COMPOSITIONAL VARIATIONS IN COOKEITE

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ABSTRACT

Assuming an ideal anionic composition, the lithium-aluminum chlorite cookeite shows a fairly constant tetrahedral population Al_2Si_6; subordinate B and Be may occasionally substitute for Al. Some Na, Ca, Mg, and K, Fe^{2+} can play the role of octahedral cations; the large cations may be accommodated between the 2:1 sandwiches and "brucite" sheets. The main octahedral substitution is $3(Li, alk.)^{1+}/Al^{3+}$, probably extending up to Li-low and Li-free donbassite and sudoite, and that involving the bivalent cations is $3R^{2+}/2Al^{3+}$. Some fluorine substitutes frequently for OH. There seems to be no need for the name "hydrocookeite".

INTRODUCTION

Cookeite, a di/trioctahedral Li,Al-chlorite with idealized formula $Li_2Al_8[Al_2Si_6O_{20}(OH)_{16}]$, is a fairly frequent constituent of many lithium-bearing pegmatites and has been encountered also in other parageneses. Unfortunately, in most instances its mode of occurrence does not permit thorough investigation. The separation of pure cookeite for chemical analysis is particularly difficult because its flakes are often intimately intergrown with other minerals.

Seventeen years ago, Ginzburg (1953) was the first author to draw attention to the variations in the chemical composition of cookeite, particularly in its octahedral occupancy. However, he could discuss only two new analyses of his own and five analyses taken from literature, some of them of doubtful quality. Since that time much more information has accumulated. The crystallochemical evaluation of these and earlier data is presented here.

AVAILABLE DATA AND THEIR TREATMENT

Chemical analyses of 16 cookeites, and one of the boron-rich manandonite, have been collected from the available literature. Fourteen of them are used in this study, and three are rejected. Penfield's (1893) analysis indicates that the composition of the Hebron, Maine cookeite is more complicated than suggested by Brush's data (1866); of two analyses

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published by Quensel (1937, 1956) one refers to a cookeite contaminated with quartz, and the correction of the other for a high quartz admixture does not seem to be reliable. Some of the other analyses used here are quite old, and are questionable as to the accuracy of the lithium and aluminum determinations. However, they compare well with modern data and their potential faults could not be excessive.

This prescreening of available chemical analyses always tends to be subjective, and the recalculations described below are inevitably based on a series of assumptions. Hence all analyses published to date are presented in Table 1, to give the reader a chance to draw his own conclusions.

In this study, the chemical analyses were recalculated to atoms per 1-layer unit cell, on the basis of 56 cationic valences required by the theoretical $O_{20}(OH)_{16}$ content (Foster 1962). For obvious crystallochemical reasons, beryllium and boron were coupled with silicon (*cf.* Strunz 1957), and enough aluminum was added to bring the total number of cations in the tetrahedral group to 8. The remainder of the aluminum and all other cations were allocated to the octahedral sites, more or less rigorously as discussed below. Trivalent iron was placed in this group deliberately; its possible tetrahedral coordination would not influence the conclusions derived here. The alkali and alkaline earth elements are assumed to belong to cookeite itself, and no attempts were made to deduct them in some fashion since there is no sound basis for doing so.

The ionic compositions of 13 cookeites, arranged according to decreasing lithium content, are listed in Table 2; manandonite is also shown for comparison. Some important relations among the octahedral cations are illustrated in Figs. 1 and 2.

DISCUSSION

Tetrahedral substitutions

The formulae calculated by Ginzburg (1953) show considerable variation in the Si/Al ratio. However, this is due to an evidently erroneous formula of the Lipovka cookeite (with very low total cationic charge and low Si content), and to the Varuträsk cookeite contaminated by quartz (*cf.* Quensel 1956).

The present results show that the silicon content of the idealized formula, $Li_2Al_8[Al_2Si_6O_{20}(OH)_{16}]$, is closely approached in all natural cookeites. The mean value is 6.08, with variation range 5.86–6.33. Consequently, the Al^{IV}-content is also rather constant, but can be considerably decreased by boron and/or beryllium substitution. The cookeites from Muiane and Radkovice show considerable content of these elements.

The sum of tetrahedral (Al + Be + B) is close to 2 in both cases,

TABLE 1. CHEMICAL ANALYSES OF COOKEITE

	1	3	4	5	6	7	8	9
SiO_2	34.00	34.81	33.31	34.08	34.15	33.40	35.49	34.92
TiO_2	—	—	tr.	0.019	—	—	—	—
Al_2O_3	45.06	45.90	44.16	45.30	46.35	47.47	44.36	46.29
Fe_2O_3	0.45	0.72	1.72	0.192	0.02	0.00	0.12	0.07
B_2O_3	—	—	—	—	0.38	—	—	—
FeO	—	—	1.69	—	—	0.71	0.24	—
MnO	—	tr.	0.18	tr.	—	tr.	tr.	0.13
CaO	0.04	tr.	0.00	0.57	0.16	0.45	0.26	0.30
MgO	—	—	0.37	1.02	tr.	0.20	1.32	0.24
BeO	—	—	—	—	1.06	—	—	—
Li_2O	4.02	3.59	3.40	3.09	3.18	3.12	2.74	2.67
Na_2O	0.19	0.52	0.70	0.07	0.10	0.09	1.12	0.14
K_2O	0.14		0.67	tr.	tr.		0.14	—
H_2O+	14.96	14.87	13.19	14.22	14.06	14.98	13.84	14.12
H_2O-		—	0.46	0.38	0.42	0.23	0.55	0.28
F	0.46	0.13	0.00	—	0.35	tr.	—	—
total	95.30	100.54	99.85	98.998	100.30	100.65	100.28	99.05
−O = 2F	0.19	0.06			0.15			
	95.09	100.48			100.15			

1. Cookeite Hebron, Maine, U.S.A. (Penfield 1894); in pegmatite cavities.
3. Cookeite Buckfield, Maine, U.S.A. (Landes 1925); associated with quartz and minor apatite, herderite in pegmatite vugs; separated for analysis in heavy liquids.
4. Cookeite northwestern U.S.S.R. (Zvyagin & Nefedov 1954); replaces, and is associated with, coarse-flaked lepidolite in pegmatite; no admixtures in the analyzed material.
5. Cookeite Dobrá Voda, Czechoslovakia (Černý *et al.* 1970); cavity lining in pegmatite, associated with quartz, apatite, tourmaline, and cassiterite; contamination of analyzed sample lower than 1%; the total includes 0.005 Ga_2O_3, 0.052 NiO.
6. Cookeite Muiane, Mozambique (Sahama *et al.* 1968); cavity lining in pegmatite with negligible quartz; no admixtures in the analyzed material.
7. Cookeite Kalbinski Range, U.S.S.R. (Ginzburg 1953); from pegmatite.
8. Cookeite Lipovka, Urals, U.S.S.R. (Ginzburg 1953); from pegmatite.
9. Cookeite Manono, Katanga (Herman *et al.* 1961); from pegmatite; contains 0,005% P_2O_5.

indicating that the boron and beryllium can enter the aluminum sites more easily than those of silicon. The same relations have been recognized also in other beryllium-bearing silicates (bityite—Ginzburg 1957, Beus 1960, bavenite—Switzer & Reichen 1960, Beus 1960, Berry 1963; cordierite—Černý & Povondra 1966) and in borosilicates (*e.g.* reedmergnerite—Milton *et al.* 1960, synthetic boron-gehlenite—Bauer 1962).

The charge balance in the Muiane cookeite can be maintained by the $[AlO_4]^{-5}/[BeO_3(OH)]^{-5}$ substitution, advocated by Beus (1960) particularly for sheet silicates. However, this substitution can be proved only if accurate water determinations are possible, and this is usually not the case with chlorite-like minerals. The high content of octahedral aluminum (Table 2, No. 6; Figs. 1 and 2) suggests that it may compensate for the

TABLE 1 (*Continued*)

10	11	12	13	14	15	16	17	18
34.7	34.68	34.72	32.00	25.20	35.20	35.25	38.22	34.52
—	0.03	0.02	—	—	—	—	—	
48.4	48.17	43.56	45.87	47.80	44.91	42.58	43.20	48.82
0.1	0.29	0.20	—	—	tr.	0.25	0.08	
—	—	1.66	—	9.25	—	—	—	
—	0.90	—	—	—	—	0.70	0.07	
—	—	0.10	—	—	—	0.06	0.03	
0.12	—	0.58	1.63	—	—	0.51	0.36	
0.05	—	0.83	0.78	—	—	0.59	0.04	
—	—	—	—	—	—	—	—	
2.45	2.45	2.28	2.10	3.97	2.82	0.80	4.33	2.86
0.01	0.04	0.07	0.65	0.48	—	0.00	0.00	
—	—	—	0.06	0.20	2.57	1.48	0.42	
14.1	13.44	14.21 }	17.29	14.10	{ 13.41	13.84	12.46	13.80
	—	1.70 }			{ 0.38	3.59	0.16	
—	—	—	0.02	—	0.34	0.34	0.33	
99.93	100.00	100.00	100.40	100.22	99.63	100.00	99.84	100.00
			0.01		0.15	0.15	0.14	
			100.39		99.48	99.85	99.70	

10. Cookeite North Little Rock, Arkansas, U.S.A. (Miser & Milton 1964); in pegmatite; averaged from a series of partial analyses.
11. Cookeite Ogofau, Carmarthenshire, England (Brammal *et al.* 1939); in gold-bearing ore veins; quartz-free, 5.97% dolomite deducted from the original analysis.
12. Cookeite Radkovice, Czechoslovakia (Černý *et al.* 1970); replaces lepidolite in pegmatite; its admixture in the analyzed sample deducted on the basis of the K_2O, Na_2O, and F; the total contains 0.011% Ga_2O_3, 0.052 GeO_2, 0.016 Cr_2O_3, 0.042 NiO.
13. Cookeite Wait-a-bit Creek, B.C., Canada (Hoffman 1895); in cavities of quartz veins.
14. Manandonite, Sahatany Valley, Madagascar (Lacroix 1922); replaces rubellite in pegmatite.
15. Cookeite Hebron, Maine, U.S.A. (Brush 1866); cavity lining in pegmatite.
16. Cookeite Varuträsk, Sweden (Quensel 1937); replaces spodumene in pegmatite; 52.4% of quartz deducted from the analyzed sample.
17. Cookeite Varuträsk, Sweden (Quensel 1937, 1956); pseudomorphous after rubellite, contaminated with "small content of quartz"; contains 0.11% P_2O_5, 0.03% Cl.
18. Ideal composition of cookeite $Li_2Al_8[Al_2Si_6O_{20}(OH)_{16}]$.

The original analysis in Norrish (1952) was not available; atomic contents given in Table 2, No. 2, were recalculated from those quoted by Radoslovich (1962).

heterovalent tetrahedral substitution—a mechanism somewhat similar to the mutual Al^{VI}/Al^{IV} equilibration in magnesium chlorites.

The fairly constant $(Al, B, Be)^{IV}/Si$ ratio is somewhat surprising in a chlorite mineral, but it seems to be well supported by all the thirteen analyses available. It may indicate that a particular type of Si, Al-ordering is preferred in the Li, Al-chlorite structure. Actually, the stacking sequence of layers in the I*a* chlorite polytype, typical of cookeite, is well suited to local charge balance between ordered Si, Al-sheets and ordered "brucite" sheets (Lister & Bailey 1967, p. 1630; an ordered

TABLE 2. UNIT CELL CONTENTS OF COOKEITE BASED ON 28 OXYGEN EQUIVALENTS

	Li	Na	K	Ca	Mg	Fe^{2+}	Al	Fe^{3+}	Σ oct.	Be	B	Al	Si	F
1.	2.88	0.06	0.03				7.59	0.06	10.62			1.91	6.09	0.12
2.	2.73						7.65		10.38			1.67	6.33	
3.	2.53	0.15					7.65	0.09	10.42			1.88	6.12	0.03
4.*	2.44	0.24	0.15		0.10	0.28	7.26	0.23	10.70			2.04	5.96	
5.	2.26	0.02		0.11	0.28		7.60	0.03	10.30			1.92	6.08	
6.	2.24	0.02		0.02			8.05		10.33	0.44	0.12	1.48	5.96	0.09
7.	2.22	0.02	0.02	0.08	0.05	0.10	7.78		10.27			2.10	5.90	
8.*	1.94	0.38	0.03	0.05	0.35	0.03	7.50	0.01	10.29			1.73	6.27	
9.	1.89	0.04		0.05	0.05		7.88	0.01	9.92		0.01	1.81	6.18	
10.	1.72			0.02	0.01		8.04	0.01	9.80			1.93	6.07	
11.	1.71	0.02				0.13	8.00	0.04	9.90			1.93	6.07	
12.	1.63			0.11	0.22	0.02	7.80	0.04	9.82		0.51	1.32	6.17	
13.*	1.54	0.24	0.02	0.32	0.22		7.76		10.10			2.14	5.86	tr.
14.	2.69	0.15	0.04				8.25		11.23		2.69	1.05	4.26	

1. Cookeite Hebron, Maine, U.S.A. (Penfield 1894).
2. Cookeite (Norrish 1952; in Radoslovich 1962).
3. Cookeite Buckfield, Maine, U.S.A. (Landes 1925).
4.* Cookeite north-western U.S.S.R. (Zvyagin & Nefedov 1954); Fe^{2+} includes 0.03 Mn.
5. Cookeite Dobrá Voda, Czechoslovakia (Černý *et al.* 1970); Mg includes 0.01 Ni.
6. Cookeite Muiane, Mozambique (Sahama *et al.* 1968).
7. Cookeite Kalbinski Range, U.S.S.R. (Ginzburg 1953).
8.* Cookeite Lipovka, Urals, U.S.S.R. (Ginzburg 1953).
9. Cookeite Manono, Katanga (Herman *et al.* 1961).
10. Cookeite North Little Rock, Arkansas, U.S.A. (Miser & Milton 1964).
11. Cookeite Ogofau, Carmarthenshire, England (Brammal *et al.* 1937).
12. Cookeite Radkovice, Czechoslovakia (Černý *et al.* 1970); Mn^{2+} 0.02 placed sub Fe^{2+}, Fe^{3+} includes 0.01 Cr.
13.* Cookeite Wait-a-bit Creek, B.C., Canada (Hoffmann 1895).
14. Manandonite Sahatany Valley, Madagascar (Lacroix 1922).

*Samples with very high (Na,K) contents.

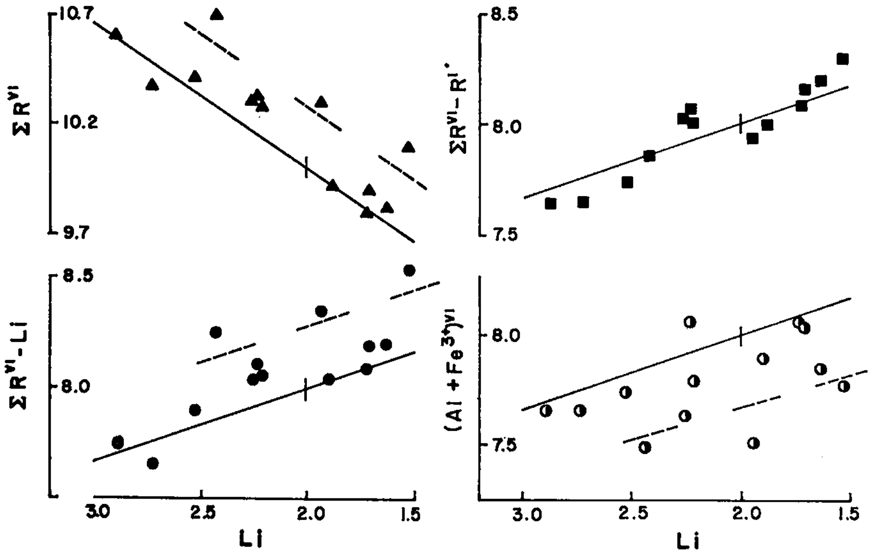

FIG. 1. Lithium content of cookeite plotted against the total R^{VI}, total R^{VI}-Li, total R^{VI}-R^{1+}, and $(Al + Fe^{3+})^{VI}$ contents, in atoms per 1-layer unit cell. Full lines follow the theoretical $3Li^{1+}/(Al, Fe)^{3+}$ substitution; the plot of the composition $Li_2Al_8[Al_2Si_6O_{20}(OH)_{16}]$ is marked by crossbar on these lines. The dashed lines separate specimens with very high contents of Na, K.

1-layer Cr-chlorite displaying a regular I*a* sequence shows the same Al_2Si_6 tetrahedral content, Brown & Bailey 1963). However, the mere existence of a very closely related manandonite warns against overemphasizing this fact: manandonite is usually idealized as $Li_2Al_8[Al_2B_2Si_4O_{20}(OH)_{16}]$ and its actual tetrahedral population is $Al_{1.05}B_{2.69}Si_{4.26}$.

Octahedral substitutions

In the idealized formula of cookeite $Li_2Al_8[Al_2Si_6O_{20}(OH)_{16}]$, Brammal *et al.* (1937), Zvyagin & Nefedov (1954), and Strunz (1966) allocated Al_4 to a dioctahedral layer within the 2:1 sandwich, and Al_4Li_2 to a trioctahedral interlayer "brucite" sheet. However, Norrish (in Eggleton & Bailey 1967) assigned $Al_{3.56}Li_{0.72}$ and Al_4Li_2 to these respective layers, and the octahedral occupancy derived here from chemical analyses shows broad variation between 10.70 and 9.80. This indicates that the distribution of cations between the two octahedral layers is not so simple as indicated earlier; for these reasons the octahedral population is treated here only as a whole group.

Generally, the octahedral occupancy is close to 10, as required in a di/trioctahedral chlorite. However, the highest octahedral contents of

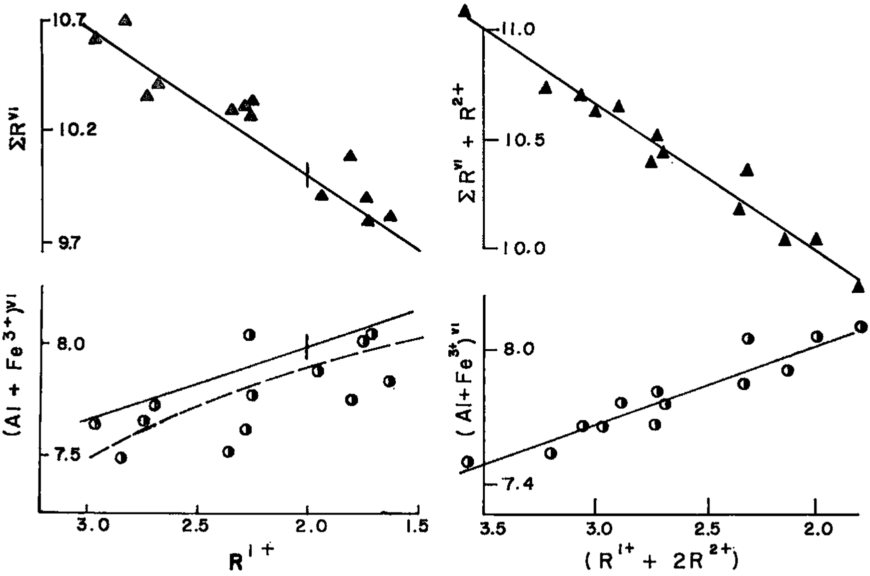

FIG. 2. Total alkali content (left side) and total alkali + doubled alkaline earth content (right side) of cookeite plotted against the total R^{VI} and $(Al + Fe^{3+})^{VI}$ contents, in atoms per 1-layer unit cell. Full lines follow the theoretical $3(Li, Na, K)^{1+}/(Al, Fe)^{3+}$ substitution in all four plots; the composition $Li_2Al_8[Al_2Si_6O_{20}(OH)_{16}]$ is marked by crossbar on these lines. The dashed line separates specimens with high contents of Ca, Mg, Fe^{2+}.

10.70 and 10.62 deviate considerably. Besides this, the single manandonite analyzed to date shows the octahedral occupancy of 11.23. This suggests that broader variations might occur in cookeite, particularly in connection with possible changes in the Si/Al ratio.

The fairly constant tetrahedral charge $(Al_2Si_6)^{+30}$ recognized in the previous paragraph suggests that—ideally—all substitutions within the octahedral sheets should maintain the total charge of +26. The mutual relations among the octahedral cations comply with this requirement. The total octahedral occupancy decreases rapidly, and the Al^{VI}-content increases slowly, with the decrease in lithium (Table 2), indicating the substitution $3Li^{1+}/Al^{3+}$. This mechanism preserves the charge balance and seems to be not restricted by space limitations, at least within the observed range of the octahedral occupancy 10.70–9.80.

The four plots illustrated in Fig. 1 show that most analyzed specimens follow closely the relations expected from the $3Li^{1+}/Al^{3+}$ substitution. There are, however, important exceptions, namely, the cookeites with high Na, K, Ca, and Mg contents. Some doubts may arise about the purity of these specimens, but at least some of them are reported as free of any mineral admixture (No. 4, 5, 12 in Tables 1, 2). Magnesium (and Fe^{2+}) can undoubtedly enter the Li,Al-chlorite structure quite easily. However, this is not the case with the large cations, and a question arises about their accommodation.

Belov (1950) suggested that small amounts of calcium, frequently found in Mg,Fe-chlorites, may occupy the octahedral sites between the 2:1 units and "brucite" sheets, adjacent to the vacant positions in the latter. The same would apply also to sodium and potassium. However, the I*a* 1-layer polytype typical of cookeite shows a superposition of tetrahedral and octahedral cation right around this proposed "intersheet" octahedral site (Brown & Bailey 1963, Lister & Bailey 1967), and the close proximity of tetrahedral cation would seem to inhibit the occupation of this position even if the regular octahedral site in the "brucite" sheet is vacated.

Besides this position proposed by Belov (1950), there is another "intersheet" site in the I*a* structure, suitable for accommodation of large cations. The cavities between the six-sided openings among the tetrahedral bases and "brucite" cations facing them have an irregular 9-fold (O, OH) coordination (*cf.* Brown & Bailey 1963, Fig. 3; Lister & Bailey 1967, Fig. 6b). They can be undoubtedly easily entered by Ca, Na, K substituting for the adjacent regular "brucite"-sheet cation, the site of which becomes vacated. Besides this possibility, it seems probable that structural imperfections in natural crystals would enable small amounts of the large cations to enter even those sites that are highly unfavourable in ideal structures, *i.e.*, regular octahedral positions and the "intersheet" sites proposed by Belov. Thus the small Na, Ca, K-contents found in cookeite have a good chance to be incorporated in its structure, and the mode of their substitution for Li and Al should be found.

In Fig. 1, the alkali-rich specimens show very high total R^{VI} and R^{VI}-Li contents, and very low Al^{VI} figures, as compared with the other cookeites concentrated along the theoretical $3Li^{1+}/Al^{3+}$ line. This suggests that large cations play the same role in the charge relations as lithium. Actually, the left side of Fig. 2 indicates that all specimens can be satisfactorily correlated with the $3R^{1+}/Al^{3+}$ substitution.

In the left part of Fig. 2, the samples falling appreciably above the theoretical line in the total R^{VI} plot, and much below that in the $(Al + Fe^{3+})^{VI}$ plot contain considerable (Ca,Mg,Fe^{2+}). Since the substitution $3R^{1+}/Al^{3+}$ seems to be the principal one, a $3R^{2+}/2Al^{3+}$ relation is more probable for bivalent cations than any other involving alkalies (*e.g.* $R^{1+} + R^{2+}/Al^{3+}$). The right side of the Fig. 2 shows the octahedral relations with R^{2+}-contents doubled, to simulate minerals with all bivalent cations substituted by alkalies. The almost perfect agreement of the plotted points with the theoretical $3R^{1+}/Al^{3+}$ line suggests that the above assumption is correct, and that the bivalent cations substitute for Al^{VI} in the ratio $3R^{2+}/2Al^{3+}$.

Actually, major irregularities in the right side of Fig. 2 are caused by the variations in the Si/Al^{IV} ratio. Specimens with $Si < 6$ plot on the upper side of the theoretical line and those with $Si > 6$ on the lower side, compensating the slightly varying tetrahedral charge.

The substitutional series of cookeite seems to be extended to much lower $(R^{1+,2+}/Al)^{VI}$ ratios in some of the donbassites (Lazarenko 1969, Drits & Lazarenko 1967, Drits & Alexandrova 1968), and sudoites (*e.g.* Müller 1963). Their idealized "end-member" composition is $Al_{8.67}[Al_2Si_6O_{20}(OH)_{16}]$, displaying the same tetrahedral Si/Al ratio as in cookeite. Low percentages of Fe_2O_3, MgO, CaO, Na_2O are usual, the Li_2O content reaches up to 0.78 wt. %, and the recalculated analyses plot very well along the right-side extension of the theoretical lines in Fig. 2. The *x*-ray powder patterns of some donbassites agree well with those of cookeite (Dr. S. W. Bailey, personal communication 1969). If the structural identity is proved—and there seems to be little doubt about it in some cases—the existence of donbassite would be an additional proof for the cookeite substitutional series proposed here, and Li-poor cookeites approaching dioctahedral composition could be expected to occur also in pegmatites. Maybe this is the case of the Li-poor cookeite from Varuträsk (anal. No. 16 in Table 1).

Hydroxyl and fluorine

The difficulties encountered in the determination of water in micaceous minerals are well known and are the main reason for using the theoretical anionic charge as the basis of crystallochemical calculations (*cf.* Foster 1962). However, the low fluorine content of some cookeites and the term "hydrocookeite" (Ginzburg 1953) require at least brief comment.

In contrast to the Mg,Fe-chlorites, chemical analyses of cookeite quite frequently show some fluorine. Besides specimen Nos. 1, 3, 6, and 13 recalculated in Table 2, fluorine was reported also by Brush (1866) and Quensel (1937, 1956) (Nos. 15, 16, 17 in Table 1). At least the Muiane cookeite (Sahama *et al.* 1968) and the quartz-contaminated specimen reported by Quensel were quite pure, without any admixture of mica or other fluorine-rich phases. Thus the ability of the cookeite structure to incorporate fluorine seems to be proved.

The name "hydrocookeite" was applied by Ginzburg (1953) to the cookeite from Lipovka (and other unspecified samples) which shows a slight low-temperature dehydration effect at around 150° C, refractive indices and birefringence lower than other "normal" cookeites, and slightly higher *d*-spacings in *x*-ray powder records. Strangely enough, the Lipovka "hydrocookeite" seems to contain a quite normal H_2O percentage (Tables 1 and 2, No. 8), and there is no sound reason for referring to the Li-poor Varuträsk cookeite (Quensel 1937) as an altered mineral, as Ginsburg does.

All properties given as characteristic for "hydrocookeite" by Ginzburg can be explained in other ways, without assuming changes in "hydration." Thus there seems to be no need for the term "hydrocookeite" at present. No crystallochemical basis for such a phase was found or proposed, and there is no mineral known to date which shows such a departure from the usual range of the H_2O contents as to require special classification.

CONCLUSIONS

Much more work remains to be done on cookeite but any progress depends more on better laboratory techniques rather than on accumulating data in the present way. Chemical analyses yielding reliable information about anionic water, and methods aimed at identification of adsorbed cations and minor admixed phases could eliminate most assumptions that are necessary today.

As for the present, the available chemical analyses show that cookeite has a fairly constant tetrahedral population Al_2Si_6, with Be and B substituting occasionally for Al. Octahedral occupancy varies from 9.8 to 10.7, concentrating around but deviating substantially from the strict di/trioctahedral figure of 10. The existence of manandonite shows that even larger variability in both the Si/Al^{IV} ratio and in the octahedral occupancy may be encountered, although the Al_2Si_6 tetrahedral population seems to be preferred by the prevailing 1-layer I*a* structural polytype.

Besides Li and Al, appreciable amounts of Na (+K), Ca, Mg, ($\pm Fe^{2+}$), and possibly Fe^{3+} can play the role of octahedral cations. The vacant space between the 2:1 sandwiches and "brucite" sheets seems to be suitable to accommodate the large cations, as suggested by Belov (1950). With the tetrahedral content Al_2Si_6 nearly constant, the main octahedral substitution is that of $3\ (Li > Na \gg K)^{1+}/(Al \gg Fe)^{3+}$, occasionally modified by the introduction of $3\ (Ca,Mg \gg Fe)^{2+}$ for $2\ (Al \gg Fe)^{3+}$. The substitution $3Li^{1+}/Al^{3+}$ requires considerable space for lithium accommodation. This is provided in the dioctahedral sheet in cookeite, and in vacant space of eucryptite—the only example of this substitution known to date (Mrose 1953).

Taking into account fluorine which may substitute to some extent for the (OH) groups, the general formula of cookeite may be written as

$$(\mathrm{Li,Na} \gg \mathrm{K})_{2+3x}(\mathrm{Ca,Mg} \gg \mathrm{Fe}^{2+})_{3y}(\mathrm{Al} \gg \mathrm{Fe}^{3+})_{8-x-2y+z} \times [(\mathrm{Al} > \mathrm{B,Be}_z)_2\mathrm{Si}_6\mathrm{O}_{20}(\mathrm{OH} \gg \mathrm{F})_{16}],$$

where $x = -0.15$ to $+0.30$, $y = 0$ to $+0.18$, and $z = 0$ to $+0.44$.

The cookeite substitutional series seems to be extended up to the di-octahedral Al-end member in donbassite and sudoite, with $x = -0.66$, y and $z = 0$. Further chemical analyses may broaden the variations even in true pegmatitic cookeite, and the detailed studies carried out at the University of Wisconsin (Lister 1966; Eggleton & Bailey 1967; Lister & Bailey 1967) will undoubtedly clarify the structural relations among these minerals.

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