

## THE CRYSTAL STRUCTURE OF NALIPOITE

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### ABSTRACT

The crystal structure of the new mineral species *nalipoite* has been solved by Patterson methods. Refinement of the *nalipoite* structure using 477 observed reflections ( $MoK\alpha$ ) converged at an  $R$  of 2.52,  $wR$  2.80%. *Nalipoite* crystallizes in space group  $Pmnb$ ,  $a$  6.884(2),  $b$  9.976(4),  $c$  4.927(2) Å,  $V$  338.4(2) Å<sup>3</sup>; the crystal-structure analysis gives the formula  $NaLi_2PO_4$ ,  $Z = 4$ . The structure has three cation sites; P and Li are tetrahedrally coordinated, and Na is octahedrally coordinated.  $PO_4$  and  $LiO_4$  tetrahedra form a corner-linked framework based on a stacking of two-dimensional  $(3.6.3.6)_1(3^2.6^2)_2$  nets along  $Z$ . Na occupies cages in the resulting three-dimensional net.

**Keywords:** *nalipoite*, new mineral species, crystal structure, phosphate, framework of tetrahedra, nets.

### SOMMAIRE

La structure cristalline de la nouvelle espèce minérale *nalipoite* a été déterminée par méthodes de Patterson. L'affinement de cette structure, fondé sur 477 réflexions observées (rayonnement  $MoK\alpha$ ), a convergé à un facteur  $R$  de 2.52 ( $wR$  de 2.80%). La *nalipoite* répond au groupe spatial  $Pmnb$ ,  $a$  6.884(2),  $b$  9.976(4),  $c$  4.927(2) Å,  $V$  338.4(2) Å<sup>3</sup>. Les résultats de l'analyse structurale lui attribuent la formule  $NaLi_2PO_4$ ,  $Z = 4$ . La structure possède trois sites cationiques; P et Li sont tétra-coordonnés, et le Na a une coordination octaédrique. Les tétraèdres contenant P et Li définissent une charpente à sommets partagés selon un empilement de réseaux bidimensionnels  $(3.6.3.6)_1(3^2.6^2)_2$  le long de  $Z$ . Le sodium occupe des cages dans le réseau tridimensionnel qui en résulte.

(Traduit par la Rédaction)

**Mots-clés:** *nalipoite*, nouvelle espèce minérale, structure cristalline, phosphate, charpente de tétraèdres, réseaux.

### INTRODUCTION

The new mineral species *nalipoite* (Chao & Ercit 1991) was initially an enigmatic species. Electron-microprobe analyses showed the presence of major P, Na and trace Al, but no other elements with  $Z$  greater than 10; however, analytical sums typically averaged 76%, suggesting the presence of some

undetected constituent. In keeping with the mineralogy of the type association, water was suspected to make up the difference; however, the measured density of 2.58 g/cm<sup>3</sup> did not support this hypothesis. As quantities of the mineral were not sufficient for conventional methods of water determination, crystal-structure analysis was chosen as the analytical method, a fortunate choice, as the structure analysis showed lithium to be the missing constituent!

### EXPERIMENTAL

A cleavage fragment of cotype *nalipoite*, from Mont Saint-Hilaire, measuring  $0.07 \times 0.12 \times 0.17$  mm was used in the data collection. Intensity data were collected with a Nicolet R3m four-circle diffractometer at the University of Manitoba, using the experimental method of Ercit *et al.* (1986). Twenty-three intense reflections were used to center the crystal; least-squares refinement of the setting angles gave the unit-cell parameters in Table 1, and the orientation matrix used for data collection. Two asymmetric units of data were collected to a maximum  $\sin\Theta/\lambda$  of 0.7035, and were merged ( $R = 1.6\%$ ) to give the numbers of unique reflections shown in Table 1.

On the basis of density measurements and from the results of the electron-microprobe analysis,  $Z$  was anticipated to be 4; hence the unit-cell contents were initially estimated to be  $4(H_4NaPO_3)$ , assuming that hydrogen was the only undetected constituent. This resulted in an initial estimate of  $\mu = 8.8 \text{ cm}^{-1}$  used in the empirical absorption correction.

TABLE 1. MISCELLANEOUS INFORMATION FOR NALIPOITE

$a$ (Å)	6.884(2)	Space group	$Pmnb$
$b$	9.976(4)	Density (gcm <sup>-3</sup> )	2.58
$c$	4.927(2)	Crystal size (mm)	0.07 x 0.12 x 0.17
$V$ (Å <sup>3</sup> )	338.4(2)	$\mu$ (cm <sup>-1</sup> ), radiation	7.6, $MoK\alpha$
$Z$	4	Total $F_o$ , Obs. $F_o$	526, 477
Formula	$NaLi_2PO_4$	Final $R$ , $wR$ (%)	2.52, 2.80
Extinction parameter:	$x = 0.0041(3)$ , where $F^* = F_o [1.0 + 0.002x^2/\sin(2\theta)]^{-1/4}$		
$R$ factors:	$R = \sum( F_o  -  F_c )/\sum F_o $ $wR = [\sum w( F_o  -  F_c )^2]/\sum w F_o ^2]^{1/2}$ , $w = \sigma^{-2}$		

TABLE 2. POSITIONAL AND THERMAL PARAMETERS FOR NALIPOITE

	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>	U <sub>eq</sub>
Na	1/4	0.8857(1)	0.7636(2)	103(1)	249(7)	223(6)	-79(5)	0	0	192(4)
Li	0.5002(5)	0.6541(3)	0.7915(7)	121(16)	163(15)	141(15)	-7(13)	-11(14)	-3(13)	142(9)
P	1/4	0.09802(6)	0.20247(1)	61(3)	81(3)	72(3)	5(3)	0	0	71(2)
O1	1/4	0.1198(2)	0.8911(4)	107(9)	151(10)	76(8)	5(7)	0	0	111(5)
O2	0.0668(2)	0.1623(1)	0.3243(2)	76(6)	114(6)	110(6)	3(5)	12(5)	17(5)	100(4)
O3	1/4	0.9454(2)	0.2578(4)	117(9)	79(8)	140(10)	9(7)	0	0	112(5)

All U values are in Å<sup>2</sup> × 10<sup>4</sup>

Data reduction (correction for Lorentz, polarization and background effects) was done with the SHELXTL package of programs. Crystal-structure analysis and refinement were done with the SHELXTL PC package of programs. Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively.

A sharpened Patterson map was calculated, from which the positions of all P, Na and O atoms were inferred. After several cycles of full-matrix least-squares refinement using unit weights, this model converged at values of  $R = 11.9$ ,  $wR = 14.0\%$ . The difference map calculated at this stage showed a positive maximum of approximately  $3.5 e^-/\text{Å}^3$ , located at a mean distance of  $1.97 \text{ Å}$  from four nearest-neighbor tetrahedrally coordinated oxygen atoms. On the basis of these data, the residual electron-density was assigned to Li. The refinement of this model converged at values of  $R = 3.15$ ,  $wR = 3.59\%$ ; all maxima in the difference map calculated at this stage were found to be less than  $0.6 e^-/\text{Å}^3$ , which, with the low  $R$  factors, indicated that the model accounted for all atoms. In addition, the implied formula for nalipoite is charge-balanced:  $\text{NaLi}_2\text{PO}_4$ . Final changes to the model involved conversion of all temperature factors to an anisotropic basis, modification of the weighting scheme to one involving a  $\sigma^2(F_o)$  term (Table 1), and inclusion of an isotropic extinction correction (Table 1). Refinement of the 44 parameters for this model converged at values of  $R$  of 2.52,  $wR$  2.80% ( $R = wR = 2.82\%$  for all 526 data). The observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

## RESULTS

The refined values of the positional parameters and the anisotropic and equivalent isotropic values of  $U$  for the atoms of the nalipoite structure are given in Table 2; bond lengths are listed in Table 3, and bond angles and polyhedral edge-lengths are shown in Table 4. Li and P are tetrahedrally coordinated, and Na is octahedrally coordinated by

TABLE 3. BOND LENGTHS FOR NALIPOITE

Na-O1a	2.418(2)	Li-O1g	1.973(3)	P-O1a	1.549(2)
-O1g	2.760(2)	-O2c	1.950(4)	-O2a,b	1.537(1) $\times$
-O2e,f	2.274(1) $\times$	-O2f	1.972(3)	-O3a	1.547(1)
-O3a	2.507(2)	-O3d	1.992(3)	<P-O>	1.543
-O3h	2.582(2)	<Li-O>	1.972		
<Na-O>	2.466 Å				

TABLE 4. POLYHEDRAL EDGE-LENGTHS AND ANGLES FOR NALIPOITE

O1g-Li-O2c	104.1(2), 3.094(2)	O1a-Na-O2e,f	104.6(1), 3.715(3) $\times$
-O2f	103.4(2), 3.097(2)	-O3a	61.2(1), 2.508(3)
-O3d	129.0(2), 3.579(2)	-O3h	91.6(1), 3.573(3)
O2c-Li-O2f	107.3(2), 3.158(2)	O1g-Na-O2e,f	75.2(1), 3.097(2) $\times$
-O3d	107.8(2), 3.185(2)	-O3a	119.8(1), 4.558(3)
O2f-Li-O3d	109.8(2), 3.119(2)	-O3h	87.4(1), 3.680(3)
<O-Li-O>	109.2°	O2e,f-Na-O3a	103.6(1), 3.760(3) $\times$
<O-O>	3.205 Å	-O3h	82.2(1), 3.185(2) $\times$
		<O-Na-O>	90.9
		<O-O>	3.486
O1a-P-O2a,b	109.2(2), 2.515(2) $\times$		
-O3a	108.2(2), 2.508(3)		
O2a-P-O2b	110.3(2), 2.523(3)		
O2a,b-P-O3a	110.0(2), 2.526(2) $\times$		
<O-P-O>	109.5		
<O-O>	2.519		

the oxygen atoms. An asymmetric unit of coordination polyhedra and atom labels (as referenced in Tables 3, 4) are shown in Figure 1. The  $\text{PO}_4$  tetrahedron is virtually undistorted ( $\Delta = 0.1$ ,  $\sigma^2 = 0.5$ , Robinson *et al.* 1971). The  $\text{LiO}_4$  tetrahedron is only slightly less regular in terms of its bond lengths ( $\Delta = 0.6$ ); consequently,  $\langle \text{Li-O} \rangle$  (meas.) =  $1.972 \text{ Å}$  compares well with  $\langle \text{Li-O} \rangle$  (calc.) =  $1.98 \text{ Å}$  (Shannon 1976). However, the  $\text{LiO}_4$  polyhedron is quite distorted in terms of bond angles ( $\sigma^2 = 99$ ). The  $\text{NaO}_6$  octahedron is highly distorted in both senses, but most of the distortion is angular:  $\Delta = 48$ ,  $\sigma^2 = 256$ . In overview, the degree of polyhedron distortion correlates well with bond strength; the  $\text{PO}_4$  tetrahedron is undistorted because of the vast differences in strength of P-O bonds (Pauling bond strength  $5/4$  v.u.) compared to Li-O ( $1/4$  v.u.) and Na-O ( $1/6$  v.u.) bonds.

Figure 2 is a Z-axis projection of the nalipoite structure. The figure has been drawn to emphasize tetrahedral components of the structure;  $\text{PO}_4$  tetrahedra are ruled,  $\text{LiO}_4$  tetrahedra are stippled, and Na atoms are shown as spheres. The low bond-strengths associated with Li-O bonds permit a high degree of polymerization of the tetrahedral components of the structure. The structure is a

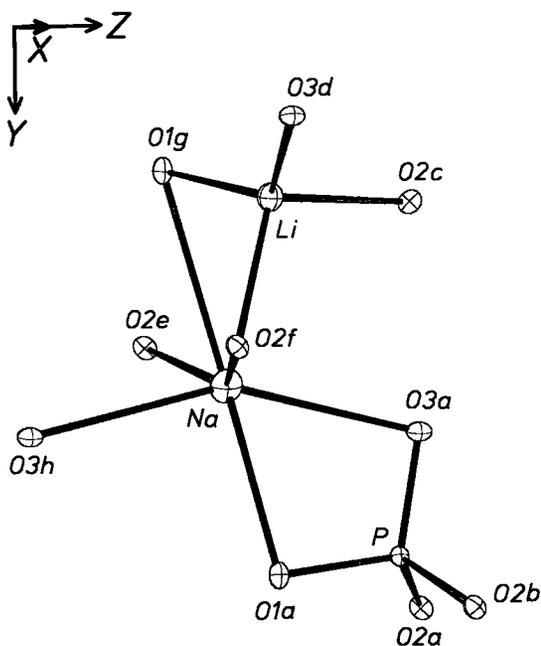
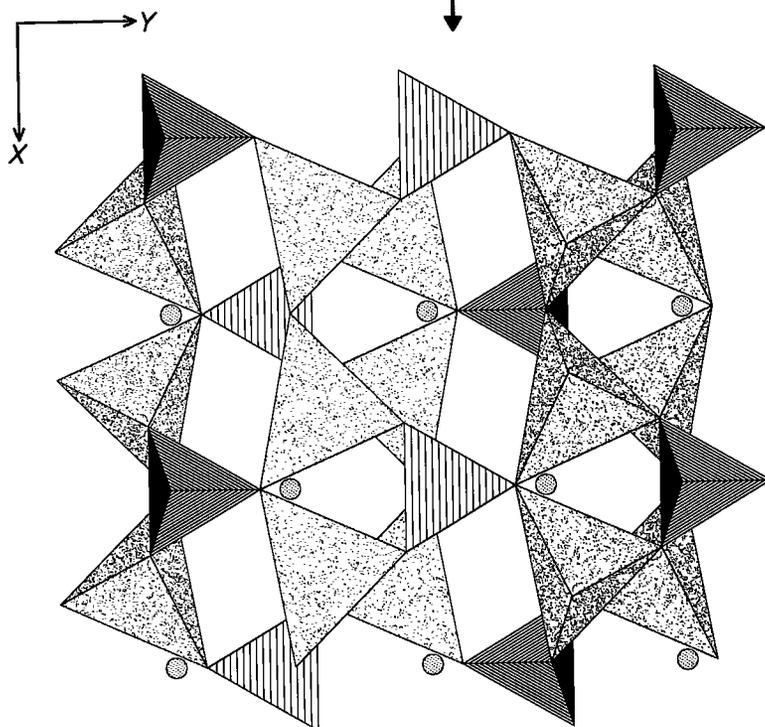


FIG. 1. An asymmetric unit of polyhedra ( $X$ -axis projection inclined by  $15^\circ$ ). Atom labels are as in Tables 3, 4.

framework in which all tetrahedra share vertices with two other tetrahedra; specifically, two  $\text{LiO}_4$  tetrahedra and one  $\text{PO}_4$  tetrahedron share each bridging oxygen.

The tetrahedral framework is perhaps better visualized in terms of nets. When viewed parallel to  $Z$ , the structure can be considered as comprised of interlinked, four-connected two-dimensional  $(3.6.3.6)_1(3^2.6^2)_2$  nets. By definition, two types of topologically distinct nodes occur in the net. Each type is surrounded by two circuits of three nodes and two circuits of six nodes. The rather complex Schläfli symbol for the net (O'Keeffe & Hyde 1980) defines the arrangement of these circuits about the two distinct types of nodes as well as the relative abundance of each type of node. Adjacent  $(3.6.3.6)_1(3^2.6^2)_2$  nets along  $Z$  are rotated  $180^\circ$  and offset relative to each other (Fig. 3 bottom). Interconnection of the nets is not achieved by perpendicular linkages; each node in any one net is linked to two nodes in both upper and lower adjacent nets; consequently, each node in the resulting three-dimensional net is eight-connected.

FIG. 2.  $Z$ -axis projection of the nalipoite structure.  $\text{LiO}_4$  tetrahedra are stippled,  $\text{PO}_4$  tetrahedra are ruled, and Na atoms are shown as spheres.



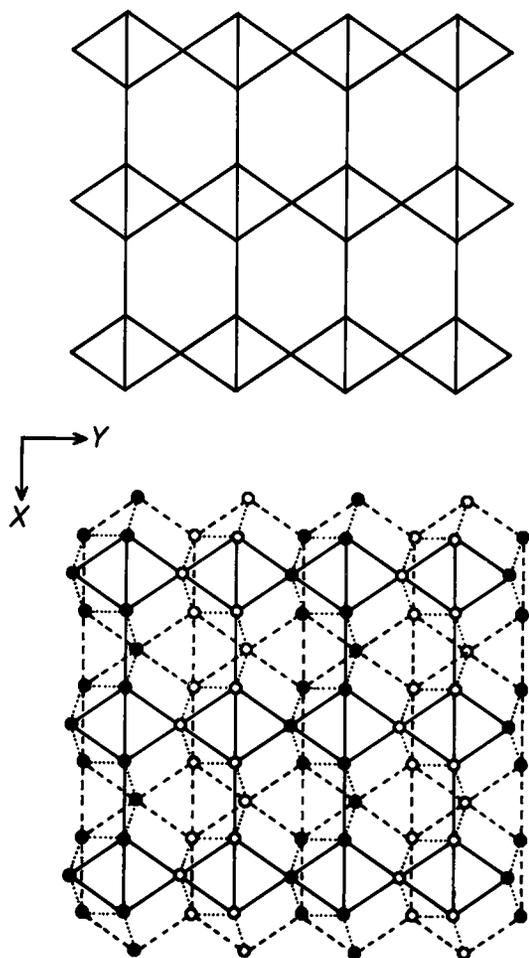
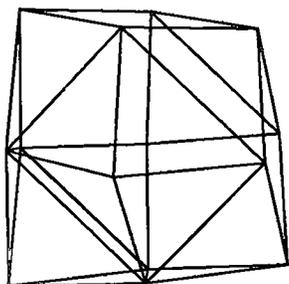


FIG. 3. The framework of tetrahedra in the nalipoite structure, shown as nets. Top: an idealized  $(3.6.3.6)_1(3^2.6^2)_2$  net, Bottom: a Z-axis projection of the framework of tetrahedra in the nalipoite structure. In solid line is one  $(3.6.3.6)_1(3^2.6^2)_2$  net, in broken line are similar nets for adjacent levels along Z, and in dotted line are linkages between adjacent nets. Open and filled circles denote opposite directions of linkage between the 2D nets (e.g., filled: upward, open: downward).



The cross-linkages between the two-dimensional nets result in circuits of three nodes and of four nodes between the nets, which produces cages of the type shown in Figure 4. The Na atom lies near the center of each cage.

Figure 5, an inclined X-axis projection of the nalipoite structure, emphasizes the layered aspects of the structure. The  $\text{LiO}_4$  tetrahedra form open, corrugated sheets (perpendicular to Y); these sheets are cross-linked and reinforced by  $\text{PO}_4$  tetrahedra and, to a lesser extent, by  $\text{NaO}_6$  octahedra, which, by alternation with the  $\text{PO}_4$  tetrahedra, form chains along X. It is undoubtedly the planar anisotropy, in the form of weak bonding within the Li layer, that results in the good  $\{010\}$  cleavage for the mineral. Re-examination of Figure 2 shows that there also are planes of weak bonding (i.e., containing Li-O bonds but not P-O bonds) perpendicular to X, hence the good  $\{100\}$  cleavage.

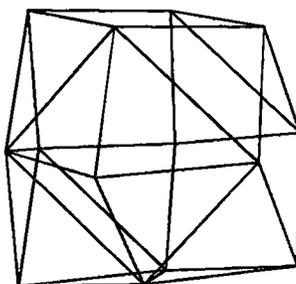
Empirical bond-valences and their sums are given in Table 5. All sums are nearly ideal, which confirms all inferences about site occupancy and coordination.

TABLE 5. BOND-VALENCE TABLE FOR NALIPOITE

	O1	O2	O3	SUM
Na	0.18	0.25 $\times 2 \rightarrow$	0.15	1.03
	0.08		0.13	
Li	0.24 $\times 2 \downarrow$	0.25	0.23 $\times 2 \downarrow$	0.97
		0.24		
P	1.22	1.26 $\times 2 \rightarrow$	1.23	4.96
SUM	1.96	2.00	1.97	

- bond valences (v.u.) from curves of Brown (1981)

FIG. 4. A stereographic projection of the Na cage in nalipoite. The three-dimensional framework of Fig. 3 produces 20-sided cages of the type shown here. A Na atom lies near the center of the cage.



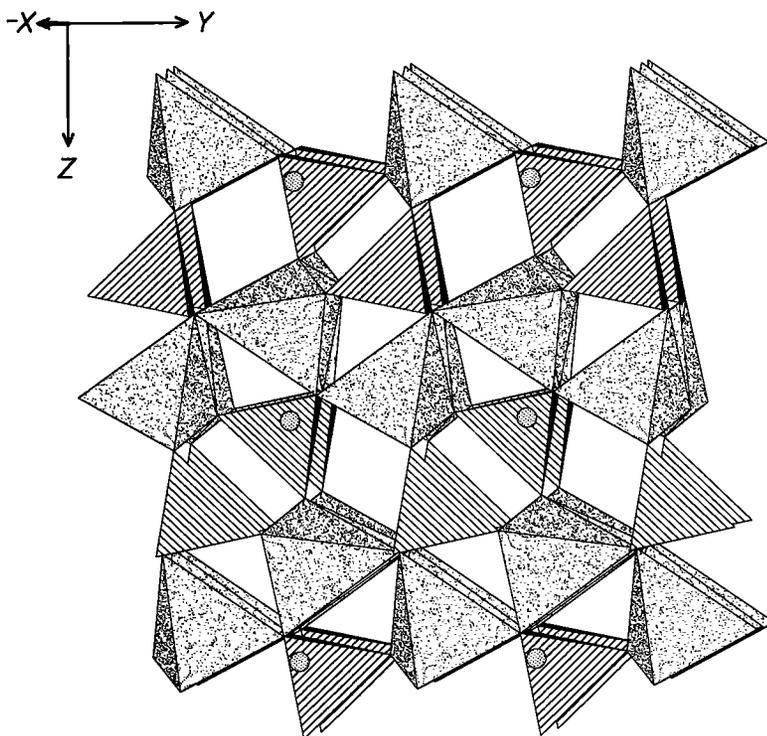


FIG. 5. An inclined X-axis projection of the nalipoite structure. Shading is as in Fig. 2.

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