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NALIPOITE, SODIUM DILITHIUM PHOSPHATE, A NEW MINERAL SPECIES FROM MONT SAINT-HILAIRE, QUEBEC

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ABSTRACT

Nalipoite, the natural analogue of $NaLi_2PO_4$, occurs as anhedral to subhedral blocky grains up to 2 mm in sodalite or analcime and as irregular grains (0.2 mm) in cavities in sodalite syenite xenoliths in the nepheline syenite, Poudrette quarry, Mont Saint-Hilaire, Quebec. It is associated with sodalite, analcime, clinoamphibole, aegirine, cancrinite, serandite, lovozerite, villiaumite, ussingite, steenstrupine-(Ce), eudialyte, thermonatrite, natrophosphate, sidorenkite, rasvumite, revdite, vuonnemite, vitusite-(Ce), chkalovite, terskite, silinaite, lintisite and others, including many unidentified minerals. The mineral is white, very pale blue or yellow with a white streak, vitreous, transparent to translucent. The mineral is brittle with a Mohs hardness about 4, and nonfluorescent in ultraviolet light. Cleavages {100}, {010}, {001} and {110} are good, with another distinct direction, possibly {101}; fracture uneven; D(meas.) 2.58(1), D(calc.) 2.612 g/cm^3. The mineral dissolves readily in 1:1 HNO_3, less readily in 1:1 HCl and slowly in 1:1 H_2SO_4. Nalipoite is biaxial (-), α 1.533(1), β 1.540(1), γ 1.541(1), $2V$(meas.) 49(1)°, $2V$(calc.) 41° (λ 589 nm). Orientation: $X = a$, $Y = c$, $Z = b$. The mineral is orthorhombic, $Pmnb$, a 6.884(2), b 9.976(4), c 4.927(2) Å. The strongest eight X-ray-diffraction lines [d in Å(I)(hkl)] are: 4.02(100)(120), 3.507(100)(021), 3.441(100)(200), 2.833(40)(220), 2.712 (40)(211), 2.493(90)(040), 2.462(90)(002), 1.721(40)(400). The chemical formula was confirmed by a crystal-structure analysis. Electron-microprobe analyses gave (average): P_2O_5 51.76, Na_2O 24.54, Al_2O_3 0.06, Li_2O (calc.) 22.12, sum 98.48 wt.%, corresponding to $Na_{1.07}Li_{2.00}P_{0.99}O_4$ based on 4 oxygen atoms, $Z = 4$. The name is derived from the composition.

Keywords: nalipoite, sodium dilithium phosphate, new mineral species, Mont Saint-Hilaire, Quebec, properties, X-ray data, composition.

SOMMAIRE

La nalipoïte, analogue naturel de $NaLi_2PO_4$, forme des cristaux xénomorphes à sub-idiomorphes jusqu'à une taille de 2 mm dans la sodalite ou l'analcime, et des grains irréguliers (0.2 mm) dans les cavités des xénolithes de syénite à sodalite dans la syénite néphélinique de la carrière Poudrette, au mont Saint-Hilaire (Québec). Elle montre une association avec sodalite, analcime, clinoamphibole, aegyrine, cancrinite, serandite, lovozerite, villiaumite, ussingite, steenstrupine-(Ce), eudialyte, thermonatrite, natrophosphate, sidorenkite, rasvumite, revdite, vuonnemite, vitusite-(Ce), chkalovite, terskite, silinaïte, lintisite, et plusieurs espèces non identifiées. C'est un minéral blanc, bleu très pâle ou jaune ayant une rayure blanche, à l'aspect vitreux, transparent ou translucide. La nalipoïte est cassante, possède une dureté de Mohs d'environ 4, et est non fluorescente en lumière ultra-violette. Les clivages {100}, {010}, {001} et {110} sont bons, et un autre, possiblement {101}, est distinct. La fracture est inégale; D(mes.) 2.58(1), D(calc.) 2.612. Le minéral se dissout rapidement dans HNO_3 (1:1), moins rapidement dans HCl (1:1), et lentement dans H_2SO_4 (1:1). Biaxe négatif, α 1.533(1), β 1.540(1), γ 1.541(1), $2V$ 49(1)° (mesuré), 41° (calculé) (λ 589 nm). Orientation: $X = a$, $Y = c$, $Z = b$. Orthorhombique, $Pmnb$, a 6.884(2), b 9.976(4), c4.927(2) Å. Les huit raies les plus intenses en diffraction X [d en Å(I)(hkl)] sont: 4.02(100)(120), 3.507(100)(021), 3.441(100)(200), 2.833(40)(220), 2.712 (40)(211), 2.493(90)(040), 2.462(90)(002), et 1.721 (40)(400). La formule chimique a été confirmée par ébauche de la structure cristalline. Les analyses à la microsonde électronique ont donné, en moyenne, P_2O_5 51.76, Na_2O 24.54, Al_2O_3 0.06, Li_2O (calculé) 22.12, total 98.48% en poids, ce qui correspond à $Na_{1.07}Li_{2.00}P_{0.99}O_4$ pour quatre atomes d'oxygène, $Z = 4$. Le nom rappelle la composition.

(Traduit par la Rédaction)

Mots-clés: nalipoïte, phosphate de sodium et de lithium, nouvelle espèce minérale, mont Saint-Hilaire, Québec, propriétés, données de diffraction X, composition chimique.

INTRODUCTION

The chemical compound $NaLi_2PO_4$ was first discovered by Gale (1945) in the process of recovering lithium from Searles Lake, California. It was later reported by Barczak (1974) as one of the products in the processing of subterranean brines. The compound has been synthesized by heating a mixture of Li_2CO_3, $NaHCO_3$ and P_2O_5

in stoichiometric proportions to 700°C (Barczak 1974). The unidentified mineral UK63 from Mont Saint-Hilaire, Quebec (Chao *et al.* 1990) has been shown to be the natural analogue of $NaLi_2PO_4$. The mineral is named nalipoite for its composition (Na–Li–P–O-ite). Both the mineral and its name have been approved by the Commission on New Minerals and Mineral Names, IMA. Cotype and metatype specimens of nalipoite are deposited at the Canadian Museum of Nature, Ottawa (CMN #56467 and CMN #56468) and at the Royal Ontario Museum, Toronto (M44516 and M44517).

Occurrence

Nalipoite was first collected in 1988 from a sodalite syenite xenolith in the nepheline syenite exposed in Poudrette quarry, Mont Saint-Hilaire, Quebec. The mineralogy of this xenolith is relatively simple; it contains mainly sodalite (75%), analcime (15%), and microcline (10%), with accessory cancrinite, clinoamphibole, aegirine, serandite, lovozerite, villiaumite, ussingite, steenstrupine-(Ce), and eudialyte. A number of rare species and as-yet-unidentified minerals also have been found in this xenolith in small quantities. These are vuonnemite, vitusite-(Ce), chkalovite, terskite, primary and secondary thermonatrite, natrophosphate, sidorenkite, rasvumite, revdite, UK38, UK53, UK55, and UK64 (Chao *et al.* 1990), and the recently established new minerals lintisite (Khomyakov *et al.* 1990) and silinaite (Chao *et al.* 1991). The presence of revdite is characteristic of this association, as the mineral has not been found in other xenoliths in this quarry. A year later, nalipoite was again found in another xenolith of sodalite syenite, in association with silinaite and seventy other minerals, as has already been briefly described by Chao *et al.* (1991).

Physical and Optical Properties

Nalipoite occurs as anhedral to subhedral blocky grains up to 2 mm in a matrix of sodalite or analcime, and as irregular grains (0.2 mm) in clusters in cavities in sodalite syenite xenoliths. The total weight of confirmed material is estimated to be less than 30 mg. The mineral is white, very pale blue or very pale yellow, with a white streak. It is vitreous and transparent to translucent. The Mohs hardness is about 4. The mineral is very brittle and is nonfluorescent in ultraviolet light. Two determinations of the density by flotation in bromoform diluted with acetone gave 2.58(1) g/cm^3. The cleavages {100}, {010}, {001} and {110} are good, with another distinct direction, possibly {101}. The fracture is uneven. The mineral dissolves readily in 1:1 HNO_3, less readily in 1:1 HCl, and very slowly in 1:1 H_2SO_4.

Optically, the mineral is; biaxial (–), α 1.533(1), β 1.540(1), γ 1.541(1), $2V$(meas.) 49(1)° and $2V$(calc.) 41°. Dispersion is not noticeable. The optical orientation is $X = a$, $Y = c$, $Z = b$. The mineral is nonpleochroic. All optical properties of nalipoite were obtained in sodium light (λ 589 nm) using a spindle stage and a crystal previously oriented by X-ray goniometry.

Synthetic $NaLi_2PO_4$ was reported (Barczak 1974) to have a prismatic habit, negative elongation, indistinct cleavage, parallel extinction, and weak birefringence (0.006). It is optically biaxial (–) with a small $2V$, and minimum and maximum indices of refraction 1.530 and 1.536, respectively. The measured density is 2.53 g/cm^3. These properties are similar to those reported here for nalipoite.

X-Ray Crystallography

X-ray single-crystal precession photographs show the mineral to be orthorhombic, space group *Pmnb* or $P2_1nb$. The cell parameters obtained on a four-circle diffractometer and refined by a least-squares method are: a 6.884(2), b 9.976(4) and c 4.927(2) A. These are in excellent agreement with the values refined from powder-diffraction data: a 6.877(3), b 9.977(6), and c 4.9255(7) A. The correct space-group is *Pmnb*, as determined by crystal-structure analysis (Ercit 1991).

X-ray powder-diffraction photographs were obtained using a 114.6-mm Gandolfi camera and Ni-filtered Cu$K\alpha$ radiation. The powder pattern of nalipoite is basically identical to that of the synthetic $NaLi_2PO_4$ and compares well with the powder pattern calculated from the crystal structure (Table 1).

Chemical Composition

Nalipoite was analyzed using a Cambridge Microscan MK5 electron microprobe at an operating voltage of 15 kV and a beam current of 30 nA. Four consecutive 5-second counts were gathered, with the beam rastering over an area of 10 × 10 μm. The mineral appears to be stable under the electron beam. Fluorapatite from Durango (P$K\alpha$), albite (Na$K\alpha$) and the Kakanui hornblende (Al$K\alpha$) were used as standards. Elements other than P, Na, and Al were not detected in a preliminary energy-dispersion scan. Results of analyses at six different spots on the same grain are given in Table 2. The analyses show a deficiency of approximately 24 wt.%, which must be due to light elements or H_2O, not detectable by the electron microprobe. The missing constituent was initially thought to be

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR NALIPOITE

	Nalipoite[1]				$NaLi_2PO_4$[2]	
hkl	$I_{calc.}$	$d_{calc.}$	$I_{est.}$	$d_{meas.}$	$I_{est.}$	$d_{calc.}$
020	4	4.9880	10	4.99	6	5.00
011	6	4.4176	10	4.42		
120	40	4.0391	100	4.02	41	4.04
101	41	4.0065			39	4.00
111	6	3.7179	10	3.715	1	3.72
021	100	3.5053	100	3.507	100	3.51
200	66	3.4420	100	3.441	36	3.42
121	12	3.1236	20	3.121	10	3.12
220	41	2.8330	40	2.833	28	2.82
211	25	2.7151	40	2.712	3	2.71
131	11	2.5588	20	2.557		
040	61	2.4940	90	2.493	51	2.50
002	64	2.4635	90	2.462	62	2.46
221	16	2.4559				
012	4	2.3917	10	2.392		
140	2	2.3448	5	2.345	3	2.35
041	1	2.2251			2	2.23
022	2	2.2088			2	2.21
231	12	2.1515	20	2.150	1	2.15
320	2	2.0846	10	2.081	4	2.07
301	2	2.0801				
311	10	2.0363	30	2.035	7	2.02
240	13	2.0196	30	2.020		
202	13	2.0033	30	2.002	7	2.00
212	3	1.9641	5	1.961	1	1.959
321	12	1.9199	30	1.918	6	1.914
132	4	1.9024	10	1.901		
241	4	1.8687			3	1.868
222	13	1.8590	30	1.860		
051	4	1.8493				
331	3	1.7635	5	1.761	7	1.757
042	14	1.7526	30	1.753		
400	21	1.7210	40	1.721	7	1.713
340	3	1.6886	5	1.689	1	1.687
251	2	1.6291	10	1.629		
420	2	1.6269			2	1.623
160	2	1.6162	5	1.615	2	1.620
103	3	1.5975	10	1.595	4	1.596
341	4	1.5974			3	1.593
322	4	1.5913			3	1.589
061	6	1.5754	10	1.577	3	1.581
242	4	1.5618	10	1.559	3	1.562
023	6	1.5599				
421	4	1.5448	10	1.546	2	1.540
123	1	1.5214	5	1.521	1	1.522
260	15	1.4971	20	1.496	6	1.501
213	9	1.4662	20	1.466	1	1.467
133	3	1.4400	10	1.440	3	1.437
351	1	1.4399				
261	8	1.4325	20	1.433		
223	11	1.4208	20	1.421	5	1.421
440	10	1.4165			5	1.414
402	11	1.4108	20	1.409	4	1.408
342	<1	1.3928			1	1.381
062	<1	1.3781			1	1.374
441	2	1.3613	5	1.361		
422	1	1.3576	10	1.355		
233	6	1.3538			1	1.355
303	1	1.3355			1	1.332
520	2	1.3272	20	1.324		
501	2	1.3260				
313	5	1.3237			1	1.321
361	7	1.2988	10	1.298	2	1.301
262	9	1.2794	20	1.280	3	1.282
442	5	1.2280			2	1.226

1. 114.6 mm Gandolfi camera, CuKα radiation (λ 1.5418Å), I_{est} visually estimated, I_{calc} from crystal-structure analysis (Ercit 1991).
2. Synthetic Li_2NaPO_4, CuKα radiation, scanning speed 1° 2θ/min. (Barczak 1974).

TABLE 2. CHEMICAL COMPOSITION OF NALIPOITE

	1	2	3	4	5	6	7	8
P_2O_5	51.93	52.56	52.32	51.13	51.38	51.26	51.76	53.83
Na_2O	24.58	24.50	24.45	24.64	24.47	24.65	24.54	23.51
Al_2O_3	0.01	0.01	0.03	0.04	0.29	0.01	0.06	-
Li_2O	22.17	22.38	22.29	21.91	22.04	21.94	22.12	22.66
Total	98.69	99.45	99.09	97.72	98.18	97.86	98.48	100.00

1-6. Li_2O calculated from stoichiometry. Oxides reported in wt.%.
7. Average of analyses 1 through 6. Li_2O calculated from stoichiometry.
8. Ideal composition for $NaLi_2PO_4$.

H_2O. The average composition (Col. 7, Table 2), with the balance assumed to be H_2O, gives an empirical formula of $Na_{1.07}P_{0.99}O_3 \bullet 1.77H_2O$ or close to $NaPO_3 \bullet 2H_2O$. However, the density calculated from the empirical formula is 2.65 g/cm^3, considerably larger than the measured value of 2.58(1) g/cm^3. As the amount of material available is very small, analysis for the missing light constituents by direct methods was not considered practical; therefore, a crystal-structure analysis was carried out (Ercit 1991). The missing light element was identified to be Li on the basis of its electron density, cation-to-oxygen interatomic distances [1.950(4) - 1.992(3), mean = 1.972 Å], its tetrahedral coordination and valence sum (0.97 *v.u.*). The structural formula of the mineral was established as $NaLi_2PO_4$, with $Z = 4$. The average composition of nalipoite (col. 7, Table 2) was, therefore, recalculated on the basis of 4 oxygen atoms per formula to yield the empirical formula $Na_{1.07}Li_2P_{0.99}O_4$, Li being taken to be present in stoichiometric proportions. Density values calculated from the ideal and empirical formulas are 2.587 and 2.612 g/cm^3, respectively, in good agreement with the measured value of 2.58(1) g/cm^3.

Discussion

Gladstone-Dale calculations, using the measured density and indices of refraction, the average results of electron-microprobe analyses, and constants given by Mandarino (1981), gave a K_P of 0.209, and a K_C of 0.213; $1 - (K_P/K_C)$ equals 0.019. Thus, the compatibility of physical and chemical data of nalipoite is superior (Mandarino 1981).

Compositionally, nalipoite appears to be intermediate between olympite (Na_3PO_4, *Pnma* or *Pn*2$_1$*a*, *a* 10.154, *b* 14.819, *c* 10.143: Khomyakov *et al.* 1980) and lithiophosphate [Li_3PO_4, *Pcmn*, *a* 4.926(3), *b* 6.129(1), *c* 10.843(4): Bondareva *et al.* 1978]. In addition, the three minerals crystallize in the same space-group (D^{16}_{2h}), with similar unit-cell parameters. However, there is no evidence of extensive solid-solution among them. Lithiophosphate from the type locality contains only 0.05 wt.% Na_2O (Matias & Bondareva 1957); material from Kings Mountain, North Carolina was reported to be 99.9% Li_3PO_4, and the sum of all the trace elements in the mineral is less than 0.1 wt.% (White 1969). On the other hand, lithium was not reported (Khomyakov *et al.* 1980) to be present in olympite from the only known occurrence, the Khibina massif, Kola Peninsula, U.S.S.R. The absence of solid solution is expected, since all Li atoms in lithiophosphate (Bondareva *et al.* 1978) and nalipoite (Ercit 1991) occupy tetrahedral sites, whereas Na normally occupies octahedral sites, as in nalipoite, or sites with higher coordination.

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