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THE EFFECT OF Mg^{2+}—Fe^{2+} SUBSTITUTION ON THE CELL DIMENSIONS OF CUMMINGTONITES

K. VISWANATHAN AND SUBRATA GHOSE, *Institut für Kristallographie und Petrographie, Eidg. Technische Hochschule, Zurich, Switzerland*

INTRODUCTION

Recently Klein (1964) has determined optical properties, chemical compositions and cell dimensions of nine cummingtonites and suggested that a linear relationship exists among cell dimensions: $a \sin \beta$ and b and the composition. He has shown that b varies considerably with composition, whereas $a \sin \beta$ and c vary very little.

Previous to the publication of this paper, we started work on the cummingtonite-grunerite series, with a view to determine the influence of $Mg^{2+} - Fe^{2+}$ substitution on the cell dimensions. Though our results are similar in nature to those of Klein, they show slight discrepancies. Klein's figures, expressing the variation in the cell dimensions, are based on the data of only 6 grunerites, whereas the figures presented in this paper depend upon the data of 21 specimens. Hence we decided to publish our results and offer a structural explanation for the anisotropic expansion of the cell dimensions due to $Mg^{2+} - Fe^{2+}$ substitution.

EXPERIMENTAL

The cummingtonites studied came from the metamorphosed iron formation of east-central Quebec and were obtained through the courtesy of Dr. R. F. Mueller. The iron formation has been investigated by

Mueller (1960, 1961, 1962) with reference to the equilibrium and solid solution relationships in mineral assemblages. For chemical analyses of the cummingtonites used in this study, see Table 1 (Mueller, 1960). These cummingtonites show a gradual variation in $Mg^{2+}/(Mg^{2+}+Fe^{2+})$ ratio and provide excellent material for the proposed study. Al_2O_3 content in these cummingtonites is very low, usually $\sim 0.2\%$, and MnO varies from 0.47 to 2.05% with an average of 1.06%.

For the determination of the cell dimensions, a Guinier type powder

TABLE 1. 2θ VALUES OF SELECTED CUMMINGTONITE-REFLECTIONS
Estimated error ± 0.02 for all except (0.12.0)
Wavelength to be used to convert these values into d-spacings is 1.5412 Å.

No.	Sp. No.	200	040	$\bar{1}11$	220	$\bar{1}31$	131	240	310	151	061	$\bar{2}02$	0.12.0
1	1 B	18.91	19.27	18.29	21.23	22.83	25.63	27.10	28.96	32.27	33.82	35.67	60.17
2	8 B	18.90	—	18.27	21.23	22.82	25.64	27.10	28.94	32.26	33.82	35.68	60.17
3	9 B	18.92	19.24	18.27	21.23	22.83	25.63	27.10	28.94	32.24	33.80	35.66	60.14
4	B 17	18.90	19.28	18.26	21.27	22.86	25.66	27.14	28.96	32.31	33.88	35.70	60.26
5	B 14	18.96	19.34	18.29	21.30	22.89	25.71	27.20	29.00	32.36	33.94	35.72	60.45
6	B 16	18.95	19.31	18.29	21.30	22.87	25.70	27.19	29.01	32.36	33.95	35.72	60.47
7	B 15	—	19.36	18.32	21.33	22.91	25.72	27.22	29.04	32.39	33.98	35.73	NM
8	B 13	—	19.37	18.32	—	22.91	25.73	27.24	29.04	32.39	33.99	35.73	60.52
9	B 19	18.97	19.35	18.30	21.32	22.91	25.72	27.24	29.03	32.41	34.00	35.75	60.56
10	DH-10-169	18.96	19.40	18.31	21.33	22.92	25.73	27.25	29.03	32.43	34.04	35.75	60.65
11	DH- 9-324	—	—	18.29	21.31	22.91	25.72	27.24	29.02	32.42	34.03	35.73	60.69
12	DH- 5- 77	18.91	—	18.34	21.34	22.94	25.76	27.26	29.03	32.44	34.04	35.73	60.68
13	6 B	—	19.39	18.31	21.33	22.93	25.74	27.25	29.05	32.43	34.02	35.75	60.61
14	DH-10-131	—	19.42	18.33	21.35	22.93	25.77	27.27	29.05	32.45	34.06	35.75	60.71
15	DH- 3-172	18.99	19.41	18.32	21.33	22.94	25.77	27.26	29.05	32.47	34.07	35.75	NM
16	7 B	—	19.43	18.36	21.37	22.96	25.79	27.31	29.09	32.48	34.09	35.80	60.80
17	B-22-A	—	19.44	18.35	21.39	22.97	25.79	27.32	29.11	32.50	34.11	35.80	60.80
18	DH- 7-490	—	19.53	18.39	21.44	23.02	25.85	27.41	29.18	32.58	34.21	35.85	61.11
19	DH-10- 78	—	19.52	18.35	21.42	23.02	25.84	27.39	29.16	32.57	34.21	35.85	61.10
20	DH-10- 95	—	19.54	18.35	21.44	23.04	25.88	27.41	29.15	32.64	34.25	35.84	61.14
21	DH- 7-482	—	19.54	18.41	21.47	23.06	25.92	27.46	29.20	32.68	34.32	35.87	61.26

NM—Not measurable

camera, developed by Hofmann and Jagodzinski (1955) has been used. The powder patterns were indexed with the aid of powder data given by Kohn and Comeforo (1955) and Jaffe *et al.* (1961). Principally monochromatic $CuK\alpha_1$ radiation has been used though in some diagrams the presence of $CuK\alpha_2$ was noticed, which was caused by a slight misalignment of the camera. In such cases, the wave length to be used for the calculation of cell dimensions was corrected, the correction being based on the intensity of the $CuK\alpha_2$ lines. Since a very good resolution is obtained in this camera ($1°\theta = 4$ mm), the lines could be measured very accurately. An aluminium filter was used for the iron-rich cummingtonites. Silicon served as an internal standard. In view of the experimental procedure adopted, it is expected that errors in the measurement of Bragg

angles of sufficiently intense lines should not exceed $\pm 0.01°$. Hence, a sin β and a are expected to be accurate to ± 0.005 Å, b to ± 0.010 Å and β to $\pm 5'$. The same degree of accuracy is not claimed for c sin β and c, since there is no sharp intense line, which contains 'l' alone or higher orders of 'l' in its indices and we had to depend on (131), ($\bar{1}$31), (151) and ($\bar{2}$02) lines. a sin β was determined chiefly from the (310) reflection which is quite intense and sharp. Though it contains 'k,' it does not seriously matter, as b could be determined accurately from (061) and (0, 12, 0) re-
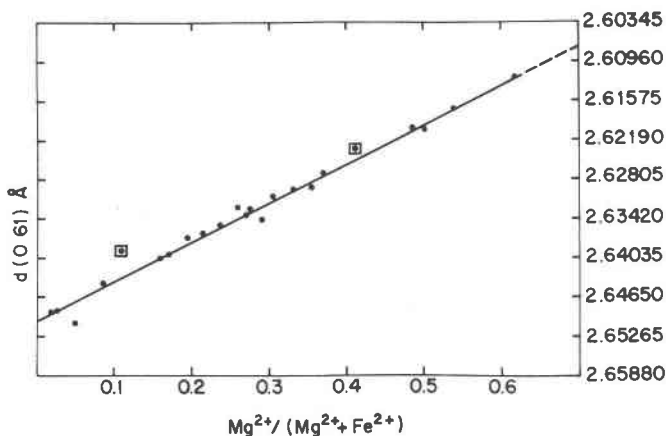

FIG. 1. X-ray determinative curve for $Fe^{2+}-Mg^{2+}$ cummingtonites. The equation of the graph is

$$d(061) = 2.65019 \text{ Å} - 0.000615 \text{ Å (mg)}$$
$$\text{where mg} = 100 \cdot Mg^{2+}/(Mg^{2+} + Fe^{2+}).$$

Error in the measurement of d-spacings ± 0.002 Å. Squares indicate Klein's (1964) values. (Klein's Nos. 1 and 10 A).

flections. The value of a sin β was checked against other reflections, such as (200), (220) and (240). Similarly, b was determined from (061) and (0, 12, 0) and checked against (040), (220), (240) and (151). The accuracy of the final cell parameters was checked for each specimen by calculating the d-spacings for all the twelve reflections, mentioned in Table 1 and by comparing them with the observed d-spacings. The agreement between the calculated and the observed d-spacings was found to be good.

RESULTS

Table 1 lists 2θ values for (200), (040), ($\bar{1}$11), (220), ($\bar{1}$31), (131), (240), (310), (151), (061), ($\bar{2}$02) and (0, 12, 0) reflections. The effective wave length to be used to convert these values to d-spacings is 1.5412 Å. The

estimated error is $\pm 0.02°$ Å (for 2θ values), except for $(0, 12, 0)$, in which case it is much higher.

Figure 1 shows a plot of d (061) *vs.* $Mg^{2+}/(Mg^{2+}+Fe^{2+})$ ratios of cummingtonites. This graph can be used to determine the composition of $Mg^{2+}-Fe^{2+}$ cummingtonites. For this purpose, (061) is preferred over $(0, 12, 0)$, since the latter is comparatively weak and sometimes fuzzy.

TABLE 2. COMPOSITIONS AND CELL DIMENSIONS OF CUMMINGTONITES
Space group $C\ 2/m$.

No.	Specimen No	$Mg^{2+}/$ $(Mg^{2+}+Fe^{2+})$	a Sin β (Å)	b (Å)	c Sin β (Å)	β	a (Å)	c (Å)
1	1 B	0.0197	9.378	18.448	5.228	101°57′	9.586	5.344
2	8 B	0.0248	9.383	18.448	5.226	102°02	9.594	5.344
3	9 B	0.0517	9.385	18.453	5.227	101°57	9.593	5.343
4	B 17	0.0854	9.379	18.413	5.224	101°58	9.588	5.340
5	B 14	0.1600	9.365	18.364	5.218	102°01	9.576	5.335
6	B 16	0.1690	9.361	18.364	5.224	102°03	9.572	5.342
7	B 15	0.197	9.354	18.348	5.217	101°58	9.562	5.333
8	B 13	0.217	9.353	18.333	5.218	102°01	9.563	5.335
9	B 19	0.235	9.356	18.332	5.220	102°00	9.565	5.337
10	DH-10-169	0.259	9.356	18.312	5.220	102°01	9.566	5.337
11	DH- 9-324	0.270	9.359	18.307	5.224	102°01	9.569	5.340
12	DH- 5- 77	0.274	9.358	18.307	5.210	102°01	9.568	5.327
13	6 B	0.292	9.349	18.317	5.216	101°59	9.557	5.332
14	DH-10-131	0.305	9.349	18.296	5.213	102°05	9.561	5.331
15	DH- 3-172	0.332	9.348	18.281	5.217	102°04	9.559	5.335
16	7 B	0.354	9.339	18.271	5.210	102°02	9.549	5.327
17	B-22-A	0.369	9.331	18.268	5.211	101°58	9.539	5.327
18	DH- 7-490	0.483	9.312	18.189	5.205	102°01	9.521	5.322
19	DH-10- 78	0.498	9.317	18.199	5.204	101°59	9.525	5.320
20	DH-10- 95	0.539	9.319	18.174	5.197	102°04	9.530	5.314
21	DH- 7-482	0.622	9.304	18.139	5.193	102°07	9.516	5.311

Moreover, $(0, 12, 0)$ tends to merge with comparatively more intense $(35\bar{3})$ reflection, with increasing Mg^{2+}-content. Therefore, it is advisable not to depend on the $(0, 12, 0)$ reflection for obtaining correct b values, especially in the case of cummingtonites with $Mg^{2+}/(Mg^{2+}+Fe^{2+})$ ratios higher than 0.35, as the overlapping of lines takes place somewhere between 0.40 and 0.60 of this ratio.

Table 2 lists cell dimensions against composition. The values of a, a sin β, b and c are plotted against composition in Fig. 2. Within the limits of error, the relationships are linear. The variation of c should be taken with caution, since the accuracy in the determination of c is low. Our curves for a sin β and b lie about 0.01 Å higher than those of Klein.
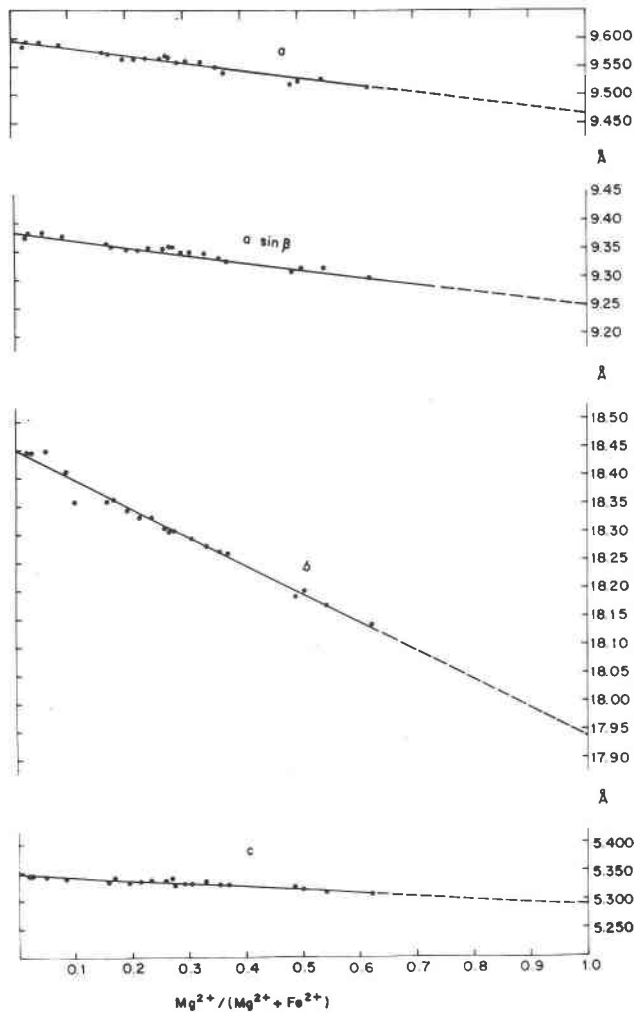
FIG. 2. Cell dimensions *vs.* composition of cummingtonites.

The linear relationships among cell dimensions and composition of cummingtonites can be expressed by the following equations:

$$a = 9.467 \text{ Å} + 0.00128(100 - mg) \text{ Å}$$
$$a \sin \beta = 9.252 \text{ Å} + 0.00133(100 - mg) \text{ Å}$$
$$b = 17.935 \text{ Å} + 0.00517(100 - mg) \text{ Å}$$
$$c = 5.292 \text{ Å} + 0.00055(100 - mg) \text{ Å}$$
$$\text{where } mg = 100 \cdot \text{Mg}^{2+}/(\text{Mg}^{2+} + \text{Fe}^{2+}).$$

DISCUSSION

It is interesting to compare the above equations with those given by Hess (1952) for orthopyroxenes. His equations are:

$$a = 18.228 \text{ Å} + 0.00205(100 - mg) \text{ Å}$$
$$b = 8.805 \text{ Å} + 0.00255(100 - mg) \text{ Å}$$
$$c = 5.185 \text{ Å} + 0.00073(100 - mg) \text{ Å}$$
$$\text{where } mg = 100 \cdot Mg^{2+}/(Mg^{2+} + Fe^{2+} + Fe^{3+}).$$

It should be noted that the ratios of the coefficient of expansion, α to the corresponding cell dimension in both minerals are approximately the same; *e.g.* α/a of cummingtonite is 0.000135, α/a of orthopyroxene 0.000113, and α/b of cummingtonite 0.000288, α/b of orthopyroxene 0.000290. The approximate equality of corresponding values indicate that the factors responsible for the expansion in these cell dimensions of both minerals are the same. The rate of expansion, however, is strongly anisotropic. In cummingtonite α/b is more than twice that $\alpha/(a)$ and $\alpha/(c)$ is less than $\alpha/(a)$.

The structure of cummingtonite (Ghose, 1961) consists of two silicate double chains, having the formula Si_4O_{11} and a strip of (Mg^{2+}, Fe^{2+}) ions in octahedral coordination with oxygen and hydroxyl ions, sandwiched between them. The silicate double chains are slightly curved away from the layer of the metal atoms to effect a better fit between the octahedral metal layer and the tetrahedral silicate layer. The resulting talc like stripes are held together by (Fe^{2+}, Mg^{2+}) ions. The structure of orthopyroxene (Ghose, 1964) is closely related to that of cummingtonite. In orthopyroxene, the silicate chains are single and sandwich a strip of (Mg^{2+}, Fe^{2+}) ions between them. In this structure also the strips are held together by (Fe^{2+}, Mg^{2+}) ions, in contrast to the clinopyroxenes, in which it is Ca^{2+}.

In both cummingtonite and orthopyroxene the silicate chains determine the c repeat distance. An extension of silicate chains would mean an increase in the Si-O-Si angle. In cummingtonite the Si-O-Si angles in question are 141.4 and 142.2° and in orthopyroxene (hypersthene) 139.5 and 132.2°. Since in cummingtonite these angles are already larger than the equilibrium value of 140° (Liebau, 1961), any further stretching of the chains would create strain in the structure and must necessarily be limited. In hypersthene the chains can be stretched somewhat further without causing strain.

The substitution of Mg^{2+} by Fe^{2+} would increase the size of the coordination octahedron. An increase in size in a reflects this overall increase in size of the octahedron. In both structures the octahedral strips lie parallel to bc (100). The strips are 2–4 octahedra wide parallel to b, the

strip transmission direction being parallel to c. But since the expansion of octahedra along c is limited for reasons stated above, the octahedra expand effectively along b. The increase in b, therefore, is due to the sum of expansions of these 2–4 octahedra.

It is interesting to note that in clinopyroxenes, the rate of expansion of b, due to $Mg^{2+} - Fe^{2+}$ substitutions (Brown, 1960) is the same as that found in cummingtonite and orthopyroxene. The considerable change in $a \sin \beta$ of clinopyroxene is caused by the substitution of Ca^{2+} by Fe^{2+} or Mg^{2+}. This can be easily explained, since Ca^{2+} in this structure holds the talc like strips together; when Ca^{2+} is replaced by a much smaller Fe^{2+} or Mg^{2+} ion, the coordination number decreases from 8 to 6 and the talc like strips are brought much closer together along a.

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