

Crystal structure of nanlingite – the first mineral with a $[\text{Fe}(\text{AsO}_3)_6]$ configuration

ZHUMING YANG¹, GERALD GIESTER^{2,*}, KUISHOU DING¹ and EKKEHART TILLMANN²

¹ Key Laboratory of Engineering Geomechanics, Institute of Geology and Geophysics, Chinese Academy of Sciences, P.O. Box 9825, Beijing 100029, China

² Institut für Mineralogie und Kristallographie, Universität Wien, Althanstr. 14, 1090 Wien, Austria

*Corresponding author, e-mail: gerald.giester@univie.ac.at

Abstract: Nanlingite was first described as a new mineral from a dolomitic limestone along a contact between greisenized granite and dolomitic limestone in the Nanling area, Hunan Province, China. The structure was solved and refined on single-crystal X-ray data in space group $R\bar{3}m$, with $a = 10.2114(10)$, $c = 25.689(3)$ Å, $V = 2319.2(6)$ Å³, to $R1 = 0.021$, $wR2 = 0.049$. The chemical formula of nanlingite is $\text{Na}(\text{Ca}, \text{Li}, \text{Na})_6(\text{Mg}, \text{Fe})_{12}(\text{AsO}_3)_2[\text{Fe}(\text{AsO}_3)_6] \text{F}_{14}$ with $Z = 3$ according to the crystal structure refinement.

The complex framework is formed by edge- and corner-sharing of distorted NaF_8 and CaF_4O_4 cubes, MgF_2O_4 octahedra, and AsO_3 trigonal pyramids. The lithium atom occupies (22 %) the split site at 0.58(2) Å from the main Ca site and exhibits a five-fold coordination with $\langle \text{Li}-(\text{O}, \text{F}) \rangle > 2.21$ Å. The iron atom (at 3*b*, site symmetry $\bar{3}m$) is surrounded by six As atoms of AsO_3 groups at a distance of 2.40 Å with the lone-pair electrons pointing towards the central atom. This $[\text{Fe}(\text{AsO}_3)_6]$ cluster is a novel configuration in the crystal chemistry of minerals. According to Mössbauer spectra and electron energy-loss spectroscopy data the oxidation state of Fe in nanlingite is mainly Fe^{II} with a low-spin state. In the configuration of arsenite groups, the distance $\langle \text{As}(2)-\text{O} \rangle = 1.73$ Å of the $[\text{Fe}(\text{AsO}_3)_6]$ clusters is shorter than the normal range. The empirical crystal-chemical formula for nanlingite is $(\text{Na}_{0.90}\text{Li}_{0.10})\Sigma_{1.00}(\text{Ca}_{4.41}\text{Li}_{1.06}\text{Mg}_{0.17}\text{Na}_{0.06}\text{Mn}_{0.05}\square_{0.25})\Sigma_{6.00}(\text{Mg}_{11.38}\text{Fe}^{3+}_{0.30}\text{Al}_{0.29}\text{Ti}_{0.03})\Sigma_{12.00}(\text{AsO}_3)_2[\text{Fe}^{\text{II}}(\text{AsO}_3)_6](\text{F}_{13.77}\text{OH}_{0.16})\Sigma_{13.93}$.

Key-words: nanlingite, arsenite, crystal structure, iron-arsenite cluster, new chemical formula.

1. Introduction

Nanlingite is a rare mineral and was first described as a new mineral (Gu *et al.*, 1976) from a dolomitic limestone along a contact between greisenized granite and dolomitic limestone in the Nanling area, Hunan Province, China. Till now this is the only occurrence known. The mineral was associated with fluorborite, fluorite, zinnwaldite, magnesian dolomite, asenopyrite, pyrrhotite, gahnite and nigerite. Nanlingite forms brownish-red tabular crystals up to 2 mm in size. It is optically uniaxial negative ($\omega = 1.82$, $\varepsilon = 1.78$) and transparent with vitreous luster, hardness about 2.3 on the Mohs scale.

The mineral was reported to be trigonal (space group $R\bar{3}m$ or $R\bar{3}m$, $a = 10.24(5)$, $c = 25.76(5)$ Å, $Z = 15$, or $a = 10.42(5)$ Å, $\alpha = 58.83^\circ$, $Z = 5$). From wet chemical analysis Gu *et al.* (1976) gave the empirical formula $(\text{Na}_{0.216}\text{Ca}_{0.775})(\text{Mg}_{2.300}\text{Li}_{0.303}\text{Mn}_{0.011}\text{Fe}^{3+}_{0.051})(\text{As}_{1.651}\text{Fe}^{3+}_{0.278}\text{Al}_{0.071})\text{O}_{5.094}(\text{OH})_{0.247}\text{F}_{2.659}$ and the general formula $\text{CaMg}_3(\text{AsO}_3)_2\text{F}_2$. The formula was also suggested as $(\text{Ca}_{0.98}\text{Na}_{0.27})(\text{Mg}_{2.83}\text{Fe}^{3+}_{0.41}\text{Li}_{0.37}\text{Al}_{0.09}\text{Mn}_{0.01})(\text{AsO}_3)_{2.04}\text{F}_{3.28}(\text{OH})_{0.30}\text{O}_{0.02}$ and the general formula $\text{CaMg}_4(\text{AsO}_3)_2\text{F}_4$ with $Z = 4$ by Fleischer *et al.* (1977). However, the crystal structure of nanlingite remained

unknown and the chemical formula unconfirmed. We have now determined the crystal structure of nanlingite for the type material and report a revised formula.

2. Experimental procedures

Crystal fragments were taken from the type nanlingite specimen found in the Nanling area, Hunan Province, China. Electron-microprobe analyses (EMPA) were performed by wavelength dispersive spectroscopy on a JXA-8100 electron microprobe analyzer. Accelerating voltage and specimen current were kept at 15 kV and 20 nA. The beam diameter was 2 µm. The following minerals and synthetic materials were used as standards: jadeite for Na and Al; fluorite for F; bustamite for Mn and Ca; rutile for Ti; kaersutite for Mg and Fe; GaAs for As.

In order to check the presence of Li in nanlingite, Cameca 1280 Secondary Ion Mass Spectroscopy (SIMS) was used. The single crystal of nanlingite was subjected to bombardment by O ions at 23 keV energies. The beam diameter was 20 µm. Specimen current was kept at 6.7 nA.

Mössbauer spectra were measured at room temperature (RT) using a constant acceleration transmission mode with a $^{57}\text{Co}/\text{Rh}$ source. The Doppler velocity was calibrated with 25 μm thick foil of natural $\alpha\text{-Fe}$, and the isomer shift (IS) is relative to the $\alpha\text{-Fe}$. The spectra were analyzed using MossWinn (Klencsár *et al.*, 1996).

The electron energy-loss spectroscopy (EELS) experiments were performed at 200 kV using a JEOI 2010F Field Emission Transmission electron microscope (TEM) with a Gatan GIF 200. The EELS spectra were acquired in the diffraction mode under the conditions of 0.1 eV/channel energy dispersion.

Single-crystal X-ray data were collected at room temperature using monochromatic $\text{MoK}\alpha$ X-radiation on an Enraf Nonius diffractometer with kappa-geometry and a CCD-area collector. The crystal structure was determined by direct methods (SHELXS-97, Sheldrick, 1997) and subsequent Fourier and difference Fourier syntheses. Based on the scattering power an occupation at site $3b$ (site symmetry $\bar{3}m$) by iron seems plausible. The incorporation of Li into the Mg(1) and Mg(2) sites was not successful during structural refinement. Part of Li has to be put on the Ca site. Because Li is much smaller and there were residual electrons close to Ca site, this position had to be split, which significantly improved the refinement. Ca occupies mainly (73 %) one position, and Li occupies (22 %) the additional site, at 0.58(2) Å from the main Ca site. The new site has much closer distances to ligands, which is more plausible for lithium. The site occupancy factors (*sof*) for the Mg(1), Mg(2) and Na sites were constrained as $\text{Mg} + \text{Fe} = 1$, $\text{Mg} + \text{Fe} = 1$, and $\text{Na} + \text{Li} = 1$, respectively. The structure was solved and refined in space group $R\bar{3}m$, with $a = 10.2114(10)$, $c = 25.689(3)$ Å, $V = 2319.2(6)$ Å³, to $R1 = 0.0208$, $wR2 = 0.0487$. The formula of nanlingite is $\text{Na}(\text{Ca}, \text{Li}, \text{Na})_6(\text{Mg}, \text{Fe})_{12}(\text{AsO}_3)_2[\text{Fe}(\text{AsO}_3)_6]F_{14}$ with $Z = 3$ according to the crystal-structure refinement.

Crystal data, data-collection information and refinement details for nanlingite are listed in Table 1. The final positional and displacement parameters are given in Table 2, and selected interatomic distances and angles in Table 3.

3. Description of the crystal structure

In the crystal structure of nanlingite as shown in Fig. 1 and 2a, b, Na and Ca are 8-coordinated by 8F and by 4F + 4O, respectively, to form distorted cubes. The split site [0.58(2) Å apart from Ca] is occupied by Li exhibiting a five-fold coordination with $\langle \text{Li}-(\text{O},\text{F}) \rangle > 2.21$ Å and forming a distorted tetragonal pyramid as shown in Fig. 3. Mg is coordinated by 2F and 4O atoms in the shape of a distorted octahedron. The As atom is coordinated by three oxygen atoms to form trigonal pyramids. AsO_3 groups can be further classified into two subgroups: the $\text{As}(1)\text{O}_3$ group has the oxygen base of the pyramid roughly parallel to (001), while the $\text{As}(2)\text{O}_3$ group has the base of oxygens roughly perpendicular to (001).

In order to illustrate the rather complex framework structure, the following, purely formal description is used.

Table 1. Crystal data, data collection information and refinement details for nanlingite.

Formula	$\text{Na}(\text{Ca}, \text{Li}, \text{Na})_6(\text{Mg}, \text{Fe})_{12}(\text{AsO}_3)_2$ [$\text{Fe}(\text{AsO}_3)_6$] F_{14}
Formula weight	1809.63
Space group	$R\bar{3}m$
a, c (Å)	10.2114(10), 25.689(3)
V (Å ³), Z	2319.8(4), 3
μ (mm ⁻¹)	10.308
Crystal dimensions (mm)	0.100 × 0.125 × 0.075
$F(000)$, ρ_{calc} (cm ⁻³)	2570, 3.886
Diffractometer	Nonius KappaCCD system
λ (MoK α)(Å), T (K)	0.71073, 293(2)
θ range for collection (°)	3.92–40.22
h, k, l ranges	–18 → 18, –15 → 15, –46 → 46
Total reflections	6439
measured	
Unique reflections	1821 [R(int) = 2.38 %]
Refinement on	F^2
$R1(F)$, $wR2(F^2)$ [$I > 2\sigma(I)$]	2.08 %, 4.87 %
$R1_{\text{all}}(F)$, $wR2_{\text{all}}(F^2)$	2.63 %, 5.02 %
Extinct. coefficient	0.00096(4)
No. of refined parameters	75
Goof on F^2	1.104
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}}$ (e/Å ³)	–1.06, 1.10

Approximately, NaF_8 distorted cubes, MgF_2O_4 octahedra and $\text{As}(1)\text{O}_3$ groups form a “sheet” of $[-\text{Na}-\text{Mg}(2)-\text{As}(1)-]$ by edge- and corner-sharing parallel to (001) as shown in Fig. 4, while CaF_4O_4 distorted cubes, MgF_2O_4 octahedra and $\text{As}(2)\text{O}_3$ groups form another “sheet”, *i.e.* $[-(\text{Ca}, \text{Li})-\text{Mg}(1)-\text{As}(2)-]$ as shown in Fig. 5. One “sheet” of $[-\text{Na}-\text{Mg}(2)-\text{As}(1)-]$ and two “sheets” of $[-(\text{Ca}, \text{Li})-\text{Mg}(1)-\text{As}(2)-]$ are alternately stacked along the c axis to form the framework of the structure shown in Fig. 1. Iron occupies the cavity at site $3b$, site symmetry $\bar{3}m$, between two $[-(\text{Ca}, \text{Li})-\text{Mg}(1)-\text{As}(2)-]$ units and is surrounded by six As atoms of $\text{As}(2)\text{O}_3$ groups as illustrated in Fig. 5 and 6.

4. Discussion

4.1. Configuration of the $[\text{Fe}(\text{AsO}_3)_6]$ cluster

The novel feature in the crystal chemistry of nanlingite is a $[\text{Fe}(\text{AsO}_3)_6]$ cluster. In this cluster, Fe as the central atom is octahedrally surrounded by six As atoms of $\text{As}(2)\text{O}_3$ groups at a distance of 2.40 Å with the lone-pair electrons pointing towards the central atom. The $\text{As}(2)$ atoms are distributed at the vertices of an octahedron (Fig. 7a). Among minerals, similar arrangements of arsenite groups coordinating cations have rarely been observed. In magnussonite, $\text{Mn}_{18}[\text{Mn}(\text{AsO}_3)_6]\text{Cl}_2$, formally monovalent Mn is bound to six As atoms with an average $\langle \text{Mn}-\text{As} \rangle$ distance of 2.65 Å as in Fig. 7b (Moore & Araki, 1979). In the $[\text{Mn}(\text{AsO}_3)_6]$ cluster the centre site is split. Cu^{1+} is bound to four As atoms of arsenite groups in distorted tetrahedral coordination (Araki & Moore, 1981) with

Table 2. Atomic coordinates and displacement parameters with e.s.d.'s in parentheses for nanlingite.

	x	y	z	U _{eq}	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
As(1)	0	0	0.340985(11)	0.00569(5)	0.00569(7)	0.00569(7)	0.00569(10)	0	0	0.00284(3)
As(2)	0.218805(9)	0.781195(9)	0.116669(6)	0.00582(4)	0.00574(5)	0.00574(5)	0.00532(6)	0.00030(2)	-0.00030(2)	0.00238(5)
Fe	0	0	0.5	0.00564(9)	0.00599(12)	0.00599(12)	0.00495(18)	0	0	0.00300(6)
Mg(1)	0.90403(6)	0.45201(3)	0.10159(2)	0.00886(13)	0.0096(2)	0.00950(17)	0.0075(2)	-0.00120(7)	-0.00240(15)	0.00481(10)
Mg(2)	0.65072(6)	0	0	0.00770(15)	0.0079(2)	0.0068(2)	0.0081(2)	0.00025(16)	0.00012(8)	0.00338(12)
Ca	0.88623(3)	0.11377(3)	0.11426(3)	0.01874(14)	0.01744(18)	0.01744(18)	0.0221(3)	0.00310(9)	-0.00310(9)	0.00928(18)
Li	0.8755(10)	0.1245(10)	0.0928(9)	0.01874(14)	0.01744(18)	0.01744(18)	0.0221(3)	0.00310(9)	-0.00310(9)	0.00928(18)
Na	0	0	0	0.0152(4)	0.0184(6)	0.0184(6)	0.0087(8)	0	0	0.0092(3)
O(1)	0.42367(6)	0.84734(13)	-0.02334(4)	0.00741(17)	0.0080(3)	0.0062(4)	0.0074(4)	0.0007(3)	0.00036(16)	0.0031(2)
O(2)	0.67253(9)	0.06133(9)	-0.07812(3)	0.00957(13)	0.0096(3)	0.0086(3)	0.0077(3)	0.0029(2)	0.0007(2)	0.0025(3)
O(3)	0.86125(8)	0.13875(8)	-0.1542(5)	0.0135(2)	0.0164(4)	0.0164(4)	0.0095(5)	-0.0030(2)	0.0030(2)	0.0095(5)
F(1)	0	0	0.08423(11)	0.0330(6)	0.0382(9)	0.0382(9)	0.0226(12)	0	0	0.0191(5)
F(2)	0.23719(8)	0.76281(8)	-0.11937(5)	0.0194(2)	0.0142(3)	0.0142(3)	0.0193(5)	-0.0029(2)	0.0029(2)	-0.0007(4)
F(3)	0.27621(13)	0.13811(6)	0.02104(4)	0.01185(18)	0.0155(5)	0.0093(3)	0.0128(4)	0.00020(18)	0.0004(4)	0.0077(2)

Note: Site symmetries with Wyckoff positions in parentheses are $\bar{3}m$ (3a) for Na; $\bar{3}m$ (3b) for Fe; $3m$ (6c) for As(1) and F(1); m (18h) for As(2), Mg(1), Ca, Li, O(1), O(3), F(2) and F(3); 2 (18f) for Mg(2); and I (36i) for O(2), respectively. Occupancy: Mg(1) = 0.846Mg+0.154Fe; Mg(2) = 0.982Mg+0.018Fe; Ca = 0.727Ca+0.050Na; Li = 0.223Li; Na = 0.918Na+0.082Li.

2.26 and 2.40 Å distances of $\langle\text{Cu}-\text{As}\rangle$ in dixenite, $\text{CuMn}_{14}\text{Fe}(\text{OH})_6(\text{AsO}_3)_5(\text{SiO}_4)_2(\text{AsO}_4)$. In freedite, $\text{Pb}_8\text{Cu}(\text{AsO}_3)_2\text{O}_3\text{Cl}_5$, the Cu^{1+} atom is tetrahedrally coordinated to two Cl atoms and two As atoms belonging to (AsO_3) groups with a 2.38 Å distance of $\langle\text{Cu}-\text{As},\text{Cl}\rangle$ (Pertlik, 1987). In the synthetic compound, $\text{Pb}_6\text{Cu}(\text{AsO}_3)_2\text{Cl}_7$, the distance of $\langle\text{Cu}-\text{As}\rangle$ is 2.42 Å (Pertlik, 1986). The distance of $\langle\text{Fe}-\text{As}\rangle$ in nanlingite is close to $\langle\text{Cu}-\text{As}\rangle$ in dixenite and freedite, but shorter than $\langle\text{Mn}-\text{As}\rangle$ in magnussonite, as shown in Table 4.

The Fe–As distance of 2.40 Å in the $[\text{Fe}(\text{AsO}_3)_6]$ cluster in nanlingite can be compared to the Fe–As distances (2.36~2.38 Å) in löllingite (FeAs_2), which possesses the marcasite (FeS_2) type structure (Ondruš *et al.*, 2001). In the löllingite structure, the Fe atoms are surrounded by six As atoms in an almost regular octahedral coordination, and the As atoms are surrounded by three Fe and one As atoms in a distorted tetrahedral coordination.

The character of the chemical bond between the metal atom and the As atom as well as the valence state of the two elements are not clearly defined (Pertlik, 1986). In dixenite, Araki & Moore (1981) mentioned “metallic $[\text{As}^{3+}-\text{Cu}^{1+}]$ clusters in an oxide matrix”. But it was argued by Pertlik (1986) that the crystals of freedite and $\text{Pb}_6\text{Cu}(\text{AsO}_3)_2\text{Cl}_7$ are transparent, and a covalent bond between the As and Cu atoms was assumed. According to As atoms of $\text{As}(2)\text{O}_3$ groups with the lone-pair electrons pointing towards the central atom with similar Fe–As distance in löllingite, we assume that in the $[\text{Fe}(\text{AsO}_3)_6]$ cluster of nanlingite a coordinate covalent bond between Fe and As exists.

In magnussonite, the stability of the $[\text{Mn}(\text{AsO}_3)_6]$ cluster was interpreted as satisfying the 18-electron rule with $2 \times 6 = 12$ electrons donated by As^{3+} plus six $3d^6$ electrons from Mn^{1+} (Moore & Araki, 1979). In dixenite, for the $[\text{Cu}(\text{AsO}_3)_4]$ cluster all lone-pair electrons ($2 \times 4 = 8$ electrons) from As^{3+} point into the central cavity which houses Cu^{1+} (d^{10}) and the cluster is believed to be stabilized by the 18-electron rule (Araki & Moore, 1981).

The stability of the $[\text{Fe}(\text{AsO}_3)_6]$ cluster in nanlingite can also be understood according to the 18-electron rule. In the $[\text{Fe}(\text{AsO}_3)_6]$ cluster there are $2 \times 6 = 12$ electrons contributed by As^{3+} plus 6 electrons contributed by $3d^6$ Fe^{2+} .

According to Hybridisation theory, Fe octahedrally surrounded by six As atoms has d^2sp^3 hybridisation orbitals. For hybridisation the six $3d^6$ electrons of Fe^{2+} must spin pairs to vacate d^2 orbitals. Based on this assumption, the oxidation state of iron in the $[\text{Fe}(\text{AsO}_3)_6]$ cluster should be divalent with a low-spin state.

4.2. Interpretation of the Mössbauer and EELS data

The RT Mössbauer spectrum of the nanlingite sample is a single close quadrupole doublet (Fig. 8). The refined hyperfine parameters are IS (isomer shift) = 0.33(2) mm/s, QS (quadrupole splitting) = 0.25(2) mm/s, and FWHM (full width at half maximum) = 0.33(2) mm/s.

It has been concluded that iron atoms with lower IS values belong to Fe^{3+} , and those with higher IS values are Fe^{2+} . But

Table 3. Selected interatomic distances (Å) and angles (°) for nanlingite.

As(1)O ₃		Fe[As(2)O ₃] ₆		CaO ₄ F ₄	
As(1)–O(1) × 3	1.7851(11)	As(2)–O(3)	1.7309(12)	Ca–F(1)	2.1551(11)
<As(1)–O>	1.7851	–O(2) × 2	1.7359(8)	–F(2)	2.1868(15)
O(1')–As(1)–O(1) × 3	101.63(4)	<As(2)–O>	1.7342	–F(3)	2.4329(12)
<O'–As(1)–O>	101.63	O(3)–As(2)–O(2) × 2	97.17(4)	–F(2)	2.5804(15)
		O(2')–As(2)–O(2)	103.03(6)	–O(3) × 2	2.5003(11)
		<O'–As(2)–O>	99.12	–O(2) × 2	2.6315(10)
				<Ca–O,F>	2.4524
Mg(1)O ₄ F ₂		Fe–As(2) × 6	2.3985(2)		
Mg(1)–F(2) × 2	1.9841(7)	<Fe–As(2)>	2.3985	LiO ₂ F ₃	
–O(3)	1.9926(13)	As(2)–Fe–As(2) × 6	85.9997(10)	Li–F(3)	1.86(2)
–O(1)	2.0714(12)	As(2)–Fe–As(2) × 6	94.0002(10)	–F(2)	2.107(19)
–O(2'') × 2	2.0969(9)	<As–Fe–As>	90.0000	–F(1)	2.213(18)
<Mg(1)–O,F>	2.0377			–O(2) × 2	2.430(6)
		NaF ₈		<Li–O,F>	2.21
Mg(2)O ₄ F ₂		Na–F(1) × 2	2.164(3)		
Mg(2)–F(3) × 2	1.9723(7)	–F(3) × 6	2.5017(12)		
–O(2) × 2	2.0808(8)	<Na–F>	2.417		
–O(1) × 2	2.1333(9)				
<Mg(2)–O,F>	2.0621				

Note: For LiO₂F₃ only Li–O and –F bonds shorter than 2.8 Å are given.

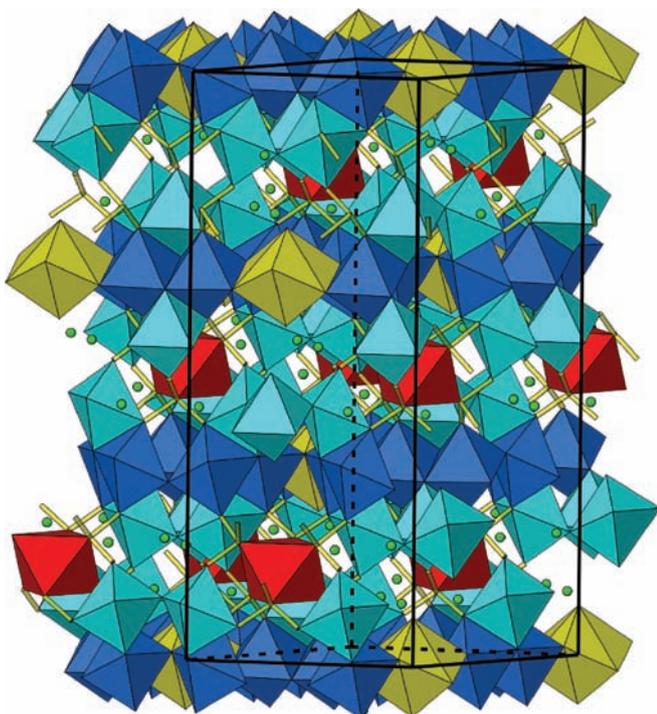


Fig. 1. Perspective view of the nanlingite structure. The red octahedra are occupied by Fe. The yellow distorted cubes illustrate NaF₈. The light and dark blue octahedra are occupied by Mg. The Ca atoms are shown as small green spheres. As–O bonds are given in yellow.

if iron is in low-spin state the IS values are even lower in both valence states (Li & Ying, 1996). The refined hyperfine parameters indicate that the iron in nanlingite is in the range of Fe^{II} with a low-spin state, or Fe³⁺ with a high-spin state in octahedral coordination. There are two octahedral sites in nanlingite occupied or partially occupied by iron, but only one single doublet with an isomer shift of octahedral Fe³⁺. This indicates that the isomer shifts of octahedral Fe in the two structural sites are overlapped.

The Fe *L*₂₃ edges from nanlingite, pyrite (FeS₂) and Fe₂O₃ containing Fe^{II} and Fe³⁺ in six-fold coordination are shown in Fig. 9. The measured separation of the Fe *L*₃ and *L*₂ maxima from FeS₂ and Fe₂O₃ are: 723.6 – 710.8 = 12.8 eV and 728.4 – 715.2 = 13.2 eV for Fe²⁺ and Fe³⁺, respectively, which are in good agreement with the published data (van Aken & Liebscher, 2002). The Fe^{II} *L*₃ edges in pyrite display a sharp maximum at 710.8 eV and a weak shoulder at 715.4 eV. The Fe³⁺ *L*₃ edge in Fe₂O₃ shows a sharp maximum at 715.2 eV.

The measured separation of the Fe *L*₃ and *L*₂ maxima for nanlingite is 724.8 – 712.0 = 12.8 eV. The Fe *L*₃ edges in nanlingite display a sharp maximum at 712.0 eV and a weak shoulder at 715.6 eV. The Fe *L*₂₃ edges from nanlingite are similar to those from pyrite. This indicates again that Fe in nanlingite is mainly Fe²⁺. However, the Fe *L*₃ edges from nanlingite show a chemical shift of 1.2 eV with a maximum at 712.0 eV compared to pyrite at 710.8 eV, suggesting that the Fe *L*₃ edges contain a superposition of Fe³⁺ *L*₃ edge spectrum. According to the analyses from the EELS and Mössbauer spectrum, it can be concluded that the oxidation state of Fe in nanlingite is mainly Fe^{II} with a low-spin state, and minor Fe is Fe³⁺ with a high-spin state.

Therefore, the main Fe^{II} in nanlingite can be assigned to the Fe site in the [Fe(AsO₃)₆] cluster. It is in agreement with the assumption from hybridization orbitals of *d*⁷*sp*³ in Fe octahedrally surrounded by six As atoms, where six 3*d*⁶ electrons of Fe²⁺ must spin pairs to vacate *d*² orbitals. The minor Fe³⁺ with a high-spin state can be assigned to the Mg(1) and Mg(2) sites.

The oxidation state of Fe in the [Fe(AsO₃)₆] cluster is similar to that in löllingite, which possesses the marcasite-type structure, and is a low-spin Fe^{II} compound (Ondruš *et al.*, 2001). The refined hyperfine parameters for löllingite are IS = 0.30 mm/s, QS = 1.68 mm/s. The IS value for löllingite is close to that (IS = 0.33) for nanlingite. The larger QS value can be interpreted by the stronger distortion of octahedral coordination polyhedron in löllingite (Fe–As distances: 2.36~2.38 Å) than that in nanlingite (Fe–As distances = 2.40 Å).

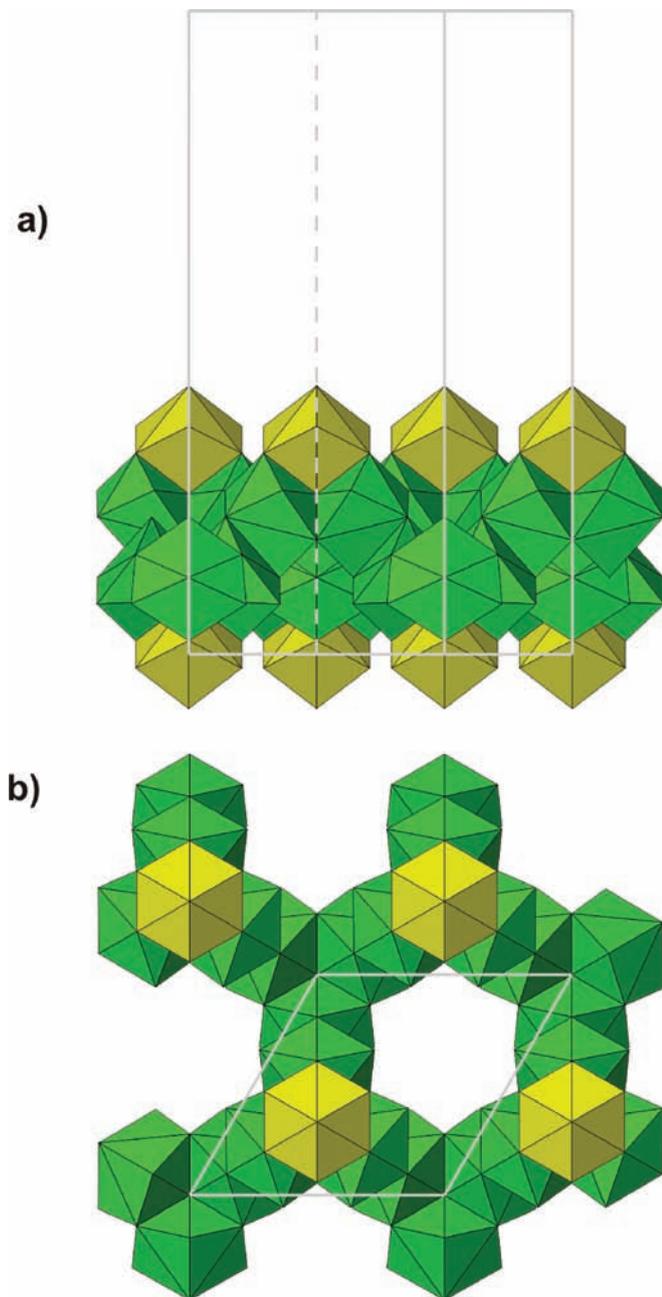


Fig. 2. Schematic drawing of the nanlingite structure in projections on (a) (100) and (b) (001), emphasizing only the arrangement of distorted NaF_8 (yellow) and CaF_4O_4 (green) “cubes”.

4.3. Geometry of the arsenite group

In the crystal structure of nanlingite, both $[\text{As}(1)\text{O}_3]$ and $[\text{As}(2)\text{O}_3]$ groups are trigonal pyramids. Compared with the non-cluster $\text{As}(1)\text{O}_3$ group, the $\text{As}(2)\text{O}_3$ group in the $[\text{Fe}(\text{AsO}_3)_6]$ cluster is somewhat distorted. In the non-cluster (AsO_3) group the $\langle \text{As}(1)-\text{O} \rangle$ bond length is 1.78 Å and the $\langle \text{O}-\text{As}(1)-\text{O} \rangle$ angle is 101.63°. The $\langle \text{As}(2)-\text{O} \rangle$ bond length of the $[\text{Fe}(\text{AsO}_3)_6]$ cluster is 1.73 Å and the $\langle \text{O}-\text{As}(2)-\text{O} \rangle$ angle is 99.12°. The $\langle \text{As}-\text{O} \rangle$ bond distance in the $[\text{Fe}(\text{AsO}_3)_6]$ cluster is shorter than that in the non-cluster (AsO_3) group, and the $\langle \text{O}-\text{As}(2)-\text{O} \rangle$ angle in the

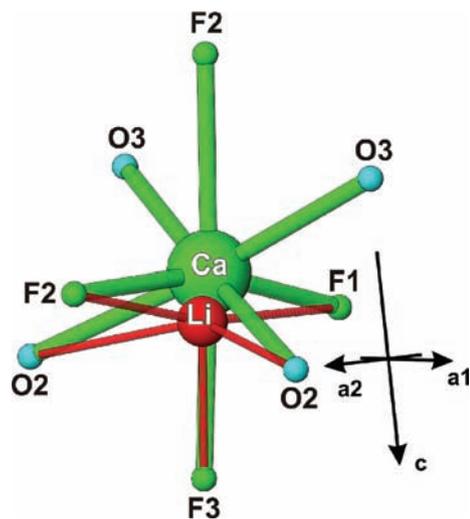


Fig. 3. Drawing of the split Ca site. Ca is 8-coordinated to form a distorted CaO_4F_4 cube; Li, separated by 0.58(2) Å from the main Ca site and with a site occupation of 22 %, forms a distorted tetragonal pyramid.

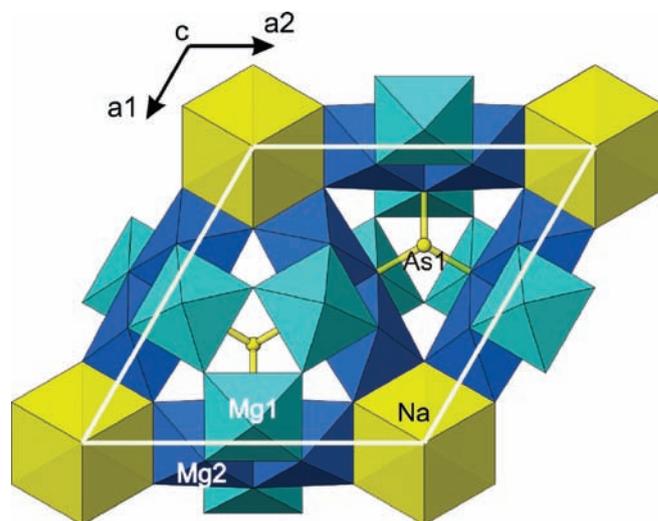


Fig. 4. View of the nanlingite structure along the c -axis illustrating structure details around $z \sim 0$, a “sheet” of $[-\text{Na}-\text{Mg}(2)-\text{As}(1)-]$.

$[\text{Fe}(\text{AsO}_3)_6]$ cluster is smaller than that in the non-cluster (AsO_3) group. The comparable $\langle \text{As}-\text{O} \rangle$ bond length of $[\text{Mn}(\text{AsO}_3)_6]$ in magnussonite is 1.76 Å and the $\langle \text{O}-\text{As}-\text{O} \rangle$ angle in the cluster is 98.3° (Moore & Araki, 1979).

The bond distances and angles of 25 (AsO_3) groups from 11 arsenite minerals have been summarized by Hawthorne (1985). The individual As-O bond lengths and O-As-O angles are in the range of 1.72 to 1.85 Å and 89.3° to 106.6°, the respective mean values are between 1.76 to 1.80 Å and 94.8° to 102.8°. In addition, in trippkeite, CuAs_2O_4 , the As-O distances are: 1.89(×2) and 1.69 Å (av. 1.82 Å) (Zemann, 1951).

In nanlingite the individual As-O distances (1.73–1.78 Å), $\langle \text{As}(1)-\text{O} \rangle$ (1.78 Å), the individual O-As-O angles (97.17°–103.01°), and $\langle \text{O}-\text{As}-\text{O} \rangle$ angles (99.12°–101.63°)

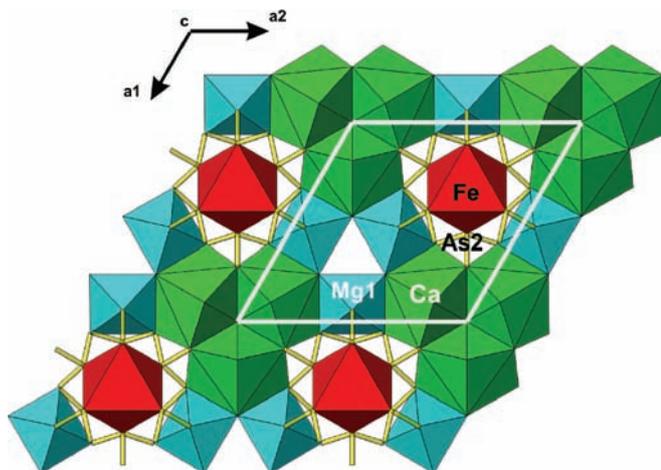


Fig. 5. View of the nanlingite structure along the c -axis at around $z \sim 1/9$, a “sheet” of $[-(\text{Ca}, \text{Li})-\text{Mg}(1)-\text{As}(2)-]$ along with the $[\text{Fe}(\text{AsO}_3)_6]$ cluster.

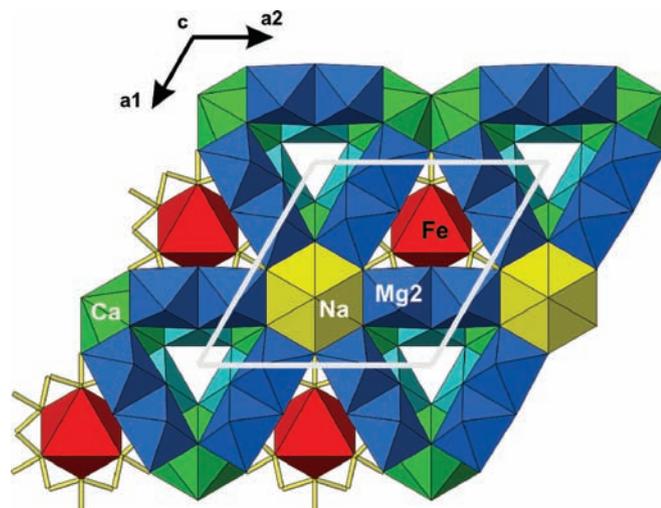


Fig. 6. View of the nanlingite structure along the c -axis between $z \sim 1/9$ and $z \sim 2/9$.

are in good agreement with the known values. However, $\langle \text{As}(2)\text{-O} \rangle = 1.73 \text{ \AA}$ is somewhat shorter than the typical average range.

4.4. Crystal-chemical formula of nanlingite

The analytical results of nanlingite by (EMP + SIMS) analyses are shown in Table 5. The present results are similar to the originally reported composition (Gu *et al.*, 1976). The differences between all those data obviously result from the respective standards and corrections used. A small, quite variable amount of Ti was detected in the present study. Li was proven by SIMS analyses. The F and As contents are reasonable. The formulae were calculated on the basis of 38 (O + F + OH) atoms per formula unit (*apfu*). The total cation number is 27.73 *apfu* for sample Nan3, indicating that there exists a cation deficiency in the formula as compared to the ideal value of 28 *apfu*. A

detailed cationic distribution is given in Table 6. The assigned populations were calculated taking into account the unit formula as well as the refined site-scattering.

As(2) and As(1) sites are filled by As exclusively. The Fe site is occupied by Fe^{II} with a low-spin state according to Mössbauer and EELS analyses. On the basis of the determination of the crystal structure, the Mg(2) site is close to be fully occupied by Mg^{2+} .

The Mg(1) site is an octahedral site. The coordination numbers for both of the Ca site and Na site are eight. According to Shannon (1976), the effective ionic radius for Mg^{2+} is 0.72 Å in six-fold coordination. Based on ionic radius and valence, Al^{3+} ($r = 0.535 \text{ \AA}$), Ti^{4+} ($r = 0.605 \text{ \AA}$) and Fe^{3+} ($r = 0.645 \text{ \AA}$), compared with Li ($r = 0.76 \text{ \AA}$), are preferentially incorporated at the smaller Mg(1) site in six-fold coordination. The Mg(1) site is fully occupied by these cations. Li is distributed to the Ca site and the Na site in eight-fold coordination.

The calculated site-scattering values at the Mg(1) site and the Ca site are 12.80 and 15.89 *epfu*, respectively, about 9 and 1 % different from the refined values [Mg(1) site = 14.10, Ca site = 15.81 *epfu*]. These discrepancies can be related to the replacements of different cations at these sites.

Calculated bond-valencies and the assigned site populations are given in Table 7. The bond-valence at the Ca site is lower than expected. This can be interpreted by the presence of monovalent cations and deficiency of cations. The bond-valence at the As(2) site is higher than normal due to the shorter As-O distance.

On the basis of 38 (O+F+OH) (*apfu*), the empirical crystal-chemical formula for nanlingite is $(\text{Na}_{0.90}\text{Li}_{0.10}) \sum_{1.00}(\text{Ca}_{4.41} \text{Li}_{1.06} \text{Mg}_{0.17} \text{Na}_{0.06} \text{Mn}_{0.05} \square_{0.25}) \sum_{6.00}(\text{Mg}_{11.38} \text{Fe}^{3+}_{0.30} \text{Al}_{0.29} \text{Ti}_{0.03}) \sum_{12.00}(\text{AsO}_3)_2 [\text{Fe}^{\text{II}}(\text{AsO}_3)_6]$ ($\text{F}_{13.77} \text{OH}_{0.16}$) $\sum_{13.93}$. The general formula can be expressed as $\text{Na}(\text{Ca}_5\text{Li}) \sum_6 \text{Mg}_{12}(\text{AsO}_3)_2 [\text{Fe}^{\text{II}}(\text{AsO}_3)_6] \text{F}_{14}$, $Z = 3$. Monovalent cations may replace Ca in the Ca site in order to maintain charge balance.

5. Conclusions

Nanlingite is the first mineral with a $[\text{Fe}(\text{AsO}_3)_6]$ configuration. The cluster of $[\text{Fe}(\text{AsO}_3)_6]$ is the third example of a rare metal-As cluster besides $[\text{Cu}(\text{AsO}_3)_4]$ and $[\text{Mn}(\text{AsO}_3)_6]$. The iron in nanlingite was interpreted to be Fe^{II} in a low-spin state based on RT Mössbauer spectrum and EELS data.

Lithium is an important constituent in nanlingite, where it occupies (22 %) the split site at 0.58(2) Å distance from the main Ca site and exhibits a five-fold coordination with $\langle \text{Li}(\text{O},\text{F}) \rangle > 2.21 \text{ \AA}$.

The revised formula obtained in the present work by crystal-structure refinement is $\text{Na}(\text{Ca}_5\text{Li}) \sum_6 \text{Mg}_{12}(\text{AsO}_3)_2 [\text{Fe}^{\text{II}}(\text{AsO}_3)_6] \text{F}_{14}$, indicating that the previous formulae, either $\text{CaMg}_3(\text{AsO}_3)_2 \text{F}_2$ or $\text{CaMg}_4(\text{AsO}_3)_2 \text{F}_4$, are erroneous and should be corrected.

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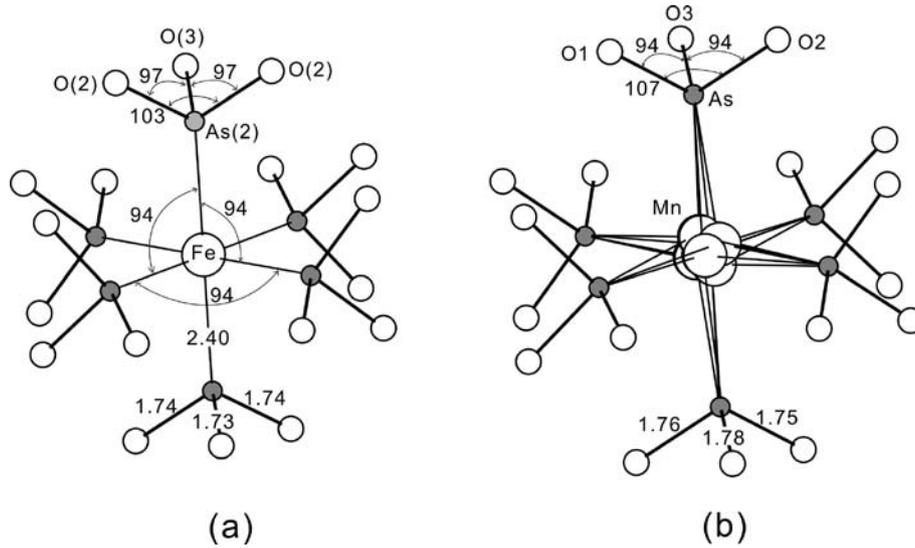


Fig. 7. Topological comparison of the $[\text{Fe}(\text{AsO}_3)_6]$ cluster in the nanlingite structure (a) with the $[\text{Mn}(\text{AsO}_3)_6]$ cluster in the magnussonite structure (b). Selected interatomic distances (Å) and angles ($^\circ$) are indicated.

Table 4. $\langle \text{As}-\text{O} \rangle$ and $\langle \text{Me}-\text{As}, \text{Cl} \rangle$ in selected arsenite minerals with the clusters

Mineral name	Cluster	$\langle \text{As}-\text{O} \rangle$	$\langle \text{Me}-\text{As} \rangle$	$\langle \text{Me}-\text{Cl} \rangle$	References
$\text{Pb}_6\text{Cu}(\text{AsO}_3)_2\text{Cl}_7$	$[\text{Cu}(\text{AsO}_3)\text{Cl}_3]$	1.76	2.34	2.44	Pertlik (1986)
Freedite	$[\text{Cu}(\text{AsO}_3)_2\text{Cl}_2]$	1.78	2.32	2.43	Pertlik (1987)
Dixenite	$[\text{Cu}(\text{AsO}_3)_4]$	1.78	2.26		Araki & Moore (1981)
	$[\text{Cu}(\text{AsO}_3)_4]$	1.76	2.40		
	Non-cluster (AsO_3)	1.75			
Magnussonite	$[\text{Mn}(\text{AsO}_3)_6]$	1.76	2.65		Moore & Araki (1979)
Nanlingite	$[\text{Fe}(\text{AsO}_3)_6]$	1.73	2.40		This work
	Non-cluster (AsO_3)	1.79			

Note: Formula of freedite, $\text{Pb}_8\text{Cu}(\text{AsO}_3)_2\text{O}_3\text{Cl}_5$; dixenite, $\text{CuMn}_{14}\text{Fe}(\text{AsO}_3)_5(\text{SiO}_4)_2(\text{AsO}_4)(\text{OH})_6$; magnussonite, $\text{Mn}_9[\text{Mn}(\text{AsO}_3)_6]\text{Cl}$; nanlingite, $\text{Na}(\text{Ca}, \text{Li}, \text{Na})_6(\text{Mg}, \text{Fe})_{12}(\text{AsO}_3)_2 [\text{Fe}(\text{AsO}_3)_6]\text{F}_{14}$.

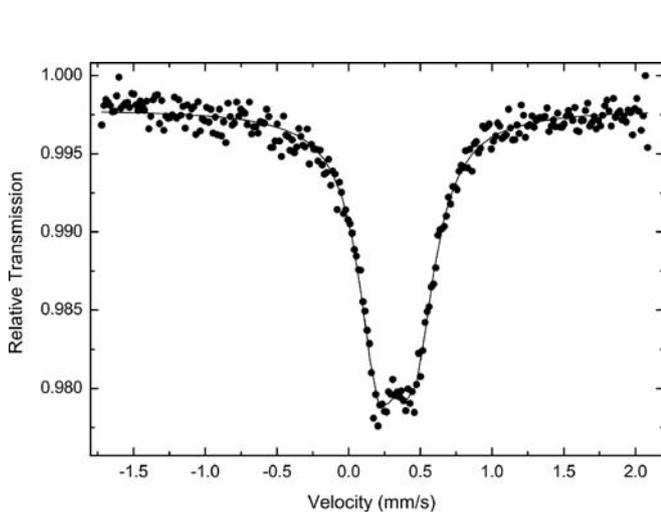


Fig. 8. Room-temperature Mössbauer spectrum of nanlingite.

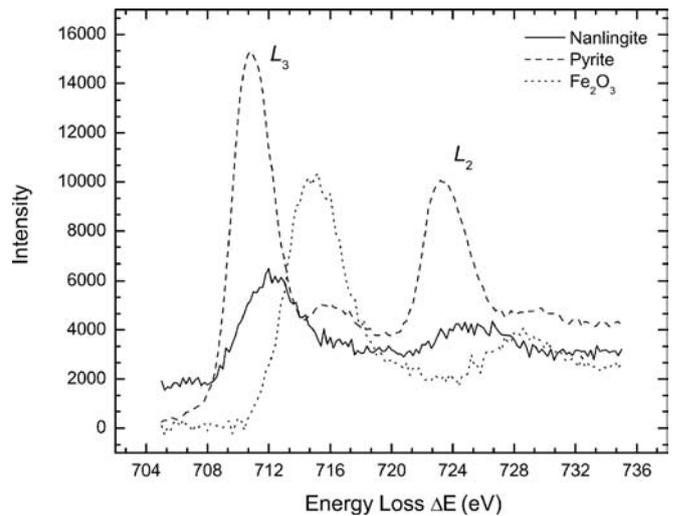


Fig. 9. $\text{Fe } L_{23}$ edges from nanlingite, pyrite and Fe_2O_3 .

Table 5. Chemical composition and unit formulae of nanlingite.

	N1	N2	Nan1	Nan2	Nan3
Na ₂ O	1.81	1.86(12)	1.88(10)	1.51(8)	1.64(6)
CaO	11.74	13.40(44)	12.30(18)	13.73(19)	13.61(22)
Li ₂ O	1.22	1.00	1.13	0.95	0.95
MgO	25.04	24.10(54)	23.27(43)	25.77(22)	25.61(25)
MnO	0.21	0.15(3)	0.16(4)	0.16(3)	0.19(3)
FeO _{total}		5.41(32)	5.69(17)	5.10(11)	5.13(11)
Fe ₂ O _{3total}	7.09				
FeO ^a	3.97	3.81	3.95	3.95	3.95
Fe ₂ O ₃ ^a	2.59	1.82	1.97	1.31	1.34
Al ₂ O ₃	0.98	0.70(78)	0.46(7)	0.51(24)	0.82(15)
As ₂ O ₃	44.11	40.36(41)	43.72(27)	43.45(21)	43.53(27)
TiO ₂		0.91(97)	3.24(35)	0.28(5)	0.14(4)
H ₂ O	0.60	0.00	0.06	0.09	0.08
F	13.64	14.10(41)	14.07(19)	14.36(10)	14.39(17)
O=F	-5.74	-5.94	-5.92	-6.05	-6.06
Sum	100.16	96.27	100.29	100.01	100.19
Na	1.058	1.131	1.103	0.888	0.962
Ca	3.793	4.504	3.987	4.460	4.413
Mn ^b	0.054	0.040	0.041	0.041	0.049
Li	1.479	1.262	1.375	1.158	1.156
Mg	0.191	0.172		0.192	0.182
Sum	6.575	7.109	6.506	6.740	6.762
Mg	11.056	11.098	10.495	11.456	11.371
Fe ³⁺ ^a	0.587	0.428	0.449	0.298	0.304
Ti		0.215	0.737	0.064	0.032
Al	0.348	0.259	0.164	0.182	0.292
Sum	12.000	12.000	11.845	12.000	12.000
Fe ^{II} ^a	1.0	1.0	1.0	1.0	1.0
As	8.079	7.690	8.034	8.002	8.001
OH	1.207	0.0	0.121	0.182	0.161
F	13.008	13.989	13.463	13.770	13.772
Sum	14.215	13.989	13.584	13.952	13.933

Note: Formulae were calculated for O + OH + F = 38 *apfu*. Sample N1: Gu *et al.* (1976); N2: Average of nine EMP analyses; Li₂O was estimated by semi-quantitative SIMS analysis (by Beijing group); Nan1: Average of 20 EMP analyses; Li₂O, H₂O, B (0.14 ppm) and Be (0.06 ppm): 1 SIMS analysis (by Vienna group); Nan2: Average of 29 EMP analyses; Li₂O, H₂O, B (0.18 ppm) and Be (0.02 ppm): 1 SIMS analysis (by Vienna group); Nan3: Average of 37 EMP analyses; Li₂O, H₂O, B (0.20 ppm) and Be (0.05 ppm): 1 SIMS analysis (by Vienna group); Si, Cl, Cr and Sb are below detection limit.

^aFeO and Fe₂O₃ were calculated, Fe^{II} was fixed to 1.0 *apfu* on the basis of the crystal-chemical formula, Mössbauer and EELS analyses.

^bMn was calculated as MnO.

Table 6. Refined site populations (RSP, *apfu*), refined site-scattering values (RSS, *epfu*), assigned site populations (ASP, *apfu*), and calculated site-scattering values (CSS, *epfu*) for nanlingite.

Site	RSP	RSS	ASP	CSS
As(1)	1.00As	33.00	1.00As	33.00
As(2)	1.00As	33.00	1.00As	33.00
Fe	1.00Fe	26.00	1.00Fe	26.00
Mg(1)	0.85Mg + 0.15Fe	14.10	0.90Mg + 0.05Fe + 0.05Al + 0.01Ti	12.80
Mg(2)	0.98Mg + 0.02Fe	12.25	1.00Mg	12.00
Ca	0.73Ca + 0.22Li + 0.05Na	15.81	0.74Ca + 0.18Li + 0.03Mg + 0.01Mn + 0.01Na + 0.04□	15.89
Na	0.90Na + 0.10Li	10.20	0.90Na + 0.10Li	10.20

Note: The assigned site populations were calculated from Sample Nan3.

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Table 7. Bond-valence table (vu) for nanlingite.

	As(1)	As(2)	Mg(1)	Mg(2)	Ca	Na	Σ
O(1)	$1.011 \times 3\downarrow$		0.379	0.304×2			2.00
O(2)		$1.154 \times 2\downarrow$	$0.354 \times 2\downarrow$	$0.351 \times 2\downarrow$	$0.103 \times 2\downarrow$		1.96
O(3)		1.170	0.469		0.147×2		1.93
F(1)					$0.274 \times 3\rightarrow$	$0.246 \times 2\downarrow$	1.07
F(2)			0.355×2		0.251, 0.087		1.05
F(3)				0.347×2	0.129	$0.099 \times 6\downarrow$	0.92
Σ	3.03	3.48	2.27	2.00	1.24	1.08	

Note: The bond-valences were calculated from the bond lengths given in Table 4, and from the assigned site populations of Table 6, with the parameters of Brese & O'Keeffe (1991).

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