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THE CRYSTAL CHEMISTRY OF THE [$M_3\phi_{11–14}$] TRIMERIC STRUCTURES: FROM HYPERAGPAITIC COMPLEXES TO SALINE LAKES

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ABSTRACT

The crystal structures of nacaphite, Na (Na,Ca)$_2$ (PO$_4$) F, *a* 5.3232(2), *b* 12.2103(4), *c* 7.0961(2) Å, α 90.002(1), β 89.998(1), γ 89.965(1)°, *V* 461.23(5) Å^3, and quadruphite, Na$_{14}$ Ca$_2$ Ti$_4$ [Si$_2$O$_7$]$_2$ (PO$_4$)$_4$ O$_4$ F$_2$, *a* 5.4206(2), *b* 7.0846(2), *c* 20.3641(7), α 86.89(1), β 94.42(1), γ 89.94(1)°, *V* 778.54(7) Å^3, from the Khibina–Lovozero alkaline complex, Kola Peninsula, Russia, have been solved by direct methods for the holotype single crystals in the space groups *P*1 (*Z* = 4) and *P*1 (*Z* = 1) and refined to residual *R* values of 5.6 and 3.1%, respectively, using 2293 and 7303 observed ($|F_o| > 4\sigma F$) reflections collected with a single-crystal diffractometer fitted with a CCD detector and Mo*K*α X-radiation. Nacaphite is twinned; this twinning of the true nacaphite unit-cell emulates the *C*-centered unit-cell previously described for nacaphite. The chemical formulae of both minerals have been slightly revised. There is a close relation between the structures of nacaphite and quadruphite. The main fragment of the nacaphite structure is a cluster of three octahedra with a common F–F edge. These trimeric clusters link to form chains extending along [100] that are connected into a framework by (PO$_4$) tetrahedra. The structure of quadruphite consists of two structural blocks (*TS* and *AC*) stacked along [001]. The Ti silicate (*TS*) block has a three-layered structure consisting of a central sheet of octahedra and two adjacent Ti–Si sheets. The *AC* block of alkali cations can be described in terms of nacaphite-like trimeric clusters; as in nacaphite, these trimeric clusters link along [100] to form an infinite chain. Trimeric clusters of the form [$M\phi_{11–14}$], *M* = Na, Ca; ϕ: O, OH, F, Cl, are common in a group of alkali sulfates, phosphates (and silicates), occurring in sulphohalite, Na$_6$ (SO$_4$)$_2$ F Cl, galeite, Na$_{15}$ (SO$_4$)$_5$ F$_4$ Cl, schairerite, Na$_{21}$ (SO$_4$)$_7$ F$_6$ Cl, kogarkoite, Na$_3$ (SO$_4$) F, the synthetic compound (Na$_2$Ca) (PO$_4$) F (a dimorph of nacaphite), arctite, (Na$_5$Ca) Ca$_6$ Ba (PO$_4$)$_6$ F$_3$, the synthetic compound Na$_2$ Fe (PO$_4$) (OH), polyphite, Na$_{17}$ Ca$_3$ Mg (Ti,Mn)$_4$ [Si$_2$O$_7$]$_2$ (PO$_4$)$_6$ O$_2$ F$_6$, and sobolevite, Na$_{11}$ (Na,Ca)$_4$ (Mg,Mn)Ti$_4$ [Si$_2$O$_7$]$_2$ (PO$_4$)$_4$ O$_3$ F$_3$. Bond-valence considerations suggest that Si analogues of some of these structures should be stable, and several phases of tricalcium silicate, Ca$_3$ (SiO$_4$) O, contain such trimeric clusters.

Keywords: nacaphite, quadruphite, crystal structure, Khibina–Lovozero, Kola Peninsula, Russia.

SOMMAIRE

Nous avons résolu les structures cristallines des échantillons holotypes de la nacaphite, Na (Na,Ca)$_2$ (PO$_4$) F, *a* 5.3232(2), *b* 12.2103(4), *c* 7.0961(2) Å, α 90.002(1), β 89.998(1), γ 89.965(1)°, *V* 461.23(5) Å^3, et la quadruphite, Na$_{14}$ Ca$_2$ Ti$_4$ [Si$_2$O$_7$]$_2$ (PO$_4$)$_4$ O$_4$ F$_2$, *a* 5.4206(2), *b* 7.0846(2), *c* 20.3641(7), α 86.89(1), β 94.42(1), γ 89.94(1)°, *V* 778.54(7) Å^3, provenant du complexe alcalin de Khibina–Lovozero, dans la péninsule de Kola, en Russie, par méthodes directes dans les groupes spatiaux *P*1 (*Z* = 4) et *P*1 (*Z* = 1); nous les avons affinées jusqu'à un résidu *R* de 5.6 et 3.1%, respectivement, en utilisant 2293 et 7303 réflexions observées ($|F_o| > 4\sigma F$) prélevées avec un diffractomètre à cristal unique muni d'un détecteur CCD et avec rayonnement Mo*K*α. La nacaphite est maclée; ces macles de la vrai maille simulent une maille à *C* centré, attribuée antérieurement à la nacaphite. Les formules chimiques des deux minéraux ont été légèrement corrigées. Une relation étroite existe entre les deux structures. Le fragment principal de la structure de la nacaphite est un groupement de trois octaèdres partageant une arête F–F commune. Ces groupements trimériques sont rattachés en chaînes le long de [100], à leur tour rattachées par des tétraèdres (PO$_4$) pour former une trame. La structure de la quadruphite contient deux blocs structuraux (*TS* et *AC*) empilés le long de [001]. Le bloc à silicate de Ti (*TS*) possède une structure à trois niveaux contenant un feuillet central d'octaèdres et deux feuillets adjacents Ti–Si. On peut décrire le bloc *AC* contenant des cations alcalins en termes de structures trimériques ressemblant à la nacaphite; tout comme dans la nacaphite, ces groupements trimériques sont liés le long de [100] pour former une chaîne infinie. Des groupements trimériques répondant à la formule [$M\phi_{11–14}$], *M* = Na, Ca; ϕ: O, OH, F, Cl, sont répandus dans un groupe de sulfates, phosphates (et silicates) alcalins, par exemple sulphohalite, Na$_6$ (SO$_4$)$_2$ F Cl, galéite, Na$_{15}$ (SO$_4$)$_5$ F$_4$ Cl, schairerite, Na$_{21}$ (SO$_4$)$_7$ F$_6$ Cl, kogarkoïte, Na$_3$ (SO$_4$) F, le composé synthétique (Na$_2$Ca) (PO$_4$) F (dimorphe de la nacaphite), arctite, (Na$_5$Ca) Ca$_6$ Ba (PO$_4$)$_6$ F$_3$, le composé synthétique Na$_2$ Fe (PO$_4$) (OH), polyphite, Na$_{17}$ Ca$_3$ Mg (Ti,Mn)$_4$ [Si$_2$O$_7$]$_2$ (PO$_4$)$_6$ O$_2$ F$_6$, et sobolevite, Na$_{11}$ (Na,Ca)$_4$ (Mg,Mn)Ti$_4$

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$[Si_2O_7]_2$ $(PO_4)_4$ O_3 F_3. D'après les considérations des valences de liaison, les analogues silicatés de certaines de ces structures devraient être stables, et plusieurs phases du silicate de tricalcium, Ca_3 (SiO_4) O, contiennent de tels agencements trimériques.

(Traduit par la Rédaction)

Mots-clés: nacaphite, quadruphite, structure cristalline, Khibina–Lovozero, péninsule de Kola, Russie.

INTRODUCTION

Structural relations of Ti silicate minerals from the Khibina–Lovozero alkaline complex have been discussed extensively in recent years. Of particular importance in these structures is a three-layered Ti silicate block consisting of a close-packed layer of octahedra and two adjacent sheets of tetrahedra and octahedra. Hyperagpaitic rocks of the Khibina–Lovozero complex formed at the last stages of pneumatolitic activity, with constituent minerals that have prominent stable clusters of alkali-cation coordination polyhedra. Such clusters are also found in minerals from saline-lake environments.

Nacaphite, Na_2 Ca (PO_4) F, and the structurally related minerals quadruphite, Na_{14} Ca Mg Ti_4 $[Si_2O_7]_2$ $(PO_4)_4$ O_4 F_2, polyphite, Na_{17} Ca_3 Mg $(Ti,Mn)_4$ $[Si_2O_7]_2$ $(PO_4)_6$ O_2 F_6, and sobolevite, Na_{11} Na_4 (Mg,Mn) Ti_4 $[Si_2O_7]_2$ $(PO_4)_4$ O_3 F_3, have been described from pegmatitic hyperagpaitic rocks of the Khibina–Lovozero alkaline complex, Kola Peninsula, Russia (Khomyakov *et al.* 1980, 1983, 1992, Khomyakov 1995). The crystal structures of nacaphite, quadruphite, polyphite and sobolevite (Sokolova *et al.* 1987a, b, 1988, 1989) consist of two types of blocks that differ both in chemistry and topology: (1) titanosilicate (*TS*), and (2) (Na,Ca) phosphate (*AC*). The Ti silicate block corresponds to the structure of seidozerite, Na_4 Mn Ti $(Zr_{1.5}Ti_{0.5})$ $[Si_2O_7]_2$ O_2 $(F,OH)_2$; the (Na,Ca)-phosphate block corresponds to a fragment of the structure of nacaphite. The seidozerite–nacaphite series includes at least 18 minerals, and can be regarded as a polysomatic series (Egorov-Tismenko & Sokolova 1990, Ferraris 1997, Sokolova 1998, Christiansen *et al.* 1999) or a merotype series (Makovicky 1997). Quadruphite, polyphite and sobolevite commonly form intergrowths with lomonosovite, Na_{10} Ti_4 $[Si_2O_7]_2$ $[PO_4]_2$ O_4; from a structural perspective, they also can be regarded as lomonosovite derivatives. The ratio P:Si varies from 1:2 in lomonosovite to 1:1 in quadruphite and sobolevite to 3:2 in polyphite.

The original crystal-structure determinations of nacaphite and quadruphite are not completely satisfactory. The original work on nacaphite was done on a twinned crystal at a time when there was no software available to adequately cope with this problem. Moreover, the structure was refined in the non-centrosymmetric space-group *C*1, and the refinement was very unstable. In the original work on quadruphite, no absorption correction was done, and there was some ambiguity as to the ordering of Mn and Mg at the junction of the *TS* and *AC* blocks. In order to resolve these problems, we have refined the structures of nacaphite and quadruphite, and discuss the relations among these minerals, focusing on the key role of alkali cations in their structural arrangements.

ELECTRON-MICROPROBE ANALYSIS

Chemical analysis of holotype single crystals of nacaphite and quadruphite was done with a Cameca SX–50 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 kV and a specimen current of 20 nA. The following standards were used: apatite: Ca; maricite: Na, P; forsterite: Mg; diopside: Si; titanite: Ti; spessartine: Mn; $SrTiO_3$: Sr; zircon: Zr; $MnNb_2O_6$: Nb; barite: Ba; Hf metal: Hf; fayalite: Fe; manganotantalite: Ta; fluorite: F (nacaphite); fluorapatite: F (quadruphite). Data were reduced using the $\phi(\rho z)$ procedure of Pouchou & Pichoir (1985). The chemical compositions of holotype nacaphite and quadruphite crystals are given in Table 1 (mean of

TABLE 1. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA (*apfu*) OF NACAPHITE AND QUADRUPHITE

	Nacaphite	Quadruphite		Nacaphite	Quadruphite
P_2O_5	35.73	19.12	P	1.01	3.98
Nb_2O_5	–	3.92			
Ta_2O_5	–	0.36	Si	–	4.07
SiO_2	–	16.57			
HfO_2	–	0.07	Nb	–	0.44
TiO_2	–	13.81	Ta	–	0.02
ZrO_2	–	3.96	Zr	–	0.47
Fe_2O_3	–	0.53	Hf	–	0.00
MnO	0.35	4.08	Ti^{4+}	–	2.55
MgO	–	1.37	Fe^{3+}	–	0.10
CaO	27.70	5.45	Mn^{2+}	–	0.44
SrO	–	0.41	Σ	–	4.02
BaO	–	0.05			
Na_2O	30.25	27.92	Mn^{2+}	0.01	0.41
F	9.03	2.72	Mg	–	0.50
O=F	–3.80	–1.15	Ca	1.00	1.44
Total	99.26	99.19	Sr	–	0.06
			Ba	–	0.00
			Na	1.97	13.32
			Σ	2.98	15.73
			F	0.96	2.11
			O	4.04	33.89

eleven determinations for each fragment), and the unit formulae were calculated on the basis of 5 (4 O + F) and 36 (34 O + 2F) anions *pfu* (per formula unit), respectively. The formulae (Table 1) differ slightly from the following empirical formulae on which the first structure determinations of nacaphite and quadruphite were based (Sokolova *et al.* 1987a, 1989): $Na_{1.99}$ ($Ca_{0.94}Sr_{0.01}$ $Mn_{0.01}$) $P_{1.00}$ $O_{3.97}$ $F_{0.97}$ and $Na_{12.66}$ $Ca_{1.42}$ $Mg_{0.39}$ $Ti_{2.44}$ $Mn_{0.86}$ $Zr_{0.46}$ $Nb_{0.42}$ $Si_{4.02}$ $P_{3.84}$ O_{33} F. We did not detect any Sr in nacaphite; the minor Sr previously reported in this mineral (Khomyakov *et al.* 1980) was probably due to inclusions of apatite; such inclusions of apatite occur in a synthetic hexagonal dimorph of nacaphite grown from a melt (Kirova *et al.* 1987, Sokolova *et al.* 1999).

COLLECTION OF X-RAY DATA AND STRUCTURE REFINEMENT

Single-crystal X-ray-diffraction data for holotype nacaphite and quadruphite were collected with a Siemens *P*4 diffractometer fitted with a CCD detector, using Mo*K*α X-radiation. An empirical absorption-correction (SADABS, Sheldrick 1996) was applied. The SHELX–97 program was used for solution and refinement of the structures. Scattering factors for neutral atoms were taken from the International Tables for X-ray Crystallography (Ibers & Hamilton 1974). The details of X-ray data collection and structure refinement are given in Table 2. Final observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

TABLE 2. MISCELLANEOUS DATA CONCERNING REFINEMENT OF NACAPHITE AND QUADRUPHITE

	Nacaphite*		Quadruphite*
	Twinned cell	Real cell	
a (Å)	10.6464(4)	5.3232(2)	5.4206(2)
b	24.4206(9)	12.2103(4)	7.0846(2)
c	7.0961(2)	7.0961(2)	20.3641(7)
α (°)	90.002(1)	90.002(1)	86.89(1)
β	89.998(1)	89.998(1)	94.42(1)
γ	89.965(1)	89.965(1)	89.94(1)
V (Å³)	1844.9(2)	461.23(5)	778.54(7)
Space group	*C*1	$P\bar{1}$	*P*1
Z	16	4	1
Absorption coefficient (mm⁻¹)	1.91	1.83	2.24
D (meas) (g.cm⁻³)	2.85***		3.12**
F(000)	1557.1	392	710.2
Crystal size (mm)	0.09 x 0.08 x 0.05		0.075 x 0.125 x 0.35
Radiation	MoKα		Mo*K*α
2θ-range for data collection (°)	60.08		59.94
R(int) (%)	2.78	4.00	0.00
Reflections collected	15824		13274
Unique reflections	9507	2662	8007
$F_o > 4\sigma F$	7484	2293	7303
Refinement method	Full-matrix least squares on F^2; fixed weights proportional to $1/\sigma(F^2_o)$		
Goodness of fit on F^2	1.067	1.144	1.063
Final *R* index [$F_o > 4\sigma F$]	7.3	5.57	3.06
R index (all data)	8.87	6.29	3.46
wR_2	21.1	16.41	8.8
GooF	1.067	1.143	1.064

* data were collected from holotype crystals.
** Khomyakov *et al.* (1992). *** Khomyakov *et al.* (1980).

Nacaphite

The intensities of 15824 reflections with $\bar{7} \le h \le 7$, $17 \le k \le 17$, $9 \le l \le 9$ were collected out to $2\theta = 60°$ using 30 s per frame. The refined unit-cell parameters were obtained from 6457 reflections ($I > 10\sigma I$) and are given in Table 2. Refinement of the structure of nacaphite was initiated in space group *C*1, and the site occupancies were refined for all alkali (*Na* and *Ca*) sites. The resultant occupancies indicated the presence of vacancies at the *Na* sites, vacancies that were not observed by Sokolova *et al.* (1989); moreover, the site-refinement results did not agree very well with the newly obtained chemical data for nacaphite (Table 1). While looking for some reason for these discrepancies, we discovered evidence of twinning in nacaphite. This led to the identification of a new unit-cell and space group (Table 2). The matrix 1 0 0 / 0 1 0 / 0 0 1 defines the twin law for nacaphite; this twin law is common for monoclinic crystals with β ≈ 90°, and emulates orthorhombic symmetry. Twinning of the true cell of nacaphite emulates the larger *C*-centered unit-cell previously ascribed to this mineral (Khomyakov *et al.* 1980). The crystal structure of nacaphite was refined to an *R* index of 5.6% and a GooF of 1.14 for a total of 176 refined parameters. A volume ratio of 0.733 : 0.267 for the two twin-fractions was found by refinement. Final atom parameters for nacaphite are given in Table 3, selected interatomic distances are listed in Table 4, and bond valences are presented in Table 5.

Quadruphite

The integrated intensities of 13274 reflections with $7 \le h \le 7$, $9 \le k \le 9$, $28 \le l \le 28$ were collected out to $2\theta = 60°$ using 30 s per frame. The refined unit-cell parameters (Table 2) obtained from 10128 reflections ($I > 10\sigma I$) are in accord with the parameters reported earlier by Sokolova *et al.* (1987a). The crystal structure of quadruphite was refined to an *R* index of 3.1% and a GooF of 1.06 for a total of 594 refined parameters. Final atom parameters for quadruphite are given in Table 6, selected interatomic distances are given in Table 7, refined site-scattering values are given in Table 8, and bond-valences are given in Table 9.

NACAPHITE

Coordination of the cations

In the newly refined structure of nacaphite, there are two unique *P* sites with mean bond-lengths <*P*(1)–O> = 1.521, <*P*(2)–O> = 1.528 Å, both somewhat less than the grand <*P*–O> distance of 1.537 Å reported by Baur

TABLE 3. FINAL ATOM PARAMETERS FOR NACAPHITE

	Site occupancies	x	y	z	U_{eq}*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M(1)	0.50(2) Ca + 0.50(3) Na	−0.2336(3)	0.8298(1)	0.4894(2)	0.0160(6)	0.0180(8)	0.0147(8)	0.0154(8)	−0.0029(5)	0.0042(5)	−0.0029(5)
M(2)	0.53(3) Na + 0.47(2) Ca	−0.2334(3)	0.8297(1)	0.0106(2)	0.0150(6)	0.0176(8)	0.0133(8)	0.0140(8)	0.0028(5)	−0.0027(5)	−0.0027(5)
M(3)	0.95(3) Na + 0.05(2) Ca	0.2365(4)	0.9096(2)	0.2501(3)	0.0203(9)	0.0245(14)	0.0182(13)	0.0183(12)	0.0001(8)	0.0011(9)	−0.0003(9)
M(4)	0.55(3) Na + 0.45(2) Ca	0.2465(4)	0.6691(1)	0.0139(2)	0.0239(7)	0.0503(13)	0.0111(9)	0.0103(8)	−0.0002(5)	0.0052(7)	0.0010(7)
M(5)	0.51(3) Na + 0.49(2) Ca	0.2465(4)	0.6691(1)	0.4860(2)	0.0251(7)	0.0508(13)	0.0130(9)	0.0118(8)	0.0003(5)	−0.0035(7)	−0.0012(7)
Na		−0.2638(4)	0.5875(2)	0.2502(4)	0.0251(8)	0.0107(11)	0.0138(12)	0.0507(17)	0.0004(10)	0.0017(11)	−0.0012(9)
P(1)		−0.2048(2)	0.5868(1)	0.7501(2)	0.0110(3)	0.0124(6)	0.0079(5)	0.0126(5)	0.0002(4)	0.0012(5)	−0.0016(5)
P(2)		0.2956(2)	0.9165(1)	0.7500(2)	0.0094(3)	0.0079(5)	0.0098(5)	0.0104(5)	−0.0002(4)	0.0007(5)	−0.0002(5)
F(1)		0.0038(6)	0.7371(3)	0.2498(5)	0.0220(7)	0.0073(13)	0.0204(16)	0.0383(20)	0.0002(14)	0.0013(13)	−0.0027(12)
F(2)		−0.4973(6)	0.7578(2)	0.2496(5)	0.0235(7)	0.0174(15)	0.0138(15)	0.0392(21)	−0.0012(14)	0.0015(14)	−0.0028(12)
O(1)		−0.4134(7)	0.9160(3)	0.7499(6)	0.0169(7)	0.0108(15)	0.0191(18)	0.0207(16)	0.0003(14)	−0.0002(14)	−0.0013(14)
O(2)		0.2011(8)	0.8563(3)	0.9262(5)	0.0220(8)	0.0330(21)	0.0172(18)	0.0160(17)	0.0018(13)	0.0144(16)	−0.0019(16)
O(3)		0.2007(8)	0.8563(3)	0.5738(5)	0.0227(8)	0.0355(21)	0.0169(18)	0.0159(17)	−0.0016(13)	−0.0131(16)	−0.0027(17)
O(4)		0.1995(8)	0.0348(3)	0.7502(6)	0.0215(8)	0.0223(18)	0.0094(16)	0.0328(20)	0.0000(14)	0.0002(17)	0.0032(15)
O(5)		−0.3035(8)	0.4690(3)	0.7503(6)	0.0232(8)	0.0225(19)	0.0086(16)	0.0384(22)	−0.0009(15)	0.0009(18)	−0.0038(15)
O(6)		0.0803(8)	0.5864(3)	0.7500(8)	0.0304(10)	0.0130(18)	0.0157(19)	0.0624(29)	−0.0002(19)	0.0005(20)	−0.0011(15)
O(7)		−0.295(2)	0.6475(4)	0.9240(8)	0.0633(22)	0.1165(56)	0.0140(21)	0.0594(34)	−0.0120(21)	0.0701(38)	−0.0127(27)
O(8)		−0.296(2)	0.6476(4)	0.5764(8)	0.0617(21)	0.1165(56)	0.0143(21)	0.0544(32)	0.0111(21)	−0.00627(37)	−0.0129(27)

* $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i{}^* a_j{}^* a_i a_j$

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) FOR NACAPHITE

M(1)–O(1)	2.333(4)	*M*(2)–O(7)	2.332(5)
M(1)–O(8)	2.333(5)	*M*(2)–O(1)	2.334(4)
M(1)–*F*(2)	2.375(4)	*M*(2)–*F*(2)	2.371(3)
M(1)–O(4)	2.379(4)	*M*(2)–O(4)	2.377(4)
M(1)–*F*(1)	2.401(3)	*M*(2)–*F*(1)	2.399(4)
M(1)–O(3)	2.410(5)	*M*(2)–O(2)	2.411(4)
<*M*(1)–(O,F)>	2.372	<*M*(2)–(O,F)>	2.371
M(3)–O(1)	2.329(4)	*M*(4)–*F*(1)	2.271(4)
M(3)–*F*(2)	2.333(4)	*M*(4)–O(6)	2.305(5)
M(3)–O(3)	2.395(4)	*M*(4)–O(2)	2.380(4)
M(3)–O(2)	2.396(4)	*M*(4)–O(5)	2.395(4)
M(3)–O(4)	2.418(5)	*M*(4)–*F*(2)	2.414(4)
M(3)–*F*(1)	2.445(4)	*M*(4)–O(7)	2.537(7)
<*M*(3)–(O,F)>	2.386	<*M*(4)–(O,F)>	2.384
M(5)–*F*(1)	2.273(4)	*Na*–*F*(1)	2.317(4)
M(5)–O(6)	2.305(5)	*Na*–O(6)	2.336(5)
M(5)–O(3)	2.381(4)	*Na*–O(5)	2.405(5)
M(5)–O(5)	2.396(4)	*Na*–*F*(2)	2.422(4)
M(5)–*F*(2)	2.418(4)	*Na*–O(7)	2.433(7)
M(5)–O(8)	2.533(7)	*Na*–O(8)	2.434(7)
<*M*(5)–(O,F)>	2.388	<*Na*–(O,F)>	2.391
P(1)–O(7)	1.517(5)	*P*(2)–O(4)	1.532(4)
P(1)–O(6)	1.518(4)	*P*(2)–O(2)	1.536(4)
P(1)–O(8)	1.518(5)	*P*(2)–O(3)	1.536(4)
P(1)–O(5)	1.532(4)	*P*(2)–O(1)	1.549(4)
<*P*(1)–O>	1.521	<*P*(2)–O>	1.538

TABLE 5. BOND-VALENCE* TABLE FOR NACAPHITE

	P(1)	*P*(2)	*M*(1)	*M*(2)	*M*(3)	*M*(4)	*M*(5)	*Na*	Σ
F(1)			0.18	0.18	0.13	0.25	0.26	0.18	1.18
F(2)			0.20	0.19	0.18	0.17	0.17	0.11	1.02
O(1)		1.20	0.28	0.30	0.25				1.98
O(2)		1.25		0.24	0.21	0.26			2.00
O(3)		1.25	0.25		0.21		0.27		1.97
O(4)		1.26	0.27	0.27	0.20				1.96
O(5)	1.26					0.25	0.26	0.20	1.97
O(6)	1.31					0.32	0.33	0.24	1.96
O(7)	1.31			0.30		0.17		0.18	1.96
O(8)	1.31		0.28				0.18	0.18	1.95
Σ	5.19	4.96	1.46	1.48	1.18	1.42	1.47	1.09	
Ideal	5	5	1.50	1.47	1.05	1.45	1.49	1.00	

* bond valences (*vu*) from curves of Brown & Altermatt (1985)

(1974). There are six unique *M* sites, each coordinated by four O and two F atoms. Five sites *M*(1–5) contain Ca and Na cations with different ratios of Ca to Na (Table 3); the sixth site, *Na*, incorporates only Na. There is no significant difference in the <*M*–(O,F)> and <*Na*–(O,F)> distances. The refined site-occupancies show Na to be strongly to completely ordered at *M*(3) and *Na*: *M*(3) = 0.95 Na + 0.05 Ca and *Na* = 1.0 Na. The other four *M* sites are characterized by approximately 1:1 ratios of Ca to Na (Table 3). The SREF results (ΣCa = 0.98, ΣNa = 2.02 *apfu*) are in a good accord with the EMPA data of Table 1 (Ca = 1.00, Na = 1.97 *apfu*). The simplified formula of nacaphite can be written as Na (CaNa) (PO_4) F.

Structure topology

The key motif in the structure of nacaphite is the trimer of octahedra shown in Figure 1a. There are two symmetrically distinct trimers in nacaphite, but their stereochemistry is virtually the same: two ($Na_{1/2}Ca_{1/2}O_6$) octahedra and one (NaO_6) octahedron (Fig. 1a). The

TABLE 6. FINAL ATOM PARAMETERS (Å) FOR QUADRUPHITE

	x	*y*	*z*	U_{eq} *	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
A(1)	0.69487(8)	0.98405(7)	0.64379(3)	0.0091(2)	0.0068(3)	0.0074(3)	0.0129(3)	0.0000(2)	0.0009(2)	0.0001(2)
A(2)	0.41629(9)	0.32801(7)	0.33580(3)	0.0093(2)	0.0075(3)	0.0076(3)	0.0127(3)	0.0002(2)	0.0013(2)	0.0002(2)
A(3)	–0.2158(1)	0.7673(1)	0.49479(4)	0.0123(3)	0.0171(5)	0.0100(4)	0.0096(4)	0.0002(3)	–0.0002(3)	0.0002(3)
A(4)	–0.6719(1)	0.5444(1)	0.48481(4)	0.0121(3)	0.0180(5)	0.0095(4)	0.0087(4)	–0.0006(3)	–0.0005(3)	0.0016(3)
M(1)	0.8625(3)	0.1526(2)	0.07805(7)	0.0190(5)	0.0205(8)	0.0200(8)	0.0162(8)	–0.0002(5)	0.0011(5)	0.0008(5)
M(2)	0.3121(2)	0.3925(2)	0.03394(7)	0.0175(5)	0.0220(7)	0.0152(7)	0.0154(7)	–0.0018(5)	0.0018(4)	–0.0008(4)
M(3)	–0.2133(2)	0.9196(2)	0.94546(6)	0.0198(4)	0.0248(7)	0.0183(7)	0.0161(7)	–0.0006(5)	0.0000(4)	0.0004(4)
M(4)	0.3106(3)	0.1591(2)	0.90089(7)	0.0187(5)	0.0205(8)	0.0198(8)	0.0159(8)	–0.0014(5)	0.0014(5)	0.0006(5)
Na(1)	–0.2159(4)	0.4048(3)	0.9358(1)	0.0158(4)	0.0206(9)	0.0108(9)	0.0155(10)	0.0004(8)	–0.0011(7)	–0.0025(7)
Na(2)	0.7493(4)	0.6991(3)	0.7885(1)	0.0278(5)	0.0369(13)	0.0179(11)	0.0276(13)	–0.0002(10)	–0.0028(9)	0.0001(9)
Na(3)	0.4151(4)	–0.1606(4)	0.3256(1)	0.0209(5)	0.0227(10)	0.0215(12)	0.0179(12)	0.0001(9)	–0.0025(8)	0.0008(8)
Na(4)	0.2576(4)	0.9593(3)	0.7457(1)	0.0221(5)	0.0334(11)	0.0156(10)	0.0182(10)	–0.0026(8)	0.0063(8)	0.0012(8)
Na(5)	0.9032(4)	0.3512(3)	0.2341(1)	0.0212(4)	0.0285(10)	0.0160(10)	0.0185(10)	–0.0043(8)	–0.0041(8)	–0.0029(8)
Na(6)	–0.2014(4)	0.2726(3)	0.4933(1)	0.0227(5)	0.0149(9)	0.0184(11)	0.0344(13)	–0.0113(9)	–0.0066(8)	0.0037(8)
Na(7)	0.3120(4)	0.0404(3)	0.4865(1)	0.0223(5)	0.0148(9)	0.0222(11)	0.0297(12)	–0.0100(9)	–0.0063(8)	0.0042(8)
Na(8)	0.2899(4)	0.4303(3)	0.7661(1)	0.0300(5)	0.0444(13)	0.0238(10)	0.0222(10)	–0.0029(8)	0.0043(9)	–0.0029(9)
Na(9)	0.9206(4)	–0.1176(3)	0.2130(1)	0.0290(5)	0.0396(12)	0.0222(10)	0.0245(10)	–0.0024(8)	–0.0028(9)	0.0036(9)
Na(10)	–0.3005(4)	0.4737(4)	0.6537(1)	0.0205(5)	0.0230(10)	0.0244(13)	0.0141(11)	0.0019(9)	0.0032(8)	–0.0006(8)
Na(11)	0.3601(4)	0.6111(3)	0.1901(1)	0.0287(6)	0.0376(13)	0.0164(12)	0.0325(14)	0.0015(10)	0.0064(10)	0.0003(10)
Na(12)	0.3161(4)	–0.0916(3)	0.0437(1)	0.0161(4)	0.0182(9)	0.0138(10)	0.0165(11)	0.0012(8)	0.0036(7)	0.0016(7)
P(1)	0.8024(2)	0.1866(2)	0.79434(5)	0.0130(2)	0.0170(5)	0.0106(4)	0.0117(5)	–0.0012(3)	0.0015(4)	0.0005(4)
P(2)	0.8018(2)	0.6363(2)	0.08917(6)	0.0139(2)	0.0150(6)	0.0147(5)	0.0120(5)	–0.0002(4)	0.0001(4)	0.0013(4)
P(3)	0.4174(2)	0.1258(1)	0.18494(5)	0.0133(2)	0.0167(5)	0.0110(5)	0.0120(5)	–0.0007(3)	0.0003(4)	0.0010(4)
P(4)	0.2448(2)	0.6753(2)	0.89000(6)	0.0137(2)	0.0171(6)	0.0126(5)	0.0113(5)	–0.0001(4)	0.0010(4)	–0.0019(4)
Si(1)	–0.8118(2)	0.2795(2)	0.61430(6)	0.0111(3)	0.0135(6)	0.0087(6)	0.0108(6)	–0.0006(5)	0.0001(4)	0.0003(4)
Si(2)	–0.0728(2)	0.6064(2)	0.35112(6)	0.0098(2)	0.0129(5)	0.0072(6)	0.0092(6)	–0.0007(5)	0.0002(4)	0.0005(4)
Si(3)	0.1880(2)	0.7055(2)	0.62876(6)	0.0102(2)	0.0121(5)	0.0089(6)	0.0093(6)	0.0004(5)	–0.0005(4)	–0.0002(4)
Si(4)	–0.0830(2)	0.0336(2)	0.36531(6)	0.0108(2)	0.0142(6)	0.0087(6)	0.0093(6)	0.0006(5)	0.0005(4)	–0.0004(4)
F(1)	0.5627(5)	0.1563(5)	0.9980(2)	0.0211(6)	0.0152(11)	0.0224(10)	0.0258(16)	–0.0025(11)	0.0023(10)	0.0010(8)
F(2)	0.0565(5)	0.1563(5)	0.9815(2)	0.0212(6)	0.0131(10)	0.0229(10)	0.0272(16)	–0.0021(10)	–0.0015(9)	–0.0003(8)
O(1)	0.7220(6)	0.0204(5)	0.7502(2)	0.0211(6)	0.0231(16)	0.0145(17)	0.0134(16)	–0.0036(13)	0.0018(12)	–0.0028(12)
O(2)	–0.0793(6)	0.9932(5)	0.4433(2)	0.0212(6)	0.0193(16)	0.0193(18)	0.0094(15)	–0.0016(13)	–0.0003(11)	0.0021(13)
O(3)	–0.5249(6)	0.7645(5)	0.4406(2)	0.0169(7)	0.0206(15)	0.0122(16)	0.0116(16)	0.0010(13)	0.0027(11)	–0.0006(12)
O(4)	-0.8094(6)	0.3205(5)	0.5359(2)	0.0160(7)	0.0189(15)	0.0161(17)	0.0109(16)	-0.0002(13)	0.0018(12)	0.0014(12)
O(5)	–0.0280(6)	0.5860(5)	0.4313(2)	0.0148(6)	0.0197(15)	0.0117(15)	0.0114(15)	-0.0013(12)	0.0016(11)	0.0008(11)
O(6)	–0.3621(6)	0.5471(5)	0.5391(2)	0.0153(7)	0.0196(15)	0.0134(16)	0.0093(15)	0.0023(13)	0.0013(11)	0.0008(12)
O(7)	0.7162(7)	0.3788(5)	0.7633(2)	0.0142(6)	0.0421(21)	0.0117(16)	0.0187(15)	0.0031(14)	0.0025(14)	0.0047(14)
O(8)	0.6717(6)	0.9510(5)	0.5530(2)	0.0142(6)	0.0162(15)	0.0230(19)	0.0136(17)	0.0006(14)	-0.0015(11)	-0.0039(13)
O(9)	0.4397(6)	0.3613(5)	0.4264(2)	0.0243(8)	0.0185(16)	0.0234(19)	0.0112(16)	-0.0020(14)	0.0014(11)	-0.0020(13)
O(10)	0.1620(6)	0.5305(6)	0.3151(2)	0.0178(7)	0.0227(17)	0.0335(22)	0.0143(17)	-0.0037(15)	0.0008(12)	0.0161(15)
O(11)	0.9602(6)	0.7894(6)	0.6655(2)	0.0177(7)	0.0209(16)	0.0305(21)	0.0158(17)	-0.0007(15)	0.0043(12)	0.0154(14)
O(12)	0.1430(6)	0.7270(5)	0.5486(2)	0.0235(8)	0.0182(16)	0.0160(16)	0.0098(15)	0.0003(13)	-0.0022(11)	0.0004(12)
O(13)	0.4483(6)	0.7810(5)	0.6610(2)	0.0223(8)	0.0211(16)	0.0251(20)	0.0167(18)	0.0020(15)	-0.0019(13)	-0.0151(14)
O(14)	0.6733(6)	0.5238(6)	0.3184(2)	0.0149(6)	0.0300(19)	0.0344(23)	0.0116(17)	-0.0045(16)	0.0032(13)	-0.0155(16)
O(15)	0.4280(8)	0.1659(7)	0.6440(2)	0.0213(8)	0.0425(22)	0.0457(28)	0.0234(22)	-0.0049(19)	-0.0051(16)	0.0310(21)
O(16)	0.9129(6)	0.6130(5)	0.1603(2)	0.0251(8)	0.0306(18)	0.0204(15)	0.0153(15)	0.0021(12)	-0.0062(13)	0.0004(13)
O(17)	0.9339(8)	0.1840(7)	0.6339(2)	0.0371(1)	0.0447(23)	0.0425(27)	0.0270(23)	-0.0096(20)	0.0157(18)	-0.0300(20)
O(18)	–0.8032(7)	0.4799(5)	0.6515(2)	0.0195(7)	0.0364(19)	0.0090(17)	0.0126(18)	-0.0012(14)	-0.0008(13)	-0.0033(13)
O(19)	0.3408(7)	0.4841(5)	0.9212(2)	0.0309(8)	0.0325(19)	0.0283(18)	0.0307(19)	0.0120(15)	0.0052(15)	0.0106(16)
O(20)	0.8796(7)	0.8276(5)	0.0577(2)	0.0294(8)	0.0347(20)	0.0247(17)	0.0274(19)	0.0124(14)	0.0035(15)	-0.0047(15)
O(21)	0.6932(6)	0.1315(5)	0.1724(2)	0.0273(7)	0.0178(15)	0.0269(16)	0.0389(19)	-0.0098(14)	0.0077(14)	-0.0003(13)
O(22)	0.6877(7)	0.1518(4)	0.8602(2)	0.0250(7)	0.0381(19)	0.0219(15)	0.0156(14)	-0.0009(11)	0.0063(13)	-0.0023(14)
O(23)	0.0862(6)	0.1830(5)	0.8056(2)	0.0291(7)	0.0158(15)	0.0306(17)	0.0416(20)	-0.0115(15)	-0.0003(14)	-0.0030(13)
O(24)	0.8866(7)	0.4755(6)	0.0485(2)	0.0353(9)	0.0481(23)	0.0370(21)	0.0217(17)	-0.0141(15)	0.0000(16)	0.0196(18)
O(25)	0.5165(6)	0.6304(4)	0.0874(2)	0.0228(6)	0.0173(15)	0.0225(14)	0.0284(16)	0.0002(12)	0.0008(12)	0.0010(12)
O(26)	0.3149(6)	0.6990(5)	0.8188(2)	0.0235(7)	0.0363(19)	0.0197(15)	0.0155(15)	0.0000(12)	0.0090(13)	-0.0017(14)
O(27)	-0.0408(6)	0.6806(4)	0.8914(2)	0.0236(7)	0.0175(15)	0.0240(15)	0.0295(16)	0.0019(12)	0.0057(12)	0.0015(12)
O(28)	0.2618(6)	0.1613(4)	0.1189(2)	0.0241(7)	0.0335(18)	0.0236(15)	0.0137(14)	-0.0006(11)	-0.0075(13)	0.0039(14)
O(29)	0.3523(7)	-0.0645(5)	0.2163(2)	0.0240(8)	0.0426(20)	0.0130(17)	0.0164(17)	-0.0017(13)	0.0020(14)	-0.0043(14)
O(30)	0.3557(8)	0.8366(6)	0.9301(2)	0.0367(9)	0.0513(24)	0.0337(20)	0.0268(19)	-0.0120(15)	0.0056(17)	-0.0193(18)
O(31)	0.3634(6)	0.2898(5)	0.2304(2)	0.0164(7)	0.0225(16)	0.0120(16)	0.0146(16)	-0.0018(13)	-0.0005(12)	0.0025(12)
O(32)	-0.0856(7)	0.8344(5)	0.3286(2)	0.0214(8)	0.0410(20)	0.0089(17)	0.0142(19)	0.0003(14)	0.0025(14)	0.0015(14)
O(33)	-0.3295(8)	0.1395(7)	0.3357(2)	0.0425(13)	0.0509(25)	0.0470(29)	0.0277(24)	-0.0075(20)	-0.0135(18)	0.0371(23)
O(34)	0.1571(9)	0.1408(8)	0.3436(2)	0.0441(12)	0.0546(26)	0.0519(30)	0.0293(24)	-0.0139(21)	0.0175(19)	-0.0430(22)

* $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i{}^* a_j{}^* a_i a_j$

TABLE 7. SELECTED INTERATOMIC DISTANCES (Å) FOR QUADRUPHITE

A(1)–O(8)	1.872(4)	*A*(2)–O(9)	1.867(3)	*A*(3)–O(3)	1.935(4)	*A*(4)–O(9)	1.935(4)
A(1)–O(17)	1.934(4)	*A*(2)–O(33)	1.918(4)	*A*(3)–O(8)	1.936(4)	*A*(4)–O(6)	1.939(3)
A(1)–O(15)	1.937(4)	*A*(2)–O(34)	1.942(4)	*A*(3)–O(6)	1.959(3)	*A*(4)–O(3)	1.959(3)
A(1)–O(11)	2.000(3)	*A*(2)–O(10)	1.994(3)	*A*(3)–O(2)	2.036(4)	*A*(4)–O(4)	2.024(4)
A(1)–O(13)	2.000(4)	*A*(2)–O(14)	2.004(4)	*A*(3)–O(12)	2.168(3)	*A*(4)–O(5)	2.154(3)
A(1)–O(1)	2.190(4)	*A*(2)–O(31)	2.176(4)	*A*(3)–O(5)	2.177(3)	*A*(4)–O(12)	2.178(3)
<*A*(1)–O>	1.989	<*A*(2)–O>	1.984	<*A*(3)–O>	2.035	<*A*(4)–O>	2.032
M(1)–O(21)	2.190(4)	*M*(2)–O(25)	2.296(4)	*M*(3)–O(27)	2.305(4)	*M*(4)–O(23)	2.208(4)
M(1)–*F*(1)	2.211(3)	*M*(2)–*F*(1)	2.338(3)	*M*(3)–*F*(2)	2.337(4)	*M*(4)–*F*(2)	2.222(3)
M(1)–O(28)	2.260(4)	*M*(2)–O(28)	2.349(3)	*M*(3)–O(22)	2.357(3)	*M*(4)–O(22)	2.264(4)
M(1)–*F*(2)	2.299(3)	*M*(2)–O(19)	2.368(4)	*M*(3)–O(20)	2.359(4)	*M*(4)–*F*(1)	2.314(4)
M(1)–O(24)	2.340(5)	*M*(2)–*F*(2)	2.415(4)	*M*(3)–O(30)	2.411(4)	*M*(4)–O(30)	2.337(4)
M(1)–O(20)	2.365(4)	*M*(2)–O(24)	2.423(4)	*M*(3)–*F*(1)	2.412(4)	*M*(4)–O(19)	2.365(4)
<*M*(1)–(O,F)>	2.278	<*M*(2)–(O,F)>	2.365	<*M*(3)–(O,F)>	2.364	<*M*(4)–(O,F)>	2.285
Tetrahedrally coordinated *Na*-sites							
Na(2)–O(27)	2.304(4)	*Na*(8)–O(23)	2.219(4)	*Na*(9)–O(21)	2.236(4)	*Na*(11)–O(25)	2.314(4)
Na(2)–O(7)	2.358(5)	*Na*(8)–O(26)	2.236(4)	*Na*(9)–O(16)	2.239(4)	*Na*(11)–O(31)	2.377(4)
Na(2)–O(1)	2.366(5)	*Na*(8)–O(7)	2.344(4)	*Na*(9)–O(32)	2.363(4)	*Na*(11)–O(29)	2.388(5)
Na(2)–O(26)	2.480(4)	*Na*(8)–O(18)	2.357(4)	*Na*(9)–O(29)	2.367(5)	*Na*(11)–O(16)	2.453(4)
<*Na*(2)–O>	2.377	<*Na*(8)–O>	2.289	<*Na*(9)–O>	2.301	<*Na*(11)–O>	2.383
Octahedrally and [7]-coordinated *Na*-sites							
Na(1)–O(27)	2.341(4)	*Na*(3)–O(29)	2.291(4)	*Na*(4)–O(23)	2.290(4)	*Na*(5)–O(21)	2.300(4)
Na(1)–*F*(2)	2.398(4)	*Na*(3)–O(3)	2.371(5)	*Na*(4)–O(26)	2.311(4)	*Na*(5)–O(16)	2.326(4)
Na(1)–O(24)	2.398(4)	*Na*(3)–O(33)	2.547(6)	*Na*(4)–O(13)	2.479(5)	*Na*(5)–O(10)	2.485(5)
Na(1)–O(22)	2.458(4)	*Na*(3)–O(10)	2.594(5)	*Na*(4)–O(1)	2.550(4)	*Na*(5)–O(31)	2.540(4)
Na(1)–O(19)	2.459(4)	*Na*(3)–O(34)	2.610(6)	*Na*(4)–O(11)	2.555(5)	*Na*(5)–O(14)	2.559(4)
Na(1)–*F*(1)	2.477(4)	*Na*(3)–O(14)	2.654(5)	*Na*(4)–O(15)	2.693(5)	*Na*(5)–O(33)	2.861(6)
<*Na*(1)–(O,F)>	2.422	<*Na*(3)–O>	2.511	<*Na*(4)–O>	2.480	*Na*(5)–O(34)	2.872(6)
						<*Na*(5)–O>	2.563
Na(6)–O(4)	2.266(4)	*Na*(7)–O(2)	2.264(4)	*Na*(10)–O(7)	2.290(4)	*Na*(12)–O(25)	2.346(4)
Na(6)–O(9)	2.352(4)	*Na*(7)–O(8)	2.352(4)	*Na*(10)–O(6)	2.361(4)	*Na*(12)–*F*(1)	2.400(4)
Na(6)–O(2)	2.390(4)	*Na*(7)–O(4)	2.387(4)	*Na*(10)–O(17)	2.480(6)	*Na*(12)–O(30)	2.421(4)
Na(6)–O(6)	2.394(4)	*Na*(7)–O(3)	2.408(4)	*Na*(10)–O(13)	2.584(5)	*Na*(12)–O(28)	2.452(4)
Na(6)–O(8)	2.640(5)	*Na*(7)–O(9)	2.642(5)	*Na*(10)–O(15)	2.639(6)	*Na*(12)–O(20)	2.469(4)
Na(6)–O(5)	2.700(4)	*Na*(7)–O(12)	2.691(5)	*Na*(10)–O(11)	2.659(5)	*Na*(12)–*F*(2)	2.479(4)
<*Na*(6)–O>	2.457	<*Na*(7)–O>	2.457	<*Na*(10)–O>	2.545	<*Na*(12)–(O,F)>	2.428
Si(1)–O(15)	1.589(4)	*Si*(2)–O(14)	1.608(4)	*Si*(3)–O(13)	1.614(4)	*Si*(4)–O(34)	1.588(4)
Si(1)–O(17)	1.605(4)	*Si*(2)–O(10)	1.623(3)	*Si*(3)–O(11)	1.621(3)	*Si*(4)–O(33)	1.593(4)
Si(1)–O(4)	1.609(3)	*Si*(2)–O(5)	1.630(4)	*Si*(3)–O(12)	1.632(3)	*Si*(4)–O(2)	1.597(3)
Si(1)–O(18)	1.644(4)	*Si*(2)–O(32)	1.655(4)	*Si*(3)–O(18)	1.639(4)	*Si*(4)–O(32)	1.632(4)
<*Si*(1)–O>	1.612	<*Si*(2)–O>	1.629	<*Si*(3)–O>	1.627	<*Si*(4)–O>	1.603
P(1)–O(7)	1.527(3)	*P*(2)–O(16)	1.526(3)	*P*(3)–O(29)	1.514(4)	*P*(4)–O(26)	1.528(3)
P(1)–O(22)	1.530(3)	*P*(2)–O(24)	1.535(4)	*P*(3)–O(21)	1.536(3)	*P*(4)–O(19)	1.538(4)
P(1)–O(23)	1.538(3)	*P*(2)–O(20)	1.541(4)	*P*(3)–O(28)	1.539(3)	*P*(4)–O(30)	1.537(4)
P(1)–O(1)	1.562(4)	*P*(2)–O(25)	1.545(3)	*P*(3)–O(31)	1.565(4)	*P*(4)–O(27)	1.551(3)
<*P*(1)–O>	1.539	<*P*(2)–O>	1.537	<*P*(3)–O>	1.539	<*P*(4)–O>	1.539

TABLE 8. REFINED OCTAHEDRAL SITE-SCATTERING VALUES AND ASSIGNED SITE-POPULATIONS FOR QUADRUPHITE

	Scattering species	SREF value (*epfu*)	Normalized site-scattering (*epfu*)	Site population (*apfu*)	Predicted site-scattering (*epfu*)	$\langle X–\varphi\rangle_{calc}$*	$\langle X–\varphi\rangle_{obs}$
A(1)	Nb, Ti	28.1(5)	28.9	0.63 Ti + 0.22 Nb + 0.15 Zr	28.9	2.01	1.99
A(2)	Nb, Ti	28.1(5)	28.9	0.63 Ti + 0.22 Nb + 0.15 Zr	28.9	2.01	1.98
A(3)	Nb, Ti	23.5(5)	24.2	0.65 Ti + 0.22 Mn + 0.05 Fe^{3+} + 0.08 Zr	24.3	2.05	2.04
A(4)	Nb, Ti	23.9(5)	24.6	0.64 Ti + 0.22 Mn + 0.05 Fe^{3+} + 0.09 Zr	24.5	2.05	2.03
M(1)	Ca, Na	14.8(4)	15.1	0.44 Na + 0.25 Mg + 0.21 Mn + 0.10 Ca	15.1	2.27	2.28
M(2)	Ca, Na	16.9(4)	17.2	0.69 Ca + 0.31 Na	17.2	2.37	2.37
M(3)	Ca, Na	17.4(4)	17.7	0.56 Ca + 0.38 Na + 0.06 Sr	17.7	2.38	2.36
M(4)	Ca, Na	14.5(4)	14.8	0.46 Na + 0.25 Mg + 0.20 Mn^{2+} + 0.09 Ca	14.8	2.27	2.28

* Calculated by summing the constituent ionic radii; values from Shannon (1976)

TABLE 9. BOND-VALENCE* TABLE (*vu*) FOR QUADRUPHITE

	P(1)	*P*(2)	*P*(3)	*P*(4)	*Si*(1)	*Si*(2)	*Si*(3)	*Si*(4)	*A*(1) [*M*(1)]	*A*(2) [*M*(2)]	*A*(3) [*M*(3)]	*A*(4) [*M*(4)]	*Na*(1)	*Na*(2)	*Na*(3)	*Na*(4)	*Na*(5)	*Na*(6)	*Na*(7)	*Na*(8)	*Na*(9)	*Na*(10)	*Na*(11)	*Na*(12)	Σ
O(1)	1.16								0.40					0.22		0.13									1.91
O(2)								1.08			0.55							0.20	0.29						2.12
O(3)											0.70	0.68			0.22				0.19						1.79
O(4)					1.04							0.57						0.29	0.21						2.11
O(5)						0.98					0.37	0.40						0.09							1.84
O(6)											0.67	0.72						0.20				0.22			1.81
O(7)	1.28													0.22						0.23		0.27			2.00
O(8)									0.94		0.70							0.10	0.23						1.97
O(9)										0.96		0.72						0.23	0.10						2.01
O(10))						1.00				0.68					0.12		0.16								1.96
O(11)							1.01		0.66							0.13						0.10			1.90
O(12)							0.98				0.38	0.37							0.09						1.82
O(13)							1.03		0.66							0.16						0.12			1.97
O(14)						1.04				0.66					0.10		0.13								1.93
O(15)					1.10				0.78							0.09						0.10			2.07
O(16)		1.29															0.24				0.31		0.17		2.01
O(17)					1.05				0.78													0.16			1.99
O(18)					0.95		0.96													0.22					2.13
O(19)				1.24						[0.31]		[0.22]	0.17												1.94
O(20)		1.23							[0.20]		[0.32]													0.17	1.91
O(21)			1.24						[0.34]								0.26				0.31				2.15
O(22)	1.27										[0.32]	[0.27]	0.17												2.03
O(23)	1.24											[0.32]				0.27				0.32					2.15
O(24)		1.25							[0.23]	[0.26]			0.20												1.94
O(25)		1.21								[0.37]													0.25	0.23	1.96
O(26)				1.27										0.16		0.25				0.31					1.99
O(27)				1.20							[0.37]		0.23	0.27											2.07
O(28)			1.23						[0.29]	[0.32]														0.17	2.01
O(29)			1.32												0.27						0.22		0.21		2.02
O(30)				1.24							[0.28]													0.19	1.71
O(31)			1.15							0.42		[0.23]					0.14						0.21		2.15
O(32)						0.92		0.98													0.22				2.12
O(33)								1.09		0.82					0.13		0.06								2.10
O(34)								1.10		0.78					0.11		0.06								2.05
F(1)									[0.25]	[0.23]	[0.18]	[0.20]	0.12											0.14	1.12
F(2)									[0.20]	[0.19]	[0.24]	[0.25]	0.14											0.11	1.13
	4.95	4.98	4.97	4.95	4.14	3.94	3.98	4.25	4.22	4.32	3.67	3.46	1.02	0.86	0.95	1.03	1.05	1.11	1.11	1.08	1.06	0.97	0.84	1.01	
									[1.57]	[1.68]	[1.71]	[1.49]													

*bond valences (*vu*) from curves of Brown & Altermatt (1985) for Ca, Na, Sr, Mg, Nb, Ti^{4+}, Zr, P, Si, Fe^{3+}, Mn^{2+}.

** bond valences (*vu*) for the *M*-sites are in square brackets

($Na_{1/2}Ca_{1/2}O_6$) octahedra share an edge, and also each shares a face with the (NaO_6) octahedron; the central axis of each cluster is an edge (formed by two F-atoms) that is common to all three constituent octahedra. These *trimeric clusters* link to form a convoluted chain of octahedra (Fig. 1b) that extends in the *a* direction. Clusters adjacent in the chain are rotated ~60° relative to each other and connect by sharing both faces and edges: the (NaO_6) and {$M(3)O_6$} octahedra are connected to the next trimer through two common faces, and the remaining octahedra link through common edges. In total, the (NaO_6) and {$M(3)O_6$} octahedra have four faces in common, whereas the {$M(1,2,4,5)O_6$} octahedra (with a higher charge of the central cation) share two faces. The chain shows pseudohexagonal symmetry described by the 6_3 axis oriented along the sequence of [F(1)–F(2)] common edges that defines the central axis of the chain. Combination of two clusters corresponds to a sequence of two [F(1)–F(2)] edges of 2.679 and 2.668 Å (sum = 5.347 Å), defining the *a* repeat and giving an *a* cell-parameter of 5.3232(2) Å.

The chains extend along the *a* axis, and link in the (100) plane by sharing octahedron corners (Fig. 1c): triplets of chains are further linked through (PO_4) tetrahedra that point alternately up and down the *a* axis. The resultant layer occurs at $x \approx 0.25$ and ≈ 0.75. The (PO_4) tetrahedra share three vertices with octahedra of the same layer, and the fourth vertex with three octahedra from the adjacent layer (Fig. 1d).

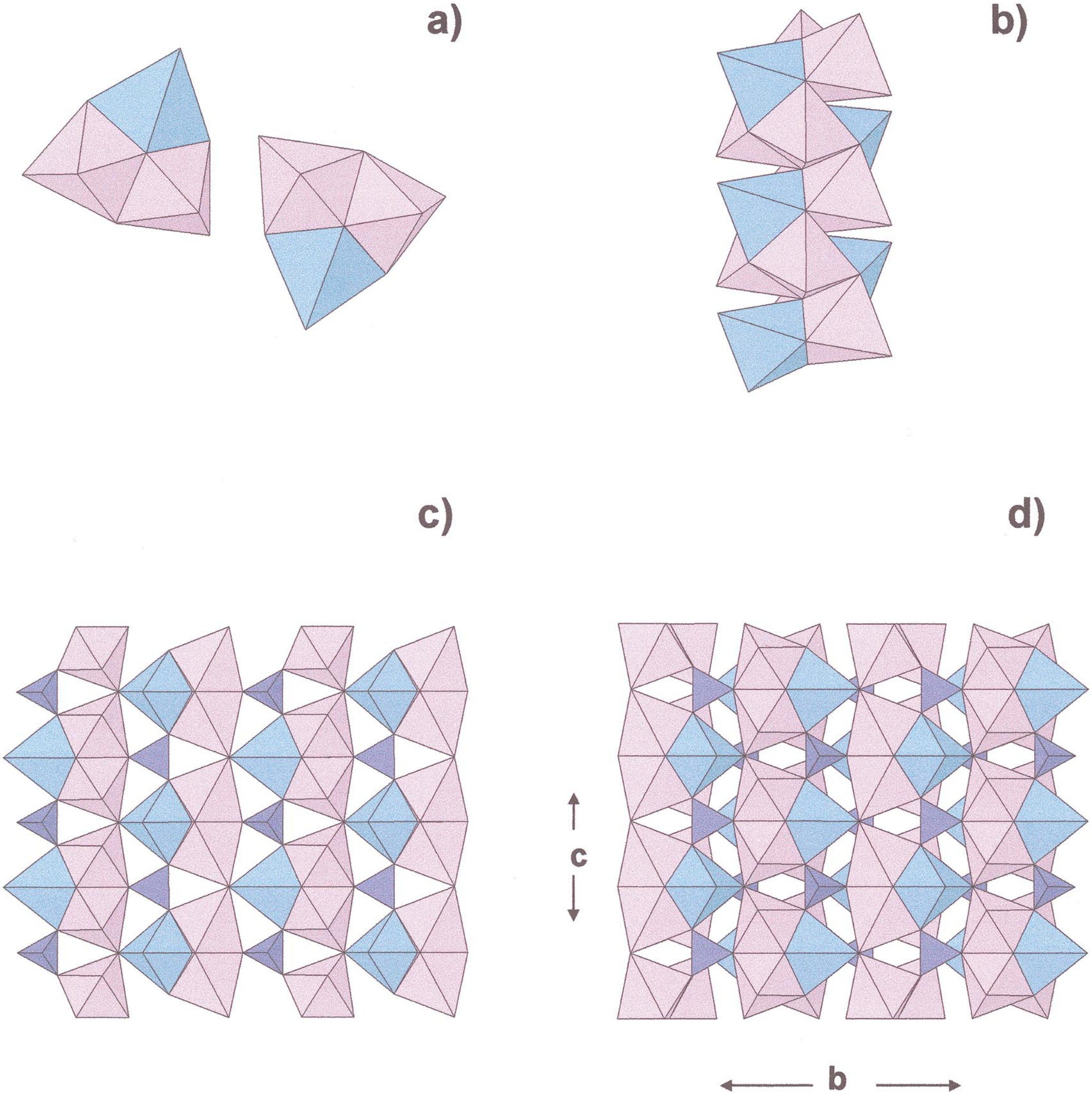

FIG. 1. The crystal structure of nacaphite: (a) the two distinct octahedron trimers, (b) the infinite chain of octahedron clusters rotated 60° relative to each other, (c) an infinite layer at $x \approx 0.25$ consisting of trimeric clusters of octahedra linked by (PO_4) tetrahedra, and (d) the crystal structure of nacaphite projected along [100]. Na octahedra are blue, *M* octahedra are pink, P tetrahedra are purple.

Quadruphite

Coordination of the cations

The structure of quadruphite consists of two blocks (*TS* and *AC*) stacked along [001] with an intermediate layer between them (Fig. 2).

The T (= Si + P) sites: There are four unique *Si* sites in the crystal structure of quadruphite, each of which is surrounded by a tetrahedral arrangement of O atoms with <*Si*–O> distances ranging between 1.603 and 1.629 Å. The *Si*(1) and *Si*(3) tetrahedra link through O(18), and the *Si*(2) and *Si*(4) tetrahedra link through O(32), forming $[Si_2O_7]$ groups with Si–O–Si angles of 136.4 and 136.9°, respectively. There is a pseudo center of inversion in the structure of quadruphite; *Si*(1) is related to *Si*(4), and *Si*(2) is related to *Si*(3): thus <*Si*(1)–O> of 1.612 Å is similar to <*Si*(4)–O> of 1.603 Å, and <*Si*(2)–O> of 1.629 Å is close to <*Si*(3)–O> of 1.627 Å. The *Si* tetrahedra are confined to the Ti silicate block of the

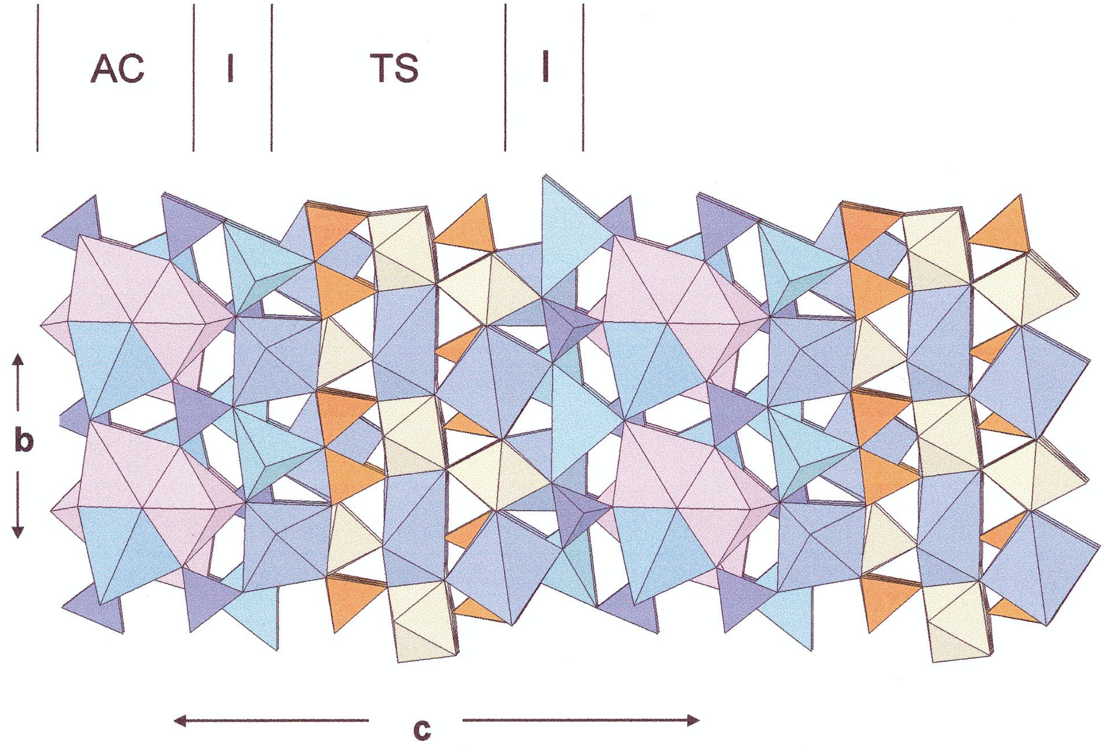

FIG. 2. The crystal structure of quadruphite projected along [100]. *A* octahedra are yellow, Na octahedra of the AC block are blue, Na ([6–8]-coordinated) polyhedra of the layer of octahedra and intermediate layers are light navy-blue, Na tetrahedra of the intermediate layer are greenish blue, P tetrahedra are purple, and Si tetrahedra are orange; *TS*: Ti silicate block; *AC*: alkali-cation block; I: intermediate layer.

structure. There are four unique *P* sites within the alkali-cation block, each of which is surrounded by a tetrahedral arrangement of O atoms with <*P*–O> distances in the range 1.537–1.539 Å, close to the grand <*P*–O> value of 1.537 Å reported by Baur (1974).

The octahedral sites of the Ti silicate block (*TS*): There are four unique *A* sites, each of which is coordinated by six anions in an octahedral arrangement; these sites can be split into two different groups: the *A*(1) and *A*(2) octahedra occur within the (*T*–*O*) sheets of tetrahedra and octahedra; the *A*(3) and *A*(4) sites belong to the (*O*) sheet of octahedra in the central part of the block. The high (>>20 *epfu*) site-scattering values and relatively short mean bond-lengths indicate that the *A* sites are occupied by Nb, Ti, Zr, and Fe of the unit formula (Table 1). The *A*(1) and *A*(2) sites are involved in shorter <*A*–O> bonds than the *A*(3) and *A*(4) sites: 1.989 and 1.984 Å, in contrast to 2.035 and 2.032 Å. As the *A*(1) and *A*(2) sites are very similar [likewise the *A*(3) and *A*(4) sites], we will treat them as similar, *i.e.*, *A*(1,2) and *A*(3,4). There is no rigorous way of assigning four scattering species (*i.e.*, Ti, Mn, Zr, Nb) over two sites. However, combining the refined site-scattering values and the observed mean bond-lengths does allow assignment of semiquantitative site-populations. The higher refined site-scattering value for *A*(1,2) indicates that most of the stronger-scattering species occur at this site. However, <*A*(3,4)–O> is significantly greater than <*A*(1,2)–O>, indicating that the larger scattering species occur at *A*(3,4), *i.e.*, Mn^{2+}, possibly with some Zr. This results in the site populations given in Table 8. There is good agreement between the observed and calculated site-scattering values, and the observed and predicted mean bond-lengths order in the correct sequence. There is some difference between the observed mean bond-lengths and the analogous sums of the constituent ionic radii (0.011–0.026 Å), but this is to be expected: the hard-sphere model predicts relative differences in bond lengths much more accurately than their actual values.

Within the *O* sheet, there are two unique *Na* sites, *Na*(6) and *Na*(7), each surrounded by an octahedral arrangement of O atoms with <*Na*–O> distances of 2.457 Å. Within the *T*–O net, there are two unique *Na* sites, *Na*(3) and *Na*(10).

The octahedrally coordinated sites of the alkali-cation block (*AC*): There are four unique *M* sites within this block, each coordinated by four O atoms and two F atoms. The total refined site-scattering at the *M* sites

(64.8 *epfu*) is close to the analogous value derived from the unit formula (63.6 *epfu*). The following cations occur at the *M* sites: Mg, Mn^{2+}, Ca, Na and Sr, ordered in terms of increasing size. The <*M*(1)–O> and <*M*(4)–O> distances (2.278 and 2.285 Å, respectively) are significantly shorter than the <*M*(2)–O> and <*M*(3)–O> distances (2.365 and 2.364 Å, respectively), and hence the smaller available cations, Mg and Mn^{2+}, must occur at the *M*(1) and *M*(4) sites. Thus the *M*(2) and *M*(3) sites are occupied by Na, Ca and Sr. We assign the minor amount of Sr to the *M*(3) site, which has the highest site-scattering value. The Na and Ca populations of *M*(2) and *M*(3) can now be calculated from the refined site-scattering values (normalized to the content of the *M* sites as indicated by the unit formula, Table 1). The resultant values (Table 8) also show reasonable agreement between observed and calculated mean bond-lengths for a hard-sphere model.

There remains Na, Ca, Mg and Mn^{2+} to assign to the *M*(1) and *M*(4) sites. There is no rigorous way in which this can be done using only one set of refined site-scattering values and mean bond-lengths (unless the site-scattering values or mean bond-lengths indicate occupancy of one site by only one cation). Here, the refined site-scattering values and mean bond-lengths at each site are essentially the same (Table 8), suggesting that the cations are disordered over the two sites; the site populations were assigned on this basis. The resultant site-populations (Table 8) show reasonable agreement between observed and calculated <*M*–O> distances. Substitution of Na and Mn at a site is unusual in these minerals, but was recently described for vuonnemite, $Na_7\ (Na,Mn^{2+})_4\ Ti^{4+}\ (Nb,Ti^{4+})_2\ [Si_2O_7]_2\ (PO_4)_2\ O_3\ (F,OH)$ (Ercit *et al.* 1998).

There are two *Na* sites, *Na*(1) and *Na*(12), each coordinated by four O atoms and two F atoms in an octahedral arrangement. In accord with a greater ionic radius of Na, the corresponding <*Na*–O> bonds of 2.422 and 2.428 Å are larger than the <*M*–O> distances. Bond-valence calculation for O and F atoms are in accord with this distribution of cations (Table 9).

The Na sites of the intermediate layer: There are four unique *Na* sites tetrahedrally coordinated by O atoms, with a range of <*Na*–O> distances from 2.289 to 2.383 Å. There is one *Na*(4) site octahedrally coordinated by O atoms with a <*Na*(4)–O> distance of 2.563 Å, and one [7]-coordinated *Na*(5) site with a <*Na*(5)–O> distance of 2.563 Å. Coordination numbers of the Na atoms are in reasonable accord with the bond-valence requirements of the O atoms (Table 9).

Based on the SREF results and bond-valence calculations, the end-member formula of quadruphite is $Na_{14}\ Ca_2\ Ti_4\ [Si_2O_7]_2\ (PO_4)_4\ O_4\ F_2$.

Structure topology

The structure of quadruphite consists of two blocks (*TS* and *AC*) stacked along [001] with an intermediate layer between them (Fig. 2). The *TS* block has a three-layered structure consisting of a central sheet of octahedra and two adjacent Ti–Si sheets. The central sheet of octahedra at $z \approx 0.5$ is a local close-packing of *Na*(6), *Na*(7), *A*(3) and *A*(4) octahedra (Fig. 3a). There are two types of chains of edge-sharing octahedra within the sheet: (1) *Na* octahedra form the first zigzag chain, and (2) *A*(3) and *A*(4) octahedra form the second chain. The size of a regular *A* octahedron is less than the size of an irregular *Na* octahedron, and substitution of Mn^{2+} (0.20 *apfu*; $^{[6]}r = 0.83$ Å) (Table 8) for Na ($^{[6]}r = 1.02$ Å) promotes linkage between the two types of chain.

Within the sheet of octahedra, the *A* and *Na* octahedra link through common edges (2.697–2.953 Å). The *Na* octahedra are also elongate along the *b* axis (to promote this linkage); this elongation is apparent in the values of the O–Na–O angles corresponding to the shortened common edges: they vary from 64.6 to 70.6°. In each of two Ti–Si sheets (located at $z \approx 0.35$ and 0.65), $[Si_2O_7]$ groups share common edges with *A*(1,2) octahedra, giving rise to large hexagonal voids that incorporate the *Na*(3) or *Na*(10) octahedra (Fig. 3b) [which share edges with *A*(2) octahedra in the plane of the sheet].

The *AC* block at $z \approx 0$ can be described in terms of nacaphite-like trimeric clusters of octahedra (Fig. 1a). As in the nacaphite structure, they form an infinite chain along [100] (Figs. 1b and 3c), and there are four *M* and two *Na* sites within the *AC* block, corresponding to two unique clusters. The *AC* block differs from nacaphite by the presence of Mg, Mn and Sr, and by partitioning of these cations over the octahedral sites. The ratio of divalent to monovalent cations is 1.47 for the *M* sites in quadruphite, and 1.0 in nacaphite. Differences in cation partitioning over the octahedral sites of the *AC* block result from the bond-valence requirements of the O(25) and O(27) anions. The O(25) and O(27) atoms are ligands of (PO_4) tetrahedra, and link to three other polyhedra, two octahedra belonging to the *AC* block, and the tetrahedron belonging to the intermediate layer. With increasing bond-valence at the *M* sites, the bond valence that O(25) and O(27) receive from cations at two other octahedral sites should decrease. In the crystal structure of quadruphite, only linkage of one *M* octahedron, two *Na* polyhedra and a (PO_4) group is possible in the *AC* block. The thickness of the *AC* block along the *c* axis is about 6 Å, corresponding to one-half of the *b* dimension of nacaphite (*i.e.*, 12.2103 Å) and to one infinite chain of octahedron clusters. The sum of two [F(1)–F(2)] edges, 2.738 + 2.724 = 5.462 Å, corresponds approximately to the *a* cell-parameter, 5.4206 Å. The *a* dimension of quadruphite is slightly larger than the *a* dimension of nacaphite, *a* = 5.3232 Å, and the two [F(1)–F(2)] edges of 2.679 + 2.668 equal 5.347 Å.

The intermediate layer at $z \approx 0.20$ and 0.75 is characterized by *Na* sites with coordination numbers of [4], [6] and [7]. The *Na* polyhedra link to *P*(1) or *P*(3) tetrahedra to form a rather irregular layer (Fig. 3d). This layer is situated at the junction of the *TS* and *AC* blocks, and

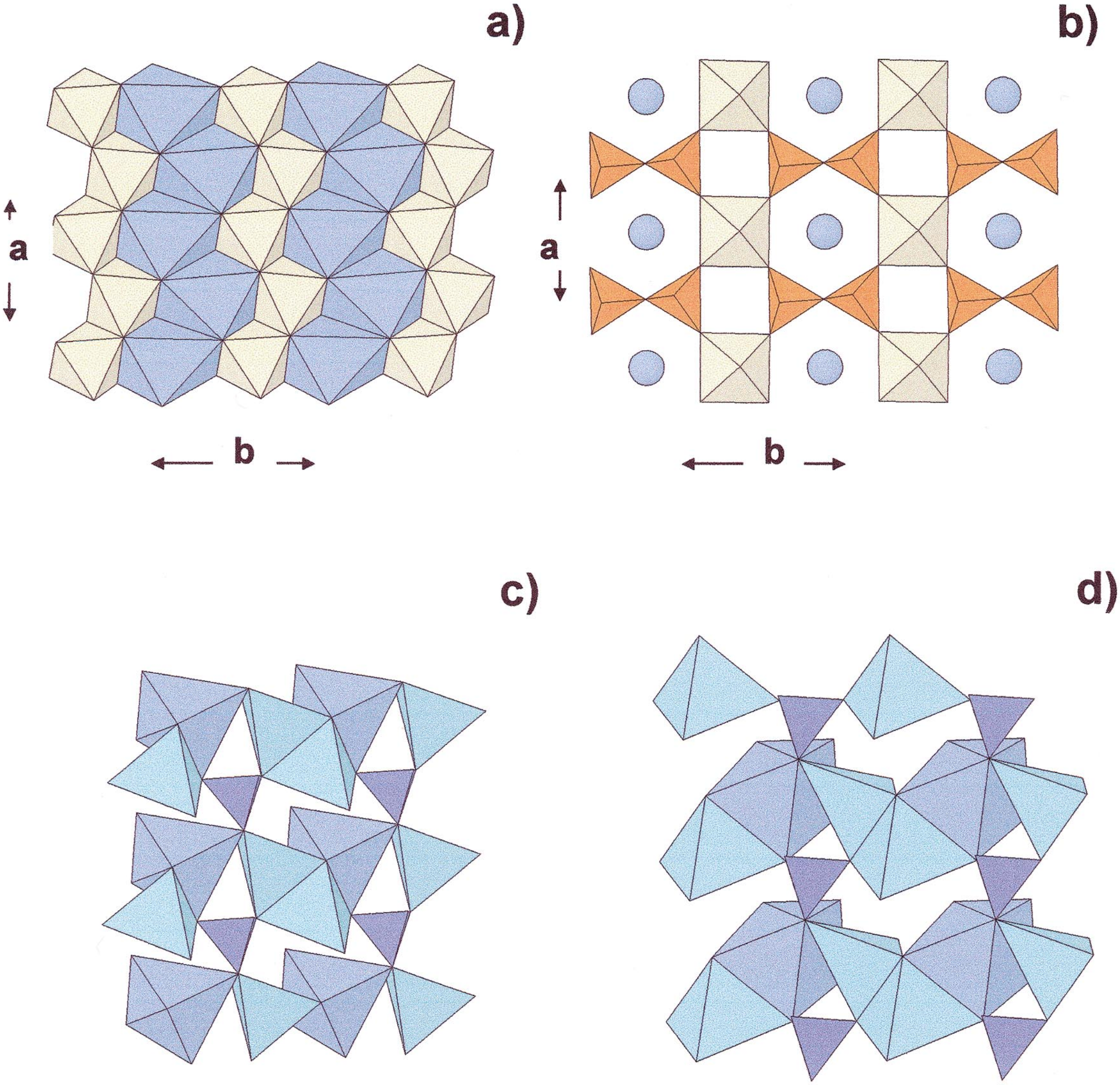

FIG. 3. The crystal structure of quadruphite. (a) The octahedron layer in the Ti silicate block; (b) the adjacent Ti silicate sheet at $z \approx 0.35$; (c) the intermediate layer at $z \approx 0.20$; (d) the intermediate layer at $z \approx 0.75$. Legend as in Figure 2. In Figure 3b, Na are shown as light navy-blue spheres.

can be regarded as a derivative of the *AC* block. The thickness of this layer is approximately that of one *Na* polyhedron. In previous work (Sokolova *et al*. 1987a), Mg was assigned to the tetrahedrally coordinated sites of the intermediate layer; we did not find any evidence of this in the present refinement. A similar intermediate layer occurs in the structures of polyphite and sobolevite (Sokolova *et al*. 1987b, 1988).

TRIMERIC CLUSTERS OF ALKALI-CATION COORDINATION POLYHEDRA

The occurrence of trimeric clusters of octahedrally coordinated alkali cations in the structures of nacaphite and quadruphite results from the key role played by alkalis in the structure of these minerals. The presence of a similar cluster in a series of crystal structures indi-

TABLE 10. SELECTED MINERALS AND SYNTHETIC COMPOUNDS WITH CLUSTERS OF OCTAHEDRALLY COORDINATED ALKALI CATIONS

Mineral	Formula	Space Group	Z	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	Bonds within octahedral clusters (Å)			Ref.
										<*M*–(O,F)>	Common edge		
											<An–An>	<An–O>	
Sulphohalite	$Na_6(SO_4)_2FCl$	$Fm3m$	4	10.071(3)	–	–	–	–	–	2.458	–	2.887	(1)
Galeite	$Na_{15}(SO_4)_5F_4Cl$	$P31m$	3	12.197(4)	–	13.96(1)	–	–	–	2.424	2.803	3.012	(2)
Schairerite	$Na_{21}(SO_4)_7F_6Cl$	$P31m$	3	12.197(4)	–	19.259(1)	–	–	–	2.396	2.890	2.954	(3)
Kogarkoite	$Na_3(SO_4)F$	$P2_1/m$	12	18.079(2)	6.958(1)	11.443(2)	–	107.71	–	2.425	3.005	3.166	(4)
Synthetic	$(Na_{0.67}Ca_{0.33})_3PO_4F$	$R3m$	15	7.0179(7)	–	40.56(4)	–	–	–	2.418	2.849	2.552	(5)
Arctite	$(Na_5Ca)Ca_6Ba[PO_4]_6F_3$	$R\bar{3}m$	3	7.094(1)	–	41.32(1)	–	–	–	2.446	2.923	2.775	(6)
Nacaphite	$Na(Na,Ca)_2(PO_4)F$	$P\bar{1}$	4	5.3232(2)	12.2103(4)	7.0961(2)	90.002(1)	89.998(1)	89.965(1)	2.382	2.382	–	(7)
Synthetic	$Na_2Fe(PO_4)(OH)$	$Pbcn$	8	5.227(1)	13.861(5)	11.774(3)	–	–	–	2.36	2.64	–	(8)
Quadruphite	$Na_{14}Ca_2Ti_4[Si_2O_7]_2[PO_4]_4O_4F_2$	$P1$	1	5.4206(2)	7.0846(2)	20.3641(7)	86.89(1)	94.42(1)	89.94(1)	2.357	2.731	–	(7)
Polyphite	$Na_{17}Ca_3Mg(Ti,Mn)_4[Si_2O_7]_2[PO_4]_6O_2F_6$	$P1$	1	5.412(2)	7.079(3)	26.56(1)	95.21(4)	93.51(2)	90.10(3)	2.372	2.727	–	(9)
Sobolevite	$Na_{11}(Na,Ca)_4(Mg,Mn)Ti_4[Si_2O_7]_2[PO_4]_4O_3F_3$	$P1$	2	5.4115(7)	7.018(1)	40.62(1)	93.19(2)	90.01(2)	90.00(1)	2.361	2.733	–	(10)

* *M* = (Na,Ca), Na, Ca, Fe^{2+}

** Axial common edge of the octahedral cluster (triplet); An = univalent anion: F^{-1}; $(OH)^{-1}$.

Refs: (1) Sakamoto (1968); (2) Fanfani *et al.* (1975b); (3) Fanfani *et al.* (1975a); (4) Fanfani *et al.* (1980); (5) Sokolova *et al.* (1999); (6) Sokolova *et al.* (1984); (7) This work; (8) Kabalov *et al.* (1974); (9) Sokolova *et al.* (1987b); (10) Sokolova *et al.* (1988)

cates its high stability as a structural motif and testifies to a highly alkaline environment of formation. Table 10 lists minerals and synthetic compounds in which such trimeric clusters occur. In all these crystals, there are large amounts of Na (or Na and Ca) and monovalent anions: F, (OH) and Cl. Excluding synthetic compounds, the minerals can be divided into two groups: (1) hydrothermal minerals of hyperagpaitic rocks of the Khibina–Lovozero complex, Kola Peninsula: arctite, kogarkoite, nacaphite, quadruphite, polyphite and sobolevite, and (2) minerals from Searles Lake, California: sulphohalite, galeite and schairerite.

In this work, we will focus on the bond topology of these structures, particularly the role of trimeric clusters. It should be emphasized that the degree of polymerization of these clusters depends on the content of monovalent anions relative to that of the alkali cations, *i.e.*, the ratio *M*:*X*, where *M* represents alkali cations, and *X* represents F and (OH) in a specific structure. This relation arises from the bond-valence requirements at the anion sites inside a cluster. The *interior* anion receives bond valence from six cations, primarily Na. With increasing content of monovalent anions, clusters can link into a chain. Moreover, to form a cluster, a polyhedron should exhibit only a *cis* configuration of the constituent monovalent anions. In this treatment, we do not include Cl because of its large size (and hence, different structural role) compared to F and OH anions.

Sulphohalite $Na_6(SO_4)_2FCl$, *M:X = 6:1*

Sulphohalite (Watanabe 1934, Sakamoto 1968) has cubic symmetry and can be described as a combination of two layers parallel to (001): (1) a layer of *Na* octahedra sharing common vertices, edges and faces at *z* = 0 and ½; (2) a layer of *Na* octahedra linked to (SO_4) tetrahedra through common corners at *z* = ¼ and ¾. Figure 4a shows linkage of (NaO_4FCl) octahedra in the layer at z = 0. There is a cluster of six *Na* octahedra at the center of the cell, and one at each of the cell corners. If viewed along one of the 3-fold axes (Fig. 4b), the clusters of octahedra in the structure of sulphohalite now appear as combinations of two trimeric clusters at an angle of 60° to each other (*cf.* Figs. 1b and 4b). The axis of the cluster along [111] is formed by a sequence of O–F–O atoms with <F–O> = 2.90 Å (Table 10). Thus the crystal structure of sulphohalite can be described as a framework of coupled trimeric clusters of octahedra. A hexagonal unit-cell with dimensions *a* 7.17, *c* 17.43 Å and space group *R*3*m* can be derived from the cubic cell of sulphohalite, and the resulting *a* cell-parameter corresponds to the distance between centers of two trimeric clusters.

Galeite $Na_{15}(SO_4)_5F_4Cl$, *M:X = 3.75:1*

The crystal structure of galeite is closely related to the crystal structure of sulphohalite (Fanfani *et al.* 1975*b*). Galeite is enriched in F compared to sulphohalite: F:Cl = 4:1 (galeite) and F:Cl = 1:1 (sulphohalite). There are ten unique *Na* sites in the structure of galeite: four (NaO_4FCl) octahedra and six (NaO_4F_2) octahedra. Of the ten octahedra, two (NaO_4FCl) octahedra are not part of the trimeric cluster: the Na atoms are disordered over the *Na*(1) and *Na*(2) sites, and exhibit a *trans* configuration for the constituent F atoms. In the structure of galeite (Fig. 5), two clusters of (NaO_4F_2) octahedra and one (NaO_4FCl) octahedron link together, with two F–F and one F–O common edges extending along the *c* axis: F(1)–F(3)–F(2)–O(9). The O(9) atom is a common vertex for two (NaO_4FCl) octahedra. Further polymerization of clusters is prevented by a layer of non-cluster (NaO_4F_2) polyhedra at z ≈ 0.71.

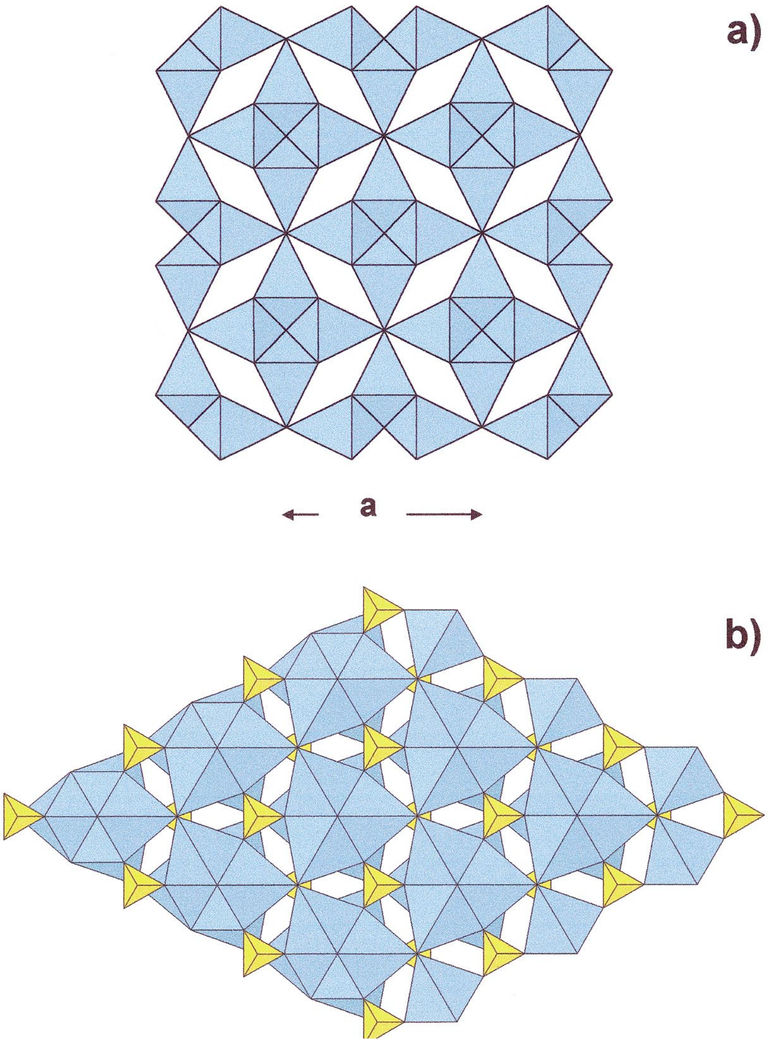

FIG. 4. The crystal structure of sulphohalite; (a) the layer of Na octahedra at *z* = 0; (b) the structure viewed down [111]. Na octahedra are blue, S tetrahedra are yellow.

Schairerite Na_{21} $(SO_4)_7$ F_6 *Cl, M:X = 3.5:1*

In general, the atomic arrangement in schairerite resembles that of galeite (Fanfani *et al*. 1975*a*). The only difference relates to the different position of the non-cluster *Na* sites in the structure of schairerite; a layer of non-cluster *Na* octahedra at z ≈ 0.52 separates two unique fragments of three linking clusters of octahedra (Fig. 6a), one of which is shown in Figure 6b. In the galeite and schairerite structures, the topology of this fragment is identical.

Kogarkoite, Na_3 (SO_4) *F, M:X = 3:1*

Kogarkoite occurs both in the Lovozero syenites, Kola Peninsula, and in hot-spring deposits at Mt. Princeton, Colorado. The crystal structure of kogarkoite has not yet been solved (Pabst & Sharp 1973), but the structure of the synthetic analogue is known (Fanfani *et al*. 1980). Na_3 (SO_4) F has many features in common with sulphohalite, galeite and schairerite. Its structure consists of close-packed *Na* octahedra; in contrast to galeite and schairerite, there are no non-cluster Na

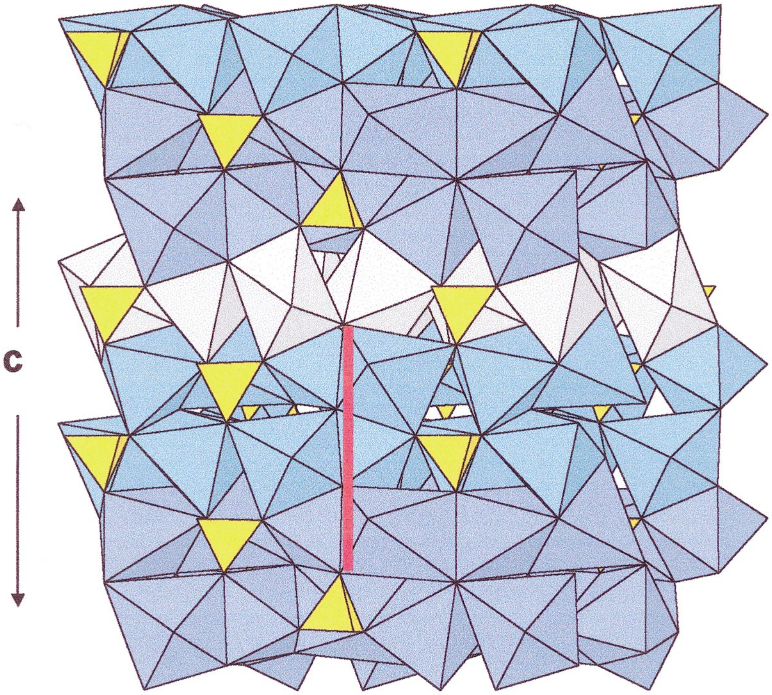

FIG. 5. The crystal structure of galeite viewed down [110]: [NaO_4F_2] octahedra are blue, disordered [NaO_4F_2] octahedra are white, [NaO_4FCl] octahedra are light navy-blue. The red line shows the axial direction of three linked trimeric clusters of octahedra.

octahedra in the structure of $Na_3 (SO_4)$ F. Fanfani *et al.* (1980) reported a trigonal subcell with *a*' 12.2, *c*' 24.4 Å, corresponding to [102] in the monoclinic cell. This subcell indicates similarity between the monoclinic structure of $Na_3 (SO_4)$ F, the cubic structure of sulphohalite, and the hexagonal structures of galeite and schairerite. Figure 7a shows the trimeric clusters in the (102) projection of the structure of $Na_3 (SO_4)$ F. Details of the linkage of three trimeric clusters are shown in Figure 7b.

Synthetic $(Na_{0.67}Ca_{0.33})_3 (PO_4)$ *F, M:X = 3:1*

This synthetic compound is a dimorph of nacaphite. The structures of nacaphite and $(Na_{0.67}Ca_{0.33})_3 (PO_4)$ F are based on trimeric clusters of octahedra (Sokolova *et al.* 1999), with differing linkage of the clusters resulting in different structure-topologies. In the structure of $(Na_{0.67}Ca_{0.33})_3 (PO_4)$ F, five trimeric clusters link to form a sequence of common edges, F(1)–F(5)–F(2)–F(3)–F(4)–O(4) along the *c* axis (Fig. 8). Four trimeric clusters are formed by *M*(1,3–5) octahedra; the fifth cluster involves [7]-coordinated *M*(2) polyhedra. All polyhedra have two F ligands. The triple-*M* columns are shifted relative to each other in accordance with the *R* symmetry-operation. Stacking of three *M* columns along [001] gives rise to the *c* cell-parameter, 40.56 Å. There is ordering of Ca and Na at six octahedrally coordinated sites in the nacaphite structure, whereas in the structure of $(Na_{0.67}Ca_{0.33})_3 (PO_4)$ F, all five unique *M* sites have the same composition ($Na_{0.67}Ca_{0.33}$).

Arctite $(Na_5Ca)\ Ca_6\ Ba\ (PO_4)_6\ F_3$ *, M:X = 3:1*

The unit-cell dimensions of arctite and $(Na_{0.67}Ca_{0.33})_3 (PO_4)$ F are practically identical (Table 10). Arctite (Khomyakov *et al.* 1981, Sokolova *et al.* 1984) differs from the other compounds discussed here as it contains Ba in addition to alkali cations. The crystal structure of arctite was previously regarded as derivative of the alunite and sulphohalite structure-types (Egorov-Tismenko *et al.* 1984). In the structure of arctite, Ba atoms (CN = [12]) are located at $z = 0$, ⅓ and ⅔. Clusters of alkali cations occur between them (Fig. 9b). There are two unique [7]-coordinated sites in arctite: *Ca* and *M* (= $Na_{0.833}Ca_{0.167}$). Two *Ca* trimers and two *M* trimers link to form a column along [001] (Fig. 9a). The axis of the column is formed by the following common edges: O(5)–F(2)–F(1)–F(2)–O(5).

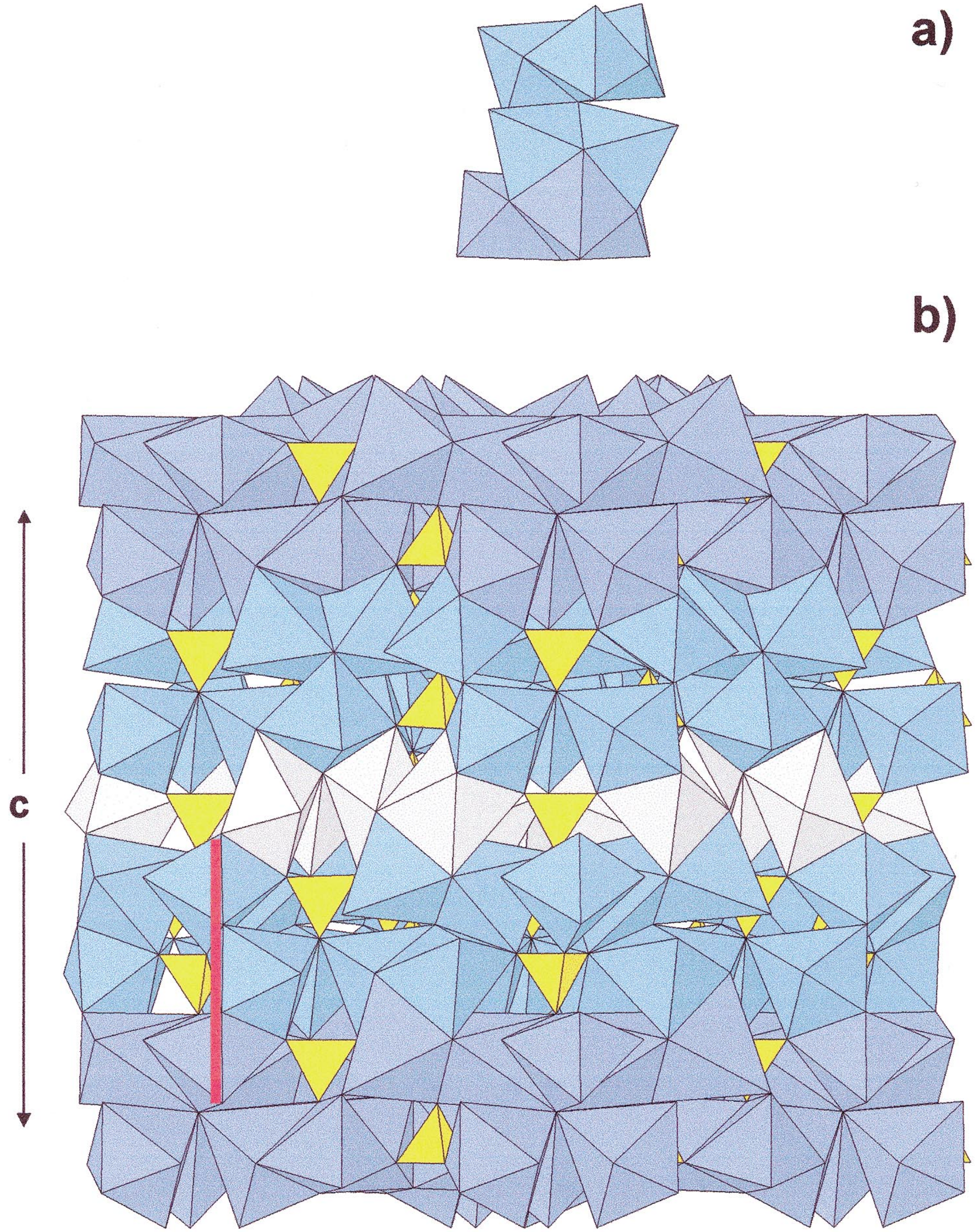

FIG. 6. The crystal structure of schairerite: (a) linkage of three clusters of octahedra, (b) general view of the crystal structure. Legend as in Figure 5.

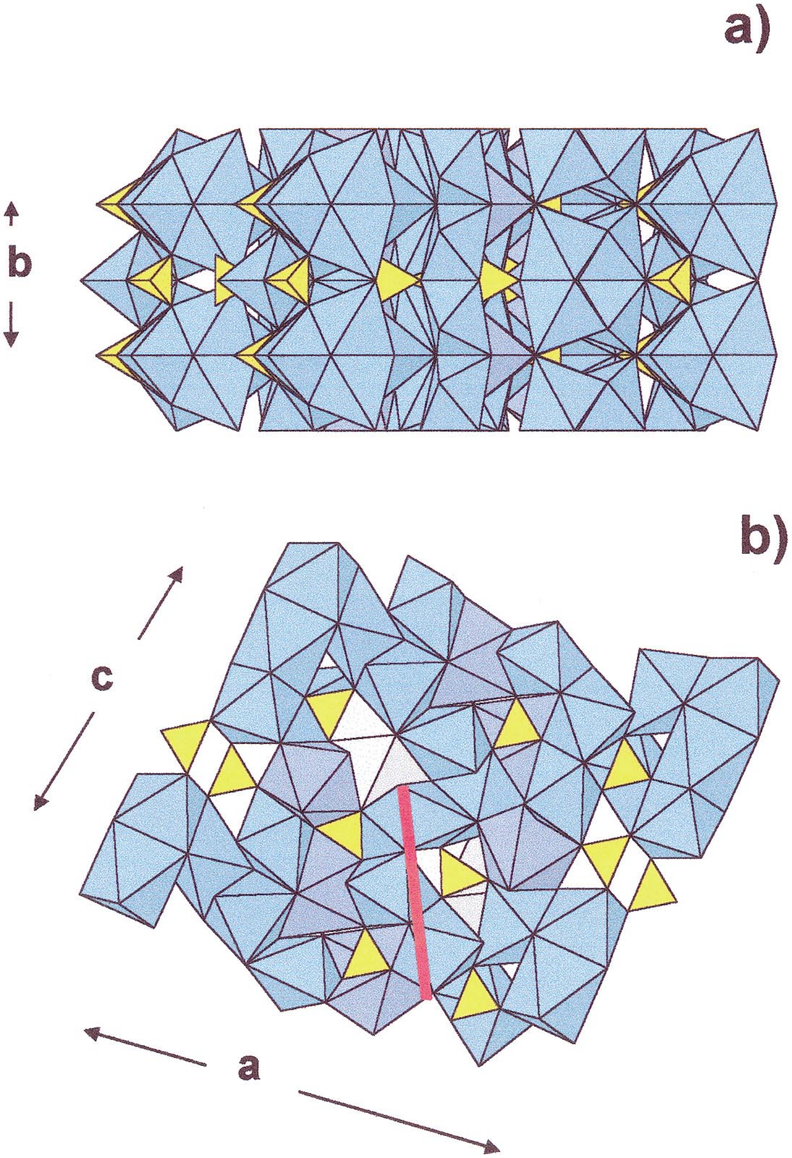

FIG. 7. The crystal structure of synthetic kogarkoite: (a) projected onto (102), (b) projected along [102]. Different types of (NaO_4F_2) polyhedra are shown as blue ([6]-coordinated), light navy-blue ([7]-coordinated) and white ([8]-coordinated).

The column of octahedra is centrosymmetric, and linkage of polyhedra within the column is more compact than in synthetic $(Na_{0.67}Ca_{0.33})_3$ (PO_4) F (*cf.* Fig. 8).

Synthetic Na_2 *Fe* (PO_4) *(OH),* $M:X = 3:1$

The crystal structure of this ferrous orthophosphate is orthorhombic (Kabalov *et al.* 1974). As in nacaphite, there are infinite chains of trimeric clusters in this structure (Fig. 10), and each cluster is formed by one *Fe* octahedron and two [7]-coordinated *Na* polyhedra. This is the first compound we have considered that contains (OH) as a monovalent anion. Sodium and Fe^{2+} are ordered at different sites in the Na_2 Fe (PO_4) (OH) structure. Different patterns of order of cations over the octahedral and [7]-coordinated sites result in a different

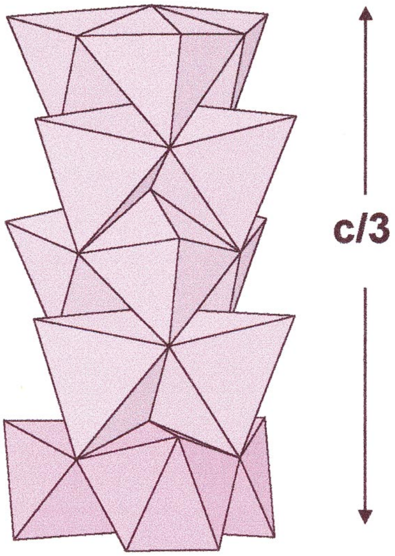

FIG. 8. A fragment of the crystal structure of synthetic $(Na_{0.67}Ca_{0.33})_3PO_4F$, a column of four clusters of octahedra (pale pink) and one cluster of [7]-coordinated polyhedra (darker pink) linked in the *c* direction.

orientation of $[PO_4]$ tetrahedra in nacaphite and Na_2 Fe (PO_4) (OH) (*cf.* Figs. 1 and 10).

Related minerals

Polyphite, Na_{17} Ca_3 Mg $(Ti,Mn)_4$ $[Si_2O_7]_2$ $(PO_4)_6$ O_2 F_6, and sobolevite, Na_{11} (Na,Ca) (Mg,Mn) Ti_4 $[Si_2O_7]_2$ $(PO_4)_4$ O_3 F_3, are closely related to quadruphite and other minerals of the lomonosovite group. Both structures consist of two types of blocks, *TS* and *AC*. By analogy with quadruphite, there are infinite chains of trimeric clusters of octahedra in the structures of these minerals. In the structure of polyphite, two infinite chains of octahedron clusters are joined together along the *c* axis. The structure of sobolevite corresponds to two quadruphite-like unit-cells that differ in the chemical composition of the *TS* and *AC* blocks. The P:Si ratio varies from 1:1 in quadruphite and sobolevite to 3:2 in polyphite.

Bond-valence considerations

These trimeric clusters occur in Na sulfates and (Na,Ca) phosphates. An O site in any structure with trimeric clusters of octahedra is characterized by four nearest neighbors: three [6]-coordinated cations and a [4]-coordinated cation (P or S). In a sulfate structure, the central O atom receives ~1.5 valence units (*vu*) from S, and needs 0.5 *vu* from the three neighboring cations. It receives ~ 3 × 1/6 = 0.5 *vu* from three $^{[6]}$Na atoms. In a phosphate structure, an O atom receives ~1.25 *vu* from P and needs ~0.75 *vu* from the three adjacent cations. A value of 0.25 *vu* from an adjacent cation requires partial substitution of Na by a divalent cation, usually Ca. For

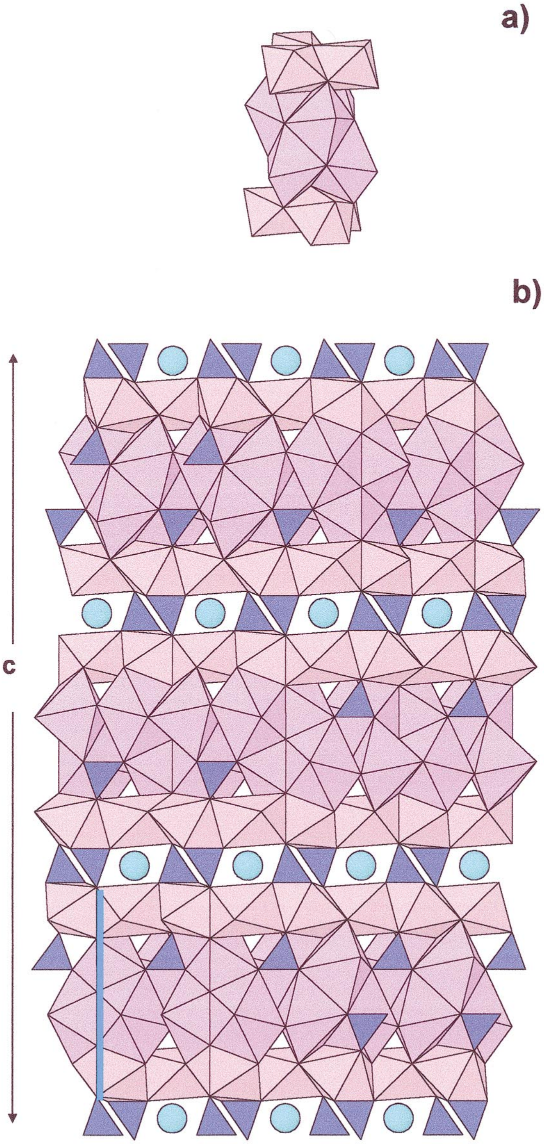

FIG. 9. The crystal structure of arctite, $(Na_5Ca)Ca_6Ba[PO_4]_6F_3$; (a) a fragment of the structure, a column of four clusters of octahedra linked together, (b) a general view of the structure. Seven-coordinated Ca and *M* polyhedra are tan and pink, P tetrahedra are purple, Ba atoms are shown as blue spheres. The greenish blue line indicates a column of four trimeric clusters linked together.

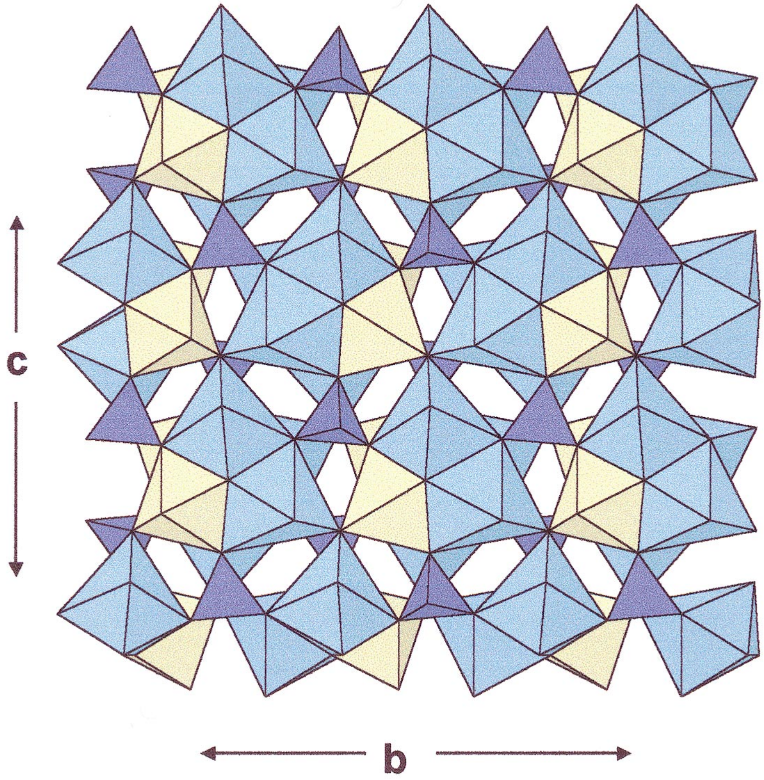

FIG. 10. The crystal structure of synthetic $Na_2Fe(PO_4)(OH)$ viewed down [100]. Fe octahedra are yellow, Na polyhedra are blue.

a silicate structure of this type, the central O atom would receive ~1.00 *vu* from Si and would need ~1.00/3 = 0.33 *vu* from each of the three adjacent cations, *e.g.*, $^{[6]}Ca$. Thus, we can conclude that silicate members of this group of structures are possible.

Possible silicate analogues

We can assume that, for a silicate structure of the triplet type, dominance of divalent cations at the alkali sites is necessary. In a silicate structure, an oxygen atom receives ~1.00 *vu* from Si^{4+} and needs ~1.00 *vu* (in total) from three nearest neighbors. A value of ~ 0.33 *vu* from one nearest-neighbor cation requires [6]-coordinated or [7]-coordinated Ca. Consider replacing Na by Ca and P by Si in the triplet structure. Substitution of F for O should be possible, as this anion receives bond valence from six adjacent alkali cations. The substitution 2Na + Ca + P + F ↔ 3Ca + Si + O produces the formula $Ca_3[SiO_4]O$. This compound is well known as the most important constituent of Portland cement clinker, tricalcium silicate: $3CaO•SiO_2$. It crystallizes in several polymorphic modifications, of triclinic, monoclinic, orthorhombic and hexagonal symmetry (Regourd 1964). Three polymorphs are strongly pseudo-rhombohedral, with hexagonal axes of *a* 7.0, *c* 25.0 Å (Jeffery 1952). The pseudo-structure with $R3m$ symmetry corresponds quite well with the triplet Na sulfate and (Na,Ca) phosphate structures. In this structure, three unique [7]-coordinated Ca atoms form two types of triplets: $[Ca_3O_{15}]$ [Ca(1)] and $[Ca_3O_{12}]$ [Ca(2) and Ca(3)] in the ratio 1:2. In the $[Ca_3O_{15}]$ triplet, Ca polyhedra share a common edge, as described above for sulfates and phosphates. In the $[Ca_3O_{12}]$ triplet, they have a central common vertex. Linkage of three clusters is shown in Figure 11a. There are three types of oxygen atoms in this structure: O atoms of the first type receive 2 *vu* from three Ca atoms and a Si atom; O atoms of the second type receive bond valence from six nearest Ca atoms; O atoms of the third type receive bond valence from one Si and four Ca atoms. For the latter case, two Ca–O bonds are short (about 2.3 Å) and two Ca–O bonds are long (about

3.0 Å). The crystal structure of $Ca_3[SiO_4]O$ can be split into nine layers (three of them unique) formed by different types of clusters (Fig. 11b).

For the synthetic compound $Ca_3[SiO_4]O$, triclinic, *a* 11.670, *b* 14.240, *c* 13.720 Å, α 105.5, β 94.3, γ 90.0°, $P1$, $Z = 18$ (Golovastikov *et al.* 1975), the triplet of octahedra $[Ca_3O_{11}]$ occurs. In this triplet, each octahedron shares two common faces with adjacent octahedra. Calcium is [6]- and [7]-coordinated; Ca polyhedra are linked to each other through common vertices, edges and faces, and zigzag chains of Ca polyhedra extend through the structure. In the crystal structure of triclinic $Ca_3[SiO_4]O$, triplets of octahedra occur as *islands* in a wild (dis)array of Ca polyhedra. Moreover, an infinite layer of Ca triplets has been previously described for arctite. These arguments suggest that the occurrence of a mineral similar to the pseudostructure of $Ca_3[SiO_4]O$ is possible.

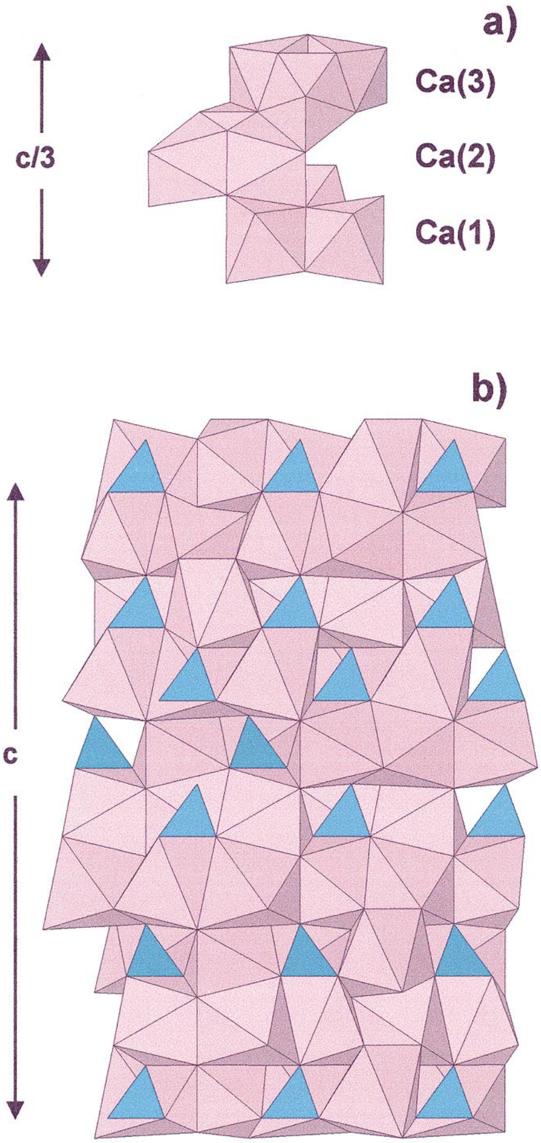

FIG. 11. $Ca_3[SiO_4]O$: (a) linkage of three trimeric clusters involving Ca; (b) general view. Ca polyhedra are pink, Si tetrahedra are blue.

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