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STRUCTURAL DATA FOR SUDOITE

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Abstract—Single crystals of sudoite from Ottré, Belgium, allow confirmation of a dioctahedral 2:1 layer and a trioctahedral interlayer in a II*b* arrangement. A regular 2-layer *s* structure is formed in which the octahedral stagger within both 2:1 layers is directed along X_1 and adjacent layers are alternately displaced by $a_2/3$ and $a_3/3$. Poor quality crystals and twinning prevented three-dimensional refinement. One-dimensional refinement suggests that the smaller d(001) value of dioctahedral chlorites relative to trioctahedral species is due primarily to the thinner dioctahedral sheet.

Key Words—Chlorite, Crystal structure, Sudoite, Symmetry, Vermiculite.

INTRODUCTION

Sudoite is a Li-poor di,trioctahedral chlorite that has been identified in clay-size particles from hydrothermal zones and low-grade metamorphic rocks from many localities. Kramm (1980) discussed its stability limits and inferred conditions of formation, and Fransolet and Schreyer (1984) synthesized sudoite at temperatures below 370°–390°C at water pressures below 7 kbar. The ideal composition of sudoite is $Al_2(Si_3Al)O_{10}(OH)_2$ for the dioctahedral 2:1 portion of the structure and $Mg_2Al(OH)_6$ for the trioctahedral interlayer. Partial structural refinement has been attempted by Eggleton and Bailey (1967) with all $k = 3n$ reflections from an X-ray film powder pattern and by Shirozu and Higashi (1976) with 00*l* reflections measured with an X-ray powder diffractometer. The two refinements differ primarily in the resulting thicknesses of the 2:1 layers and the interlayer and, as a consequence, in the interpretations of the mechanism that provides a good lateral fit between the dioctahedral and trioctahedral components.

Fransolet and Bourguignon (1978) described single crystal of sudoite from quartz veins at two localities in Belgium. Dr. Bourguignon kindly provided material from the Ottré locality, and we have used this material to characterize sudoite in more detail. The composition given in Table 1 by a combination of microprobe analysis and wet chemical analysis is $Al_{2.009}(Si_{2.999}Al_{1.001})O_{10}(OH)_2 \cdot (Mg_{2.002}Al_{0.82}Fe^{3+}_{0.184}Li_{0.015}Ti_{0.004}Mn_{0.001})(OH)_6$ based on 28 positive charges.

EXPERIMENTAL

More than 100 individual flakes of sudoite were studied by precession and Weissenberg X-ray photographs. The flakes were small, soft, and commonly rumpled, so that it was difficult to obtain crystals good enough for a structure determination. It was noted immediately that a regular 2-layer stacking sequence of layers was present. All reflections showed some mosaic spread. The $k \neq 3n$ reflections were not streaked, but were slightly more elongate than those with $k = 3n$ as a result of $\pm b/3$ stacking faults (Figure 1).

All crystals good enough to study by the Weissenberg technique proved to be twinned by the mica law with three components present. Some of the trilling reflections were discrete, but others superimposed on those of the parent crystal to give a triclinic intensity distribution in which the Friedel equivalents were not necessarily equal. The rectangular crystal used for the structural analysis measured 0.27 × 0.17 × 0.02 mm in size. Cell dimensions of $a = 5.238(1)$, $b = 9.067(2)$, $c = 28.541(2)$ Å, and $\beta = 97.34(1)°$ were obtained by least squares fit, constrained to a monoclinic cell, of a film powder pattern taken with monochromatic FeKα radiation, a 114.6-mm camera diameter, and a Straumanis-Wilson-type mount.

The intensities of reflections as high as $2\theta = 60°$ in all eight octants were measured on a Nicolet $P2_1$ automated single-crystal diffractometer with monochromatic MoKα radiation. Intensities were measured by the θ:2θ variable scan technique, with one standard reflection monitored after every 100 reflections to check crystal and electronic stability. The integrated intensities were reduced to structure amplitudes by applying Lorentz-polarization corrections by the standard method and absorption corrections by the semi-empirical technique of North *et al.* (1968). Although more than 1000 reflections were evaluated, only 283 had measurable intensities. Because of non-equivalence of many Friedel equivalents, all reflections were treated individually during refinement.

DETERMINATION OF BASIC STRUCTURE

Examination of the observed amplitudes F_o for the 20*l* reflections (Figure 1) shows clearly that the layer–

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Table 1. Microprobe analysis of sudoite.

Oxide	Wt. %	Oxide	Wt. %
SiO_2	32.90	MnO	0.01
Al_2O_3	35.40	CaO	0.00
MgO	14.73	BaO	0.03
Fe_2O_3[1]	2.69	K_2O	0.00
Li_2O[1]	0.04	Na_2O	0.01
TiO_2	0.06		

[1] Fe valency and Li_2O content from Fransolet and Bourguignon (1978). ARL microprobe operated at 15 kV with a beam of 10–15 μm. Measurements at 10 points for 30 sec each, using standards of microcline, albite, barite, wollastonite, johannsenite, MgO, Fe_2O_3, Al_2O_3, and TiO_2. Corrections made by theoretical ZAF method.

interlayer relationship for this specimen is II*b* according to the terminology of Bailey and Brown (1962). That is, the slant of the octahedral interlayer sheet is opposite in direction to that in the 2:1 layer (II), and the interlayer cations do not project onto tetrahedral cations in the layer below (*b*). By comparison with calculated values the F_o values also indicate that the 2:1 layer is dioctahedral and the interlayer is trioctahedral (Table 2). These points had been recognized previously by Eggleton and Bailey (1967) for sudoite from the Tracy Mine, Michigan, by Shirozu and Higashi (1976) for sudoite from two localities in Japan, and by Fransolet and Bourguignon (1978) for the sudoite of this study. All sudoites examined in any detail to date are similar in these respects. By contrast, donbassites with two dioctahedral sheets may crystallize with either I*a* or II*b* layer–interlayer relationships.

Examination of the reflections with $k \neq 3n$ provided the additional information that the Ottré sudoite of this study has a regular 2-layer stacking sequence and a space group that approximates *C*2/*c* or *Cc* (complicated by twinning). Mathieson and Walker (1953) showed that chlorite or vermiculite layers related by a *c*-glide plane in a monoclinic 2-layer structure can have relative arrangements designated by them as *p, q, r,* and *s*. We calculated structure amplitudes for these models using II*b* chlorite units in which 7.5° tetrahedral rotation angles were incorporated and the vacant site was expanded (Table 2). The Ottré sudoite has the *s* structure in which the *a*/3 octahedral stagger within each 2:1 layer is always along X_1 (L layers) and successive layers are displaced alternately by $a_2/3$ and $a_3/3$. This structure can be recognized readily because of its strong 020, 021, and 025 reflections. Calle *et al.* (1976) illustrated the differences in intensities of the 0k*l* reflections for these structures for vermiculite. The most stable form of vermiculite also has the *s* structure, but with I*a* type layers (Shirozu and Bailey, 1966; Calle *et al.*, 1976). In contrast to vermiculite, the $k \neq 3n$ reflections for sudoite are not as markedly elongate, although some $\pm b/3$ stacking faults are present. The ideal space group of the *s* structure is *C*2/*c*.

Table 2. Representative F_o and F_c values for unrefined *s* structure.

hk*l*	F_o	F_c	hk*l*	F_o	F_c	hk*l*	F_o	F_c
002	46	33	110	54	26	260	88	70
4	132	135	1	142	117	2	161	156
6	290	233	2	119	96	−2	64	17
8	286	277	−2	49	39	−6	243	143
10	186	171	−3	69	53	8	107	130
12	66	74	4	43	65	−8	60	31
14	166	168	5	40	42	10	154	169
16	60	50	−5	69	68			
20	162	180	7	44	57	310	88	35
			−7	106	137	1	20	3
020	120	102	8	41	33	−1	129	96
1	217	151	−8	33	67	2	42	25
2	71	46	9	26	29	−2	109	56
3	1	1	−9	67	63	3	84	78
4	39	29				−3	116	78
5	70	60	136	107	153	4	70	43
6	17	13	−6	191	180	−4	61	19
7	31	32	8	54	35	−5	4	1
8	14	43	−8	53	87	−6	20	9
9	95	94	10	153	176	7	59	61
10	35	45	12	36	32			
			−12	195	232	404	20	40
060	513	385	−14	76	91	6	41	67
4	173	149	16	54	75	12	137	207
6	155	132	18	61	55	14	71	82
8	115	92	−20	113	127	16	37	50
10	96	92				−16	46	101

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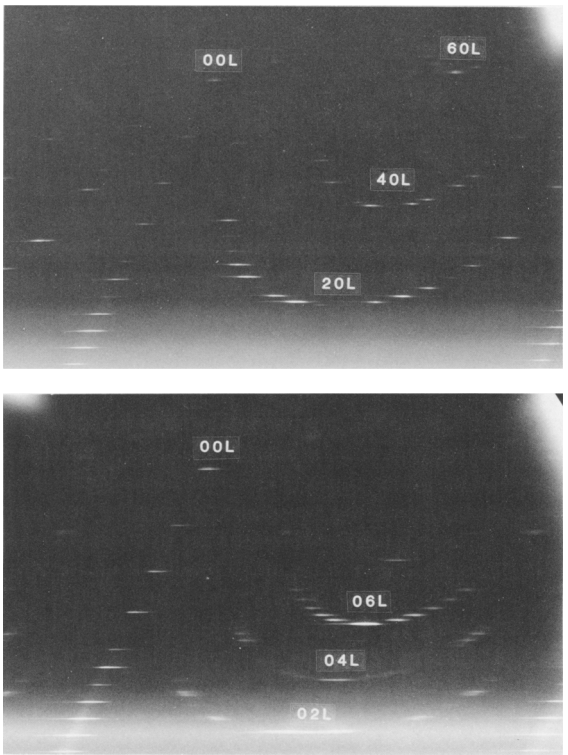


Figure 1. Weissenberg $h0l$ and $0kl$ photographs of Ottré sudoite. Twinning shows up as a doubling of certain reflections, most evident on the $02l$ festoon.

Drits and Lazarenko (1967) also recognized the s structure with IIb layers in single crystals of sudoite from the Berezovsk district, Urals (labeled donbassite crystals in their paper). Their published F^2 values and electron density maps are very similar to ours. The composition of their specimen is $Al_2(Si_{2.86}Al_{1.14})O_{10}(OH)_2$ for the 2:1 layer and $Mg_{1.96}Al_{0.9}Fe_{0.22}(OH)_6$ for the interlayer. The structure was not refined.

REFINEMENT AND DISCUSSION

Refinement of the ideal atomic positions was attempted in three ways. Normal least-square refinement using F_o values and a modified ORFLS program (Busing *et al.*, 1962) was not successful and produced bond lengths that were unrealistic. Program RAELS was then used. This program (A. D. Rae, School of Chemistry, University of New South Wales, Australia, unpublished) allows the F^2 values of superimposed twin components to be added together and also allows incorporation of stacking faults. For the crystal used, comparison of observed and calculated intensities and usage of superimposed lattice drawings identified twinning according to the mica law. Attempted refinement by programs RAELS of the atomic positions, volumes of the trilling components, and number of $\pm b/3$ stacking faults were also unsuccessful. Thus, it was primarily the poor quality of the crystal used, rather than the twinning, that prevented refinement.

Table 3. Atomic coordinates for sudoite.

	x	y	z
T(1)	0.770	0.000	0.154
T(2)	0.770	0.333	0.154
Al(1)	0.000	0.500	0.250
Al(2)	0.000	0.833	0.250
Mg(1)	0.000	0.000	0.000
Mg(2)	0.000	0.333	0.000
O(1)	0.787	0.981	0.213
O(2)	0.787	0.353	0.213
O(3)	0.480	0.397	0.132
O(4)	0.296	0.667	0.138
O(5)	0.986	0.434	0.132
OH(1)	0.348	0.167	0.213
OH(2)	0.359	0.000	0.035
OH(3)	0.359	0.333	0.035
OH(4)	0.359	0.667	0.035

Finally, because of the variance between the results of Eggleton and Bailey (1967) and Shirozu and Higashi (1976) as to the thickness of the component sheets in sudoite, refinement of the z parameters was attempted using only $00l$ reflections (not affected by mica-law twinning). Treating sudoite as a 1-layer chlorite of symmetry $C2/m$, all $00l$ and $00\bar{l}$ reflections to $2\theta = 90°$ were measured on the Nicolet $P2_1$ single crystal diffractometer, corrected for Lp effects, and the F_o values for $+l$ and $-l$ averaged. No measurable intensities were found for l greater than 16 (or 32 for a 2-layer cell). Using assumed isotropic B values of 1.0 for cations and 1.5 for anions, least-squares variation of non-fixed z parameters reduced the reliability factor, R, to 5.0%. Variation of the B values reduced R to 1.4%, but is considered unrealistic because of two B values greater than 3.0 and one negative value. Table 3 lists the experimental z values, restored to a 2-layer cell, and the unrefined x and y coordinates of the atoms for the s structure, as adjusted for tetrahedral rotation and dioctahedral distortion.

A one-dimensional electron density projection onto [001] confirmed that the 2:1 layer is dioctahedral and the interlayer is trioctahedral (Figure 2). The slightly greater density at the interlayer plane relative to the 2:1 octahedral plane (observed density ratio of 1.67) than expected for the ideal 3:2 ratio of cations suggests that the 0.189 atoms of heavy elements are in the interlayer. The one-dimensional refinement is not considered to be of high accuracy because of the poor quality of the crystal and the limited number of reflections available. The resulting sheet thicknesses appear reasonable, however, when compared with more accurate values from the literature, as derived by three-dimensional refinements of similar structures. Table 4 contains sheet thicknesses for muscovite and paragonite, which have

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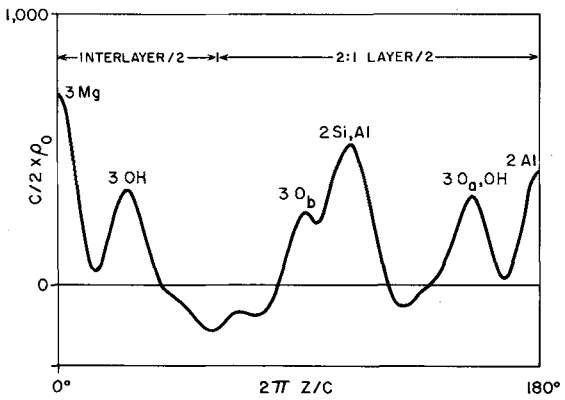


Figure 2. One-dimensional electron density projection used to document di,trioctahedral nature of sudoite and to measure sheet thicknesses.

dioctahedral 2:1 layers that should be comparable to that of sudoite, for the di,trioctahedral chlorite cookeite (unpublished data from this laboratory), the di,dioctahedral chlorite donbassite (Aleksandrova *et al.*, 1972), and the average of six trioctahedral chlorites chosen to have Al^{IV} contents similar to sudoite.

Eggleton and Bailey (1967) examined the fit of a dioctahedral 2:1 layer with a trioctahedral interlayer in sudoite by suggesting that the trioctahedral interlayer is thickened and the dioctahedral 2:1 layer is thinned to give better lateral concordance, and that the basal oxygens approach the interlayer hydroxyls more closely than in trioctahedral species. Their refinement, which involved deconvolution of overlapping lines on a powder photograph, gives sheet thicknesses more at variance with the results of three-dimensional refinements than is the case for the average of two one-dimensional refinements of sudoite (Table 4) by Shirozu and Higashi (1976). The latter authors suggested that the dioctahedral 2:1 layer is thinner than in trioctahedral species but that the interlayer O–OH separations are similar, with the lateral fit governed by the chemical composition of the sheets. The results of the present study are intermediate, but closer on average to those of Shirozu and Higashi. We found no evidence during refinement of the Ottré sudoite to suggest that the 2:1 layer may be phengitic and the interlayer incomplete, as suggested by Shirozu and Higashi (1976) for their specimens. It should be kept in mind in comparing these results that the Ottré sudoite of this study has more Al^{IV} than the other sudoites studied. We consider the problem of the lateral fit to be insignificant, however, because differences in positions of the basal oxygens and surface hydroxyls across the O–OH separation can be accommodated by changes in direction of the OH vectors and bending of the interlayer hydrogen bonds.

A more pertinent question to be considered is the magnitude of d(001) for dioctahedral vs. trioctahedral species. Eggleton and Bailey (1967), Shirozu and Higashi (1976), and Shirozu (1980) agree that the d(001) values for dioctahedral chlorites are systematically smaller than those for trioctahedral chlorite, so that existing d(001) graphs cannot be used to obtain their tetrahedral contents. The observed d(001) value of 14.153 Å for a Si_3Al tetrahedral composition for the Ottré specimen fits this same trend. Table 4 suggests that the smaller d(001) value is due on average primarily to a thinner dioctahedral sheet in the 2:1 layer plus possibly a slightly thinner total interlayer space, more evident in the cookeite and donbassite results than for the present study. The range of thicknesses shown for trioctahedral chlorite limits the validity of such comparisons pending more accurate refinements.

POSSIBLE TRICLINIC SYMMETRY

As mentioned above, the single crystal intensity distribution is triclinic; however, at least part of this effect is due to twinning, e.g., superimposing 060 on 330, etc. It was noted also in indexing the powder pattern by a monoclinic-constrained least-squares fit that a few calculated *d* values differed from those observed by

Table 4. Chlorite sheet thicknesses (Å).

	Sudoite			Avg. 10 musc.-parag.	Cookeite	Donbassite	Trioct. avg. 6	Chlorite range
	E-B	S-H	This study					
Tetrahedral sheet	2.30	2.22	2.24	2.24	2.25	2.23	2.25	2.21–2.29
Octahedral sheet	2.05	2.09	2.09	2.10	2.07	2.12	2.14	2.05–2.18
Tetrahedral sheet	2.30	2.22	2.24	2.24	2.25	2.23	2.25	2.21–2.29
Σ 2:1 layer	6.65	6.53	6.57	6.58	6.57	6.58	6.64	6.57–6.70
O–OH sep.	2.69	2.80	2.80	—	2.79	2.77	2.81	2.73–2.85
Octahedral sheet	2.15	2.04	1.98	—	1.92	2.01	1.98	1.91–2.03
O–OH sep.	2.69	2.80	2.80	—	2.79	2.77	2.81	2.73–2.85
Σ interlayer	7.53	7.64	7.58	—	7.50	7.55	7.60	7.39–7.70
Total	14.18	14.17	14.15		14.07	14.13	14.24	14.02–14.33
Al^{IV}	0.70	0.80	1.00	0.97	0.97	0.86	0.98	

E-B = Eggleton and Bailey (1967); S-H = Shirozu and Higashi (1976), average of 2 refinements.

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more than 3σ. A similar discrepancy can be seen in the pattern published by Fransolet and Bourguignon (1978) for the same specimen (e.g., 1.995 vs. 1.987 Å for $13\bar{5}$, 1.816 vs. 1.812 Å for $13\bar{6}$, and 1.549 vs. 1.553 Å for 137). These deviations disappear if triclinic geometry is allowed, and least-squares fitting of the powder pattern then gives $\alpha = 90°28(1)'$, $\beta = 97°17(1)'$, and $\gamma = 89°56(1)'$ for the crystallographic angles. A slightly triclinic unit-cell geometry, if true, would also facilitate the ubiquitous twinning that is observed. The poor quality of the crystals prevented verification of the triclinic geometry by single crystal study, and we do not consider the triclinic geometry as proven unless better data can be obtained.

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