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Crystal structure of sapphirine-1Tc

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Abstract. Both polymorphs of sapphirine, namely sapphirine-1Tc and sapphirine-2M, were found in granulites near Wilson Lake (Labrador). Both minerals can be described as consisting of equivalent layers with monoclinic symmetry, translation periods $a = 9.78$, $c = 9.93$ Å, with $\beta = 110.2°$, the width of a layer being $b_0 = 7.20$ Å. The layers are built up by octahedral walls connected by tetrahedral chains. Adjacent layers are related by translation vectors $t_1 = a/2 + b_0 - c/4$, or $t_2 = a/2 + b_0 + c/4$. Sapphirine-1Tc corresponds to the sequence $t_1 t_1 t_1 \ldots$ (or $t_2 t_2 t_2 \ldots$), whereas sapphirine-2M corresponds to the sequence $t_1 t_2 t_1 t_2 \ldots$

The structures of the two polymorphs from Wilson Lake were refined with the aim to determine the distribution of magnesium, iron, and aluminium cations in octahedral sites and of aluminium and silicon cations in tetrahedral sites. The structural data indicate for both polymorphs a substantially similar distribution, which corresponds to that obtained by P. B. Moore in his study of the sapphirine from Fiskenaesset.

Introduction

The OD character of sapphirine was indicated by Dornberger-Schiff and Merlino (1974), who showed that each structure of the whole family of possible OD-structures consists of equivalent layers having translation periods $a = 9.783$, $c = 9.929$ Å, with $\beta = 110°\ 17'$, the "width" of a single layer being $b_0 = 7.20$ Å[1]. All the layers in each structure are translationally equivalent and adjacent layers are related by vectors $t_1 = a/2 + b_0 - c/4$ or $t_2 = a/2 + b_0 + c/4$. It was shown (Dornberger-Schiff and Merlino, 1974)

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[1] The dimensions given for the single layer derive from the cell data for sapphirine from Fiskenaesset, the type locality: space group $P\,2_1/n$, $a = 9.783$, $b = 14.401$, $c = 9.929$ Å, $\beta = 110°$ 17′.

that two members of maximum degree of order exist, which are called MDO_1 and MDO_2 in the terminology of the OD-theory, the first corresponding to the succession of vectors $t_1 t_1 t_1$ ... (or $t_2 t_2 t_2$ ...), the other to the succession $t_1 t_2 t_1 t_2$ ... This last succession is realized in "normal" sapphirine or sapphirine-2M, with two layers in the monoclinic unit cell, whereas the preceding one is realized in sapphirine-1Tc, with one structural layer in the triclinic unit cell (Merlino, 1973).

Sapphirine-1Tc was found in granulites from Wilson Lake, Labrador (Canada). X-ray crystallographic investigation of sapphirine from that source (Merlino, 1973) indicated the presence of MDO_2 domains, corresponding to the monoclinic polymorph, besides MDO_1 domains, corresponding to the triclinic polymorph. Various crystal fragments presented different amounts of the two domains. Moreover whereas the MDO_1 domains were coherent throughout each fragment, the MDO_2 domains were out of phase thus giving rise to more or less diffuse reflections, which seemed indicative of solid state reactions leading from sapphirine-1Tc to an arrangment of "out of phase" MDO_2 domains.

All the diffraction patterns could be indexed with reference to a common pseudomonoclinic cell with $a_m = 9.87$, $b_m = 29.08$, $c_m = 10.04$ Å, $\beta_m = 110°\ 38'$.

The crystal structure of sapphirine-2M from the type locality, Fiskenaesset, was solved by P. B. Moore (1968, 1969) who found a substantial ordering in the distribution of silicon and aluminium cations in tetrahedral sites and of aluminium and magnesium cations in octahedral sites.

The aim of the present work was to determine whether sapphirine-1Tc from Wilson Lake presents a similar or a different ordering of tetrahedral and octahedral cations. To make the comparison more complete, the ordering scheme was determined also for a sapphirine-2M from the same locality.

Experimental

Sapphirine-1Tc

A small crystal fragment from Wilson Lake was used to collect intensity data. The cell parameters obtained with a Philips PW 1100 single-crystal diffractometer, using Mo$K\alpha$ radiation, are $a = 9.97(1)$, $b = 10.34(1)$, $c = 8.62(1)$, $\alpha = 107.4°\ (1)$, $\beta = 95.2°\ (1)$, $\gamma = 123.8°\ (1)$. The triclinic cell can be obtained by the common pseudomonoclinic cell by the transformation matrix $[00\bar{1}/\frac{1}{2}\frac{1}{4}\frac{1}{4}/\frac{1}{2}\frac{\bar{1}}{4}\frac{1}{4}]$. Intensity data were collected on the same diffractometer using graphite monocromatized Mo$K\alpha$ radiation ($\lambda = 0.7107$), scan width 1.6°, scan speed 0.08° s^{-1}, ϑ-2ϑ scan, from 3° to 30° in ϑ. All the reflections with $I_{top} - 2\sqrt{I_{top}} < I_{back}$ were skipped, I_{top} and I_{back} indicating peak and background intensities, respectively. The 2532 observed reflections were corrected for Lorentz and polarization factors; no absorption correction was made, owing to the small dimensions of the crystal.

Sapphirine-2M

A very small crystal fragment from Wilson Lake was used to obtain cell parameters and intensity data by means of a Philips PW 1100 diffractometer, with Mo $K\alpha$ radiation. The cell orientation given by Moore (1969) and obtained by the common pseudomonoclinic cell by the transformation matrix $[101/0\bar{\tfrac{1}{2}}0/00\bar{1}]$ was assumed and the following parameters were measured: $a = 11.31\ (1)$, $b = 14.48\ (1)$, $c = 9.99\ (1)$ Å, 125.4° (1). Intensity data were collected with scan width 1.4°, scan speed 0.05° sec^{-1}, ϑ-2ϑ scan, from 3° to 35° in ϑ. Weak reflections were skipped as in the case of sapphirine-1Tc. Because of the smaller volume of the crystal fragment a lower number of reflections (1812) was measured; moreover, as stated in the introduction, whereas the family reflections, namely reflections with $l = 2n$, were sharp, those with index $l = 2n + 1$ appeared diffuse. Corrections were made for Lorentz and polarization factors; correction was not made for the absorption owing to the very small dimensions of the crystal.

Refinement

Sapphirine-1Tc

The starting parameters were obtained by the final atomic coordinates given by Moore (1969): in the triclinic phase two octahedral cations M8 and M9 in special positions on inversion centers corresponded to the M8 octahedral cation in a general position in the monoclinic phase. Several full-matrix least-squares refinement cycles with isotropic temperature factors and weighting scheme based on $\sigma(F_o)$ were conducted. In the course of the refinement the cation distribution among the octahedral and tetrahedral sites was derived, taking account of: a) relative heights of the electron density in the various sites, b) thermal parameters, c) mean bond distances, d) chemical data, e) Mössbauer spectroscopic data[2].

The cation distribution which best agrees with all known data is given in Table 1, together with atomic coordinates and isotropic thermal parameters for all the atoms in the structure. The appropriate scattering curves for each site were obtained from the cation distribution; curves for the pure atomic species were obtained from International Tables for X-ray Crystallography,

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[2] The chemical and Mössbauer data were communicated to me by S. A. Morse and are based on a chemical analysis by K. Aoki and a Mössbauer study by R. G. Burns.

Table 1. Fractional atomic coordinates, isotropic thermal parameters, and cation distribution in octahedral and tetrahedral sites, in sapphirine-1Tc

Site	Cation distribution			x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B	$\sigma(B)$
M1	0.9 Al	0.1 Fe^{+3}		-0.19331	0.35014	-0.33486	0.00024	0.00024	0.00024	0.28	0.03
M2	0.9 Al	0.1 Fe^{+3}		0.28520	0.33460	-0.34992	0.00024	0.00024	0.00024	0.41	0.03
M3	0.7 Mg	0.25 Fe^{+3}	0.05 Fe^{+2}	0.09720	0.44457	-0.44134	0.00021	0.00021	0.00022	0.51	0.03
M4	0.85 Mg	0.15 Fe^{+2}		0.59581	0.44010	-0.44468	0.00025	0.00025	0.00025	0.34	0.03
M5	0.80 Mg	0.20 Fe^{+2}		-0.29206	0.14171	-0.12497	0.00024	0.00023	0.00024	0.22	0.03
M6	0.80 Mg	0.20 Fe^{+2}		0.17631	0.12642	-0.14167	0.00024	0.00024	0.00024	0.35	0.03
M7	1.0 Al			0.49504	0.24213	-0.24324	0.00029	0.00029	0.00029	0.33	0.03
M8	1.0 Al			0.50000	0.50000	0.0	0.0	0.0	0.0	0.25	0.04
M9	1.0 Al			0.50000	0.0	0.50000	0.0	0.0	0.0	0.28	0.04
T1	1.0 Al			-0.27929	0.14245	0.25324	0.00025	0.00026	0.00026	0.10	0.03
T2	0.75 Si	0.25 Al		0.23096	0.14891	0.25521	0.00024	0.00024	0.00025	0.15	0.03
T3	0.5 Si	0.5 Al		0.02972	0.25277	0.15226	0.00024	0.00025	0.00025	0.22	0.03
T4	0.75 Al	0.25 Si		-0.46944	0.25687	0.14106	0.00024	0.00025	0.00025	0.16	0.03
T5	1.0 Al			0.12785	-0.06752	0.44287	0.00026	0.00026	0.00026	0.21	0.03
T6	0.75 Al	0.25 Si		0.13158	0.44095	-0.06630	0.00025	0.00025	0.00025	0.28	0.03
O1				-0.25662	0.36907	-0.12270	0.00065	0.00066	0.00065	0.42	0.08
O2				0.25648	0.37529	-0.12070	0.00063	0.00065	0.00065	0.42	0.08
O3				-0.15357	0.55747	-0.33311	0.00064	0.00064	0.00065	0.56	0.08
O4				0.34145	0.55339	-0.32942	0.00061	0.00061	0.00061	0.37	0.07
O5				0.03568	0.45427	-0.22798	0.00067	0.00067	0.00067	0.66	0.08
O6				0.51372	0.43765	-0.22820	0.00059	0.00060	0.00060	0.29	0.07
O7				0.14863	0.66738	-0.44563	0.00063	0.00064	0.00064	0.62	0.08
O8				0.65481	0.67529	-0.43899	0.00061	0.00061	0.00061	0.38	0.08
O9				0.26021	-0.12186	0.37562	0.00062	0.00064	0.00065	0.36	0.08
O10				-0.25160	-0.12368	0.36635	0.00063	0.00064	0.00064	0.35	0.08
O11				0.35506	0.10470	0.18403	0.00059	0.00061	0.00060	0.33	0.07
O12				-0.14705	0.09620	0.17832	0.00062	0.00063	0.00063	0.46	0.08
O13				-0.05874	-0.22951	0.45478	0.00061	0.00063	0.00063	0.46	0.08
O14				-0.56642	-0.22561	0.43846	0.00059	0.00060	0.00060	0.33	0.07
O15				0.07437	-0.01327	0.28442	0.00062	0.00063	0.00062	0.48	0.08
O16				-0.45313	-0.02879	0.28135	0.00062	0.00063	0.00062	0.39	0.08
O17				-0.35526	0.18028	0.09633	0.00061	0.00062	0.00062	0.42	0.08
O18				0.14767	0.17971	0.10656	0.00061	0.00062	0.00062	0.46	0.08
O19				-0.02686	0.28527	-0.01583	0.00062	0.00062	0.00063	0.49	0.08
O20				0.45114	0.28025	-0.02978	0.00064	0.00064	0.00064	0.51	0.08

Vol. 3 (1962). The final discrepancy index R was 0.056 for the 2532 observed reflections[3].

Sapphirine-2M

The starting parameters were taken from Moore (1969) and the refinement was conducted as for sapphirine-1Tc. All the evidences pointed to a cation distribution among octahedral and tetrahedral sites strictly similar to that obtained for sapphirine-1Tc. Thus the same scattering curves for corresponding sites were used in the final stage of the refinement. Because of the diffuseness of the reflections with $l = 2n + 1$, two scale factors were used, one applied to the sharp reflections and the other to the diffuse reflections. The low number of "observed" reflections and the diffuseness of those with index $l = 2n + 1$, indicative of some disorder in the stacking of the structural layers, prevented good accuracy in the atomic parameters. The final R value for the 1812 reflections was 0.092[3].

Description and discussion

The crystal structure of sapphirine-1Tc is described in Figure 1; that of sapphirine-2M is reported in Figure 2. Both figures are idealized polyhedral diagrams and their comparison shows clearly the similarities as well as the differences between the two structures. The structure of sapphirine-1Tc is built up by the same structural units previously found by Moore (1968, 1969) in the structure of sapphirine-2M from Fiskenaesset: octahedral walls which run parallel to the *a* axis (or c_m axis of the pseudomonoclinic cell) and oriented parallel to $\{011\}$ plane; tetrahedral chains $[Al_{4.25}Si_{1.75}O_{18}]$ which run parallel to *a* (or c_m) axis; $[AlO_6]$ octahedra (corresponding to M8 and M9 sites) between walls, sharing edges with the walls above and below.

Sapphirine-1Tc is isostructural with aenigmatite $Na_2Fe_5^{+2}TiSi_6O_{20}$ whose crystal structure was determined by Merlino (1970) and by Cannillo et al. (1971) and serendibite $Ca_2M_6T_6O_{20}$ where M = (Mg,Al) and T = (Si,Al,B) according to the structural studies of Machin and Süsse (1974) and Buerger and Venkatakrishnan (1974). Three other minerals were indicated as isostructural with the preceding ones, on the basis of their crystal chemistry and crystallographic parameters: rhönite (Fleischer 1936, Walenta 1969), krinovite (Merlino, 1972) and welshite (Moore, 1978). Moreover a synthetic phase, found in titaniferous slags and named baikovite, was indicated by Machin and Süsse (1974) as a further possible member of the group on the basis of its chemical composition (Rudneva and Malysheva, 1960).

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[3] A list of the observed and calculated structure factors may be obtained from the author on request.

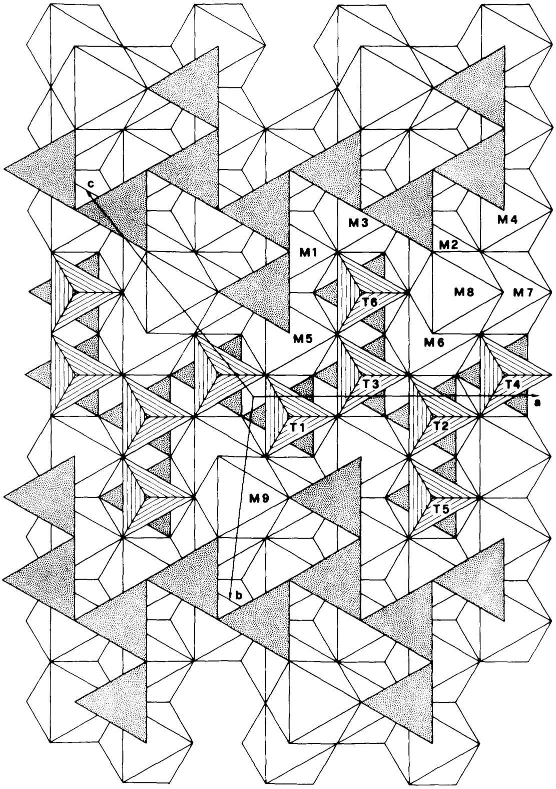

Fig. 1. Idealized polyhedral diagram of sapphirine-1Tc, as seen along a_m^*: *b* and *c* vectors end at height 1/2 $(d_{100})_m$, *m* indicating quantities which refer to the pseudomonoclinic cell

All those mineral phases were frequently or invariably polysynthetically twinned on {010} of the pseudomonoclinic cell. Among them only sapphirine-1Tc has a monoclinic counterpart, corresponding to the MDO_2 structure in the terminology of the OD-theory. Also the other minerals of the group could be found with monoclinic structure, at least on a submicroscopic scale, as restricted MDO_2 domains inside triclinic structures.

The bond lengths in the tetrahedral and octahedral sites are reported in Table 2. As previously said, these values were used together with other chemical and structural data, to determine the cation distributions in tetrahedral and octahedral sites. The mean M–O and T–O values for sapphirine-1Tc and 2M from Wilson Lake are given in Table 3 and compared with the corresponding values for sapphirine-2M from Fiskenaesset. It appears that corresponding values are strictly similar, which strongly indicates a similar cation distribution.

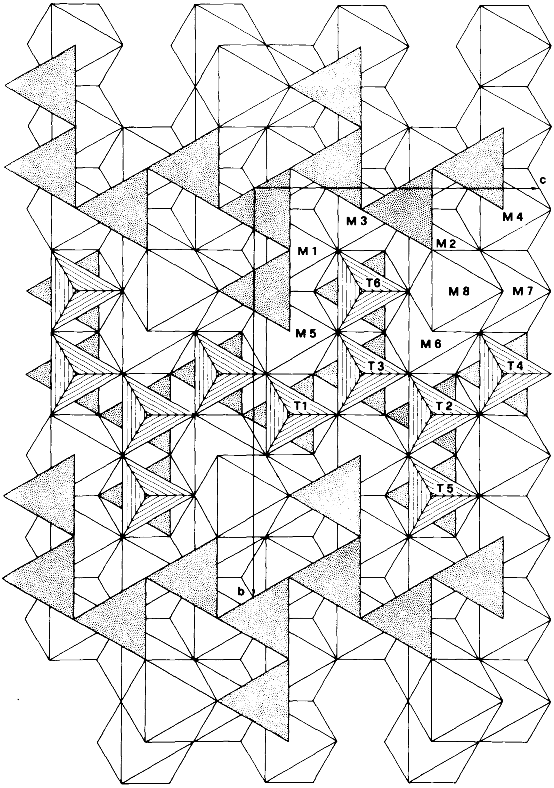

Fig. 2. Idealized polyhedral diagram of sapphirine-2M, as seen along *a**

The distortions in the polyhedral arrangement of sapphirine-2M was analyzed by Moore (1969) and explained by the cation ordering and cation repulsions: similar considerations are valid also for sapphirine-1Tc.

Conclusions

Since the discovery of the triclinic modification of sapphirine, the hypothesis was made that the two modifications could correspond to different degrees of ordering of the cations in the tetrahedral and octahedral sites, with sapphirine-1Tc as the less ordered polymorph (Merlino, 1973). On the other hand thermodynamic parameters were determined for natural 2M sapphirine and synthetic sapphirine obtained in hydrothermal experiments (Kiseleva, 1976). The differences in the values obtained in the two cases indicated a

Table 2. Octahedral and tetrahedral bond distances in sapphirine-1Tc, with the estimated standard deviations in parenthesis

M1–O1	1.978(6) Å	M4–O6	2.105(6) Å	M7–O6	1.886(8) Å	
O3	1.946(8)	O8	2.143(7)	O20	1.906(6)	
O5	1.872(6)	O3^{v}	2.032(6)	O1^{v}	2.007(6)	
O7^{ii}	1.961(6)	O4^{iv}	2.107(6)	O10^{i}	1.990(6)	
O9^{i}	1.961(7)	O8^{iv}	2.044(6)	O14^{i}	1.883(6)	
O14^{iii}	1.918(5)	O14^{i}	2.088(8)	O16^{i}	1.914(8)	
M2–O2	1.974(6)	M5–O1	2.168(8)	M8–O2	1.972(5)	x2
O4	1.948(7)	O17	2.058(6)	O6	1.920(5)	x2
O6	1.902(6)	O19	2.102(6)	O20	1.965(7)	x2
O8^{iv}	1.957(6)	O9^{i}	2.177(6)			
O10^{i}	1.970(8)	O11^{i}	2.128(7)			
O13^{i}	1.845(6)	O16^{iii}	2.183(6)			
M3–O4	1.999(6)	M6–O2	2.167(7)	M9–O9	1.955(5)	x2
O5	1.982(6)	O18	2.131(6)	O14^{v}	1.907(6)	x2
O7	2.076(8)	O20	2.171(6)	O16^{v}	1.958(6)	x2
O3^{ii}	2.069(6)	O10^{ii}	2.137(6)			
O7^{ii}	2.007(6)	O12^{i}	2.070(8)			
O13^{i}	1.998(8)	O15^{i}	2.110(6)			
T1–O12	1.748(8)	T3–O12	1.700(5)	T5–O9	1.779(8)	
O16	1.764(5)	O18	1.733(8)	O13	1.716(5)	
O17	1.737(7)	O19	1.698(7)	O15	1.767(8)	
O7^{iv}	1.764(4)	O3^{vi}	1.709(5)	O10^{ix}	1.760(5)	
T2–O11	1.648(7)	T4–O17	1.724(8)	T6–O2	1.758(8)	
O15	1.650(6)	O11^{viii}	1.754(5)	O5	1.701(8)	
O18	1.667(7)	O20^{viii}	1.751(7)	O19	1.729(6)	
O8^{vii}	1.658(4)	O4^{vi}	1.743(4)	O1^{vi}	1.746(5)	

The atoms of the different asymmetric units are related to the symmetry equivalent atoms of the fundamental unit as follows:

i	atom at	−x	−y	−z
ii	atom at	−x	1−y	−1−z
iii	atom at	−1−x	−y	−z
iv	atom at	1−x	1−y	−1−z
v	atom at	1+x	y	z
vi	atom at	−x	1−y	−z
vii	atom at	1−x	1−y	−z
viii	atom at	−1+x	y	z
ix	atom at	−x	−y	1−z

higher degree of structural order in the natural material. In connection with the preceding hypothesis it appeared likely that the synthetic sapphirine differed from the natural material in consisting of the disordered 1Tc triclinic modification (Kiseleva, 1976).

The present work clearly indicates that the kind of structural modification (monoclinic or triclinic) and the ordering of the cations are not necessarily

Table 3. Mean bond distances in sapphirine-1Tc and 2M from Wilson Lake and sapphirine-2M from Fiskenaesset

	1Tc Wilson Lake	2M Wilson Lake	2M Fiskenaesset
M1	1.939 Å	1.94 Å	1.926 Å
M2	1.933	1.94	1.930
M3	2.022	2.02	1.988
M4	2.087	2.10	2.078
M5	2.136	2.13	2.120
M6	2.131	2.13	2.115
M7	1.931	1.92	1.921
M8	1.952	1.94	1.930
M9	1.940		
T1	1.753	1.78	1.771
T2	1.656	1.66	1.658
T3	1.710	1.70	1.700
T4	1.743	1.73	1.733
T5	1.756	1.78	1.755
T6	1.734	1.73	1.736

linked, since the same degree of ordering was found in two phases characterized by different stacking sequences of the structural layers. Thus the hypothesis we noted is untenable and we may more precisely speak of polytypic relations between sapphirine-1Tc and sapphirine-2M. This does not invalidate the conclusions of Kiseleva (1976) about the different degree of order in natural and synthetic sapphirines, but forbids conclusions about the structural modification (triclinic or monoclinic) assumed for synthetic sapphirines: the question could be answered by accurate X-ray powder diffraction studies, on the basis of the different diffraction patterns of the two modifications.

As regards the genetic relations between sapphirine 1Tc and 2M at Wilson Lake, crystallographic evidence, namely the presence of sharp and diffuse spots corresponding to MDO_1 and MDO_2 domains, respectively, strongly indicates that sapphirine-1Tc was the originally formed polytype. As the previous hypothesis (Merlino, 1973) which maintained that sapphirine-2M was the ordered phase, obtained by cooling from sapphirine-1Tc, appears untenable on the basis of the present data, the 1Tc-2M transformation could be related to deformation stresses, as suggested by Higgins and Ribbe (1978) on the basis of electron optical observations.

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