinites, California Coast Ranges, and a discussion of blueschist tectonics. *In* N. L. Dobretsov (ed.), Sobolev Volume, Akad. Nauk SSSR, Sibir. Otdel., Inst. Geol. Geof.

EUGSTER, H. P., AND D. P. WONES (1962) Stability relations of the ferruginous biotite, annite. *J. Petrology* **3,** 82–125.

FINGER, L. (1969) Crystal structure and cation distribution of a grunerite. *Mineral. Soc. Amer. Spec. Pap.* **2,** 95–100.

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.

———— (1965) A scheme of cation distribution in the amphiboles. *Mineral. Mag.* **35,** 46–54.

HALL, A. L. (1930) Asbestos in the Union of South Africa. *Mem. Geol. Surv. Union S. Afr.* **12,** 329 p.

HEINRICH, E. W., AND A. A. LEVINSON (1961) Carbonatic niobium-rare earth deposits, Ravalli County, Montana. *Amer. Mineral.* **46,** 1424–1447.

HERBER, R. H. (1967) The Mössbauer effect and its application in chemistry. *In*, R. F. Gould (ed.) *Advances in Chemistry, Ser.* **68,** Amer. Chem. Soc., Washington, D.C., 1–20.

HODGSON, A. A., A. G. FREEMAN, AND H. F. W. TAYLOR (1965) The thermal decomposition of crocidolite from Koegas, South Africa. *Mineral Mag.* **35,** 5–30.

KLEIN, C. (1964) Cummingtonite-grunerite series: a chemical, optical and x-ray study. *Amer. Mineral.* **49,** 963–982.

KÜNDIG, W., H. BÖMMEL, G. CONSTABARIS, AND R. H. LINDQUIST (1966) Some properties of supported small α-Fe_2O_3 particles determined with the Mössbauer effect. *Phys. Rev.* **142,** 327.

MIYASHIRO, A. (1957) The chemistry, optics, and genesis of the alkai-amphiboles. *J. Fac. Sci. Univ. Tokyo, Sec. 2,* **11,** 57–83.

ONUKI, H., AND W. G. ERNST (1969) Coexisting sodic amphiboles and sodic pyroxenes from blueschist facies metamorphic rocks. *Mineral. Soc. Amer. Spec. Pap.* **2,** 241–250.

PAPIKE, J. J., AND J. R. CLARK (1968) The crystal structure and cation distribution of glaucophane. *Amer. Mineral.* **53,** 1156–1173.

——, M. ROSS, AND J. R. CLARK (1969) Crystal-chemical characterization of clino-amphiboles based on five new structural refinements. *Mineral. Soc. Amer. Spec. Pap.* **2,** 117–136.

PATTERSON, J. H. (1965) The thermal disintegration of crocidolite in air and in vacuum. *Mineral. Mag.* **35,** 31–37.

——, AND D. J. O'CONNOR (1966) Chemical studies of amphibole asbestos. I. Structural changes of heat-treated crocidolite, amosite, and tremolite from infrared absorption studies. *Aust. J. Chem.* **19,** 1155–1164.

PEACOCK, M. A. (1928) The nature and origin of the amphibole asbestos of South Africa. *Amer. Mineral.* **13,** 241–285.

SHANNON, R. D., AND C. T. PREWITT (1969) Effective ionic radii in oxides and fluorides. *Acta. Crystallogr. B,* **25,** 925–946.

SWITZER, G. (1951) Mineralogy of the California glaucophane schists. *Bull. Calif. Div. Mines* **161,** 51–70.

VEDDER, W. (1964) Correlations between infrared spectrum and chemical composition of mica. *Amer. Mineral.* **49,** 736–768.

——, AND R. W. T. WILKINS (1969) Dehydroxylation and rehydroxylation, oxidation and reduction of micas. *Amer. Mineral.* **54,** 482–509.

VIRGO, D., AND S. S. HAFNER (1970) Fe^{2+}, Mg order-disorder in natural orthopyroxenes. *Amer. Mineral.* **55,** 201–223.

WERTHEIM, G. K. (1964) Mössbauer effect: principles and application. *Academic Press,* New York, 116 p.

WHITFIELD, H. J., AND A. G. FREEMAN (1967) Mössbauer study of amphiboles. *J. Inorg. Nucl. Chem.* **29,** 903–914.

WHITTAKER, E. J. W. (1949) The structure of Bolivian crocidolite. *Acta Crystallogr.* **2,** 312–317.

—— (1960) The crystal chemistry of the amphiboles. *Acta Crystallogr.* **13,** 291–298.