Canadian Mineralogist
Vol. 18, pp. 85-88 (1980)

PARANATROLITE, A NEW ZEOLITE FROM MONT ST-HILAIRE, QUÉBEC

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ABSTRACT

Paranatrolite, a new zeolite from Mont St-Hilaire, Québec, is unstable in air and dehydrates to form tetranatrolite. Unaltered paranatrolite has been observed only as colorless transparent epitactic overgrowths on natrolite crystals preserved in water since the time of collection. Physical properties are: $H = 5–5\frac{1}{2}$, D(obs) $= 2.21$ g/cm^3; fracture conchoidal; cleavage unobserved. The mineral is pseudo-orthorhombic, diffraction aspect, *F*★★★, with *a* 19.07(1), *b* 19.13(1), *c* 6.580(3) Å, $Z = 8$. The true symmetry is probably monoclinic, perhaps triclinic. The diffraction spots are very diffuse, suggestive of a disordered structure. The strongest Gandolfi diffraction lines are: 6.76(20)(220), 5.92(60)(111), 4.78(30)(040,400), 4.44(40)(131,311), 3.26(15)(151,511), 3.12(15)(022,202), 2.94(100)(351,531), 2.65(15)(460,640), 2.51(15)(171,711), 1.772(15)(4.10.0, 10.4.0). The powder pattern is similar to that of gonnardite. Optically the mineral is biaxial negative, $2V < 10°$, with low birefringence and oblique extinction. The chemical formula is that of tetranatrolite except for the water content, which is calculated from the mass–density–volume relationship: $(Na_{1.75}Ca_{0.10}K_{0.09})Fe_{0.01}Al_{1.95}Si_{3.02}O_{10}\cdot 2.98H_2O$ or, ideally, $Na_2Al_2Si_3O_{10}\cdot 3H_2O$.

Keywords: paranatrolite, Mont St-Hilaire, Québec, tetranatrolite, zeolite, gonnardite.

SOMMAIRE

La paranatrolite, zéolite nouvelle du mont St-Hilaire (Québec), est instable dans l'air et se déshydrate en tétranatrolite. Inaltérée, elle ne se trouve qu'en enduits épitactiques, incolores et transparents, sur cristaux de natrolite préservés sous eau dès qu'ils sont recueillis. Propriétés physiques: *Dr.* (Mohs) $5–5\frac{1}{2}$, densité 2.21 g/cm^3; fracture conchoïde; clivage non-observé. La paranatrolite est pseudo-orthohombique, *a* 19.07(1), *b* 19.13 (1), *c* 6.580(3) Å, aspect de diffraction *F*★★★, $Z = 8$. La symétrie vraie est probablement monoclinique, peut-être triclinique. Les taches de diffraction X sont très diffuses, indice d'une structure désordonnée. Les raies de diffraction les plus intenses, à la chambre Gandolfi, sont: 6.76(20)(220), 5.92(60)(111), 4.78(30)(040,400), 4.44(40)(131, 311), 3.26(15)(151,511), 3.12(15)(022,202), 2.94 (100)(351,531), 2.65(15)(460,640), 2.51(15)(171, 711), 1.772(15)(4.10.0, 10.4.0). Le diagramme de poudre ressemble à celui de la gonnardite. Optiquement biaxe négatif, le nouveau minéral a $2V < 10°$, faible biréfringence et extinction oblique. Sa formule chimique s'obtient à partir de celle de la tétranatrolite, en calculant l'eau d'hydratation au moyen de la relation masse–densité–volume: $(Na_{1.75}Ca_{0.10}K_{0.09})Fe_{0.01}Al_{1.95}Si_{3.02}O_{10}\cdot 2.98H_2O$, soit idéalement $Na_2Al_2Si_3O_{10}\cdot 3H_2O$.

(Traduit par la Rédaction)

Mots-clés: paranatrolite, mont St-Hilaire, Québec, tétranatrolite, zéolite, gonnardite.

INTRODUCTION

In the preceding paper, Chen & Chao (1980) reported the occurrence of an unusual variety of natrolite from Mont St-Hilaire, Québec. The surface layer alters to tetranatrolite (a tetragonal, probably disordered modification of natrolite) upon exposure to air, with the rate of alteration apparently related to the humidity of the immediate environment. Investigation of the nature of this alteration, using natrolite specimens preserved in water from the time of collection, led to the discovery of a new zeolite mineral with a composition close to $Na_2Al_2Si_3O_{10}\cdot 3H_2O$. It dehydrates partly upon exposure to air to form tetranatrolite. The name *paranatrolite* is given to this mineral because of its close association with natrolite and the similarity in their chemical composition. The name and the mineral were approved by the Commission on New Minerals and Mineral Names, I.M.A., with the understanding that an earlier use of the same name by Maier *et al.* (1964) for a rehydrated natrolite produced in a dehydration experiment had been discredited by Senderov & Yukhnevich (1964). Type specimens of paranatrolite preserved in water are deposited in the collections of the Royal Ontario Museum, Toronto (*M*35546) and at the National Museum of Natural Sciences, Ottawa (37132).

OCCURRENCE AND PROPERTIES

The former presence of paranatrolite at Mont St-Hilaire, Québec, is indicated by the wide occurrence of its dehydration product *tetranatrolite,* which has been found in association with a variety of other minerals in miarolitic cavities and pegmatitic dykes in nepheline syenite (Chen & Chao 1980). Fresh, unaltered paranatrolite has been observed only as colorless, transparent epitactic overgrowths up to 1 mm in thickness on large natrolite crystals (average 5x5x25 mm) that have been preserved in water from the time of collection. Because the mineral is unstable in air, all studies have been made using water-immersion mounts. The hardness of the mineral is about 5–5½. Fractures are conchoidal. Cleavages are not observed. Dust-like particles and small crystals of natrolite are common at the interface between paranatrolite and natrolite. In fact, it was the abundance of the dustlike particles on some crystals that made the paranatrolite overgrowths detectable.

Under the polarizing microscope the mineral displays very low birefringence and slightly undulatory extinction. Interference figures are generally very poor with broad and diffuse isogyres. The mineral is optically biaxial negative with a small $2V$ of less than 10°. A composite paranatrolite–natrolite fragment broken off the prismatic zone of the crystal indicates that the indices of refraction of paranatrolite are slightly higher than those of natrolite. The paranatrolite portion of the composite fragment gives oblique extinction with an angle of 21° to the straight boundary between the two minerals, whereas the natrolite portion shows parallel extinction. This suggests that the symmetry of paranatrolite is lower than orthorhombic.

The density of the mineral was determined by flotation in bromoform, the density of which was pre-adjusted approximately to that of natrolite. The mineral grains were first checked for purity under the microscope; they were then placed momentarily on a piece of cleaning tissue to remove excess surface water and quickly transferred to the bromoform container. Two independent measurements were made using different grains and an average value of 2.21(1) g/cm^3 was obtained. There was no sign of dehydration of the grains during the measurement, and the grains remained transparent in bromoform for several hours after the measurements were made.

X-RAY STUDIES

Several fragments of paranatrolite were separated under water from the underlying natrolite crystals and were mounted in 0.3 mm capillaries filled with water. The open end of each capillary was sealed with a household cement. Precession photographs taken of these fragments showed the mineral to be pseudotetragonal and pseudo-orthorhombic. The deviation from orthorhombic symmetry occurs mainly in the intensities of presumably equivalent reflections, particularly on the upper-level c-axis precession photographs. The true symmetry, either monoclinic or triclinic, has not been ascertained owing to the poor quality of the recorded reflections, which are extremely diffuse. For the pseudo-orthorhombic cell the systematic extinctions are consistent with space groups *Fmm*2, *Fm*2*m*, *F*2*mm*, *F*222 and *Fmmm*. The space group *Fdd*2, to which natrolite belongs, can be ruled out because of the presence of reflections such as 600 and 060. The c parameter of paranatrolite is very slightly smaller than that of natrolite, whereas a and b are considerably larger than the corresponding parameters of natrolite. The cell parameters of paranatrolite refined by a least-squares method using Gandolfi diffraction data are compared in Table 1 with those of related minerals. The X-

TABLE 1. PROPERTIES OF PARANATROLITE AND RELATED MINERALS

	Natrolite(1)	Tetranatrolite(1)	Paranatrolite	Gonnardite(2)
Symmetry	*Fdd*2	$I\bar{4}2d$	Pseudo-orthorhombic	Orthorhombic
a(Å)	18.308(7)	13.098(2)	19.07(1)	13.38
b	18.632(8)		19.13(1)	13.38
c	6.589(3)	6.635(2)	6.580(3)	6.66
Vol(Å^3)	2X1123.8	1138.3	2X1200.2	1192.3
Z	8	4	8	4
D(obs)(g/cm^3)	2.254(5)	2.276(5)	2.21(1)	2.26
D(calc)	2.254	2.234		2.252
Optical sign	(+)2V≈59°	(+)	(-)2V<10°	(-)2V≈50°

(1) Chen & Chao (1980); (2) Deer *et al.* (1963).

ray powder-diffraction pattern of paranatrolite, obtained with a 114.6 mm Gandolfi camera using a water-filled capillary mount, is given in Table 2. The pattern bears the general characteristics of minerals of the natrolite group and is closest to that of gonnardite (Table 2).

The precession photographs of a composite paranatrolite–natrolite fragment (Fig. 1) show that the overgrowths of paranatrolite on natrolite are epitactic in nature. The precession photographs of the same composite fragment taken 24 hours after the removal of the seal show that paranatrolite had completely altered to tetranatrolite (Fig. 2) and that the natrolite portion had remained unaffected. The dehydration of paranatrolite to tetranatrolite resulted in a significant decrease in *a* and *b*, an increase in *c* and a significant (5.16%) reduction in the cell volume.

CHEMICAL FORMULA

As paranatrolite is unstable in air, a direct analysis of the mineral by standard methods is not possible. However, it is reasonable to assume that the dehydration of paranatrolite to tetranatrolite does not introduce other chemical changes and that the composition of paranatrolite differs from that of tetranatrolite only in the amount of water present. The formula of paranatrolite may, therefore, be written on the basis of the formula of tetranatrolite (Chen & Chao 1980) as follows: $(Na_{1.75}Ca_{0.10}K_{0.09})Fe_{0.01}Al_{1.95}Si_{3.02}O_{10}\cdot xH_2O$. For the pseudo-orthorhombic cell Z is equal to 8, as for natrolite. The number of water molecules (x) in the formula may be calculated from the mass–density(D)–volume(V) relationship as expressed by the equation $ZM = VD/1.6602$. For paranatrolite V and D are known, as given in Table 1, and the formula weight (M) is $345.773 + 18.016x$; x is therefore equal to 2.98. The formula of paranatrolite is thus $(Na_{1.75}Ca_{0.10}K_{0.09})Fe_{0.01}Al_{1.95}Si_{3.02}O_{10}\cdot 2.98H_2O$, or ideally $Na_2Al_2Si_3O_{10}\cdot 3H_2O$. The density 2.204 g/cm^3, calculated for the ideal composition using the observed cell volume (Table 1), is in good agreement with the observed value 2.21 g/cm^3.

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR PARANATROLITE, MONT ST-HILAIRE, QUEBEC

Paranatrolite (1) Mont St-Hilaire				Gonnardite (2) Chaux-de-Bergonne	
hkl	d_{calc}Å	d_{obs}Å	I_{obs}	d_{obs}Å	I_{obs}
220	6.753	6.76	20	6.70	s
111	5.915	5.92	60	5.93	vs
				5.25	w
040	4.783	4.78	30	4.74	ms
400	4.768				
131	4.453	4.44	40	4.44	s
311	4.447				
240	4.275	4.27	5	4.22	mw
420	4.267				
				3.69	vw
				3.52	vvw
151	3.259	3.26	15	3.23	ms
511	3.252				
022	3.111	3.12	15	3.12	m
202	3.110				
260	3.024	3.02	5		
620	3.016				
351	2.934	2.94	100	2.92	vvs
531	2.931				
460	2.650	2.65	15		
640	2.647				
242	2.607	2.59	5	2.61	m
422	2.605				
171	2.502	2.51	15	2.48	m
711	2.496				
080	2.391	2.39	5	2.36	w
800	2.384				
				2.33	vvw
				2.28	w
660	2.251	2.25	10	2.22	m
				2.16	vvw
133	2.062	2.07	10	2.12	vwb
313	2.061			2.07	w
191	2.011	2.01	5	1.98	wb
911	2.006				
333	1.972	1.968	5		
				1.895	mw
2.10.0	1.876	1.872	10		
10.20	1.870				
				1.851	w
				1.818	mw
4.10.0	1.775	1.772	15		
10.40	1.771				
				1.759	mwb

(1) Sample with Si standard mounted in 0.3 mm capillary filled with water. CuKα radiation (λ=1.5418Å), 114.6 mm Gandolfi camera visual intensities.
(2) Data from Meixner *et al.* (1956). 23 lines from 1.697Å to 1.032Å are omitted.

DISCUSSION

Although the characterization of paranatrolite is far from complete, the data presented here are sufficient for the mineral to be distinguished from other zeolites of the natrolite group. Paranatrolite is probably disordered with respect to Al and Si atoms, as is suggested by the diffuse single-crystal X-ray reflections and by its dehydration relationship to the disordered tetranatrolite. It is likely that the substitution of Ca for Na in the structure may have played an important role in promoting disorder during crystallization. The hydrothermal treatment of tetranatrolite (Chen & Chao 1980) suggests that the dehydration of paranatrolite to tetranatrolite is probably not reversible.

ACKNOWLEDGEMENTS

The author thanks P. Tarassoff, who collected the paranatrolite–natrolite specimens, with foresight preserved them in water and generously made them available for this study. The author also thanks R.W. Yole for his critical reading of the manuscript and J. Baker for her technical assistance. This study was made possible through NSERC grant A5113.

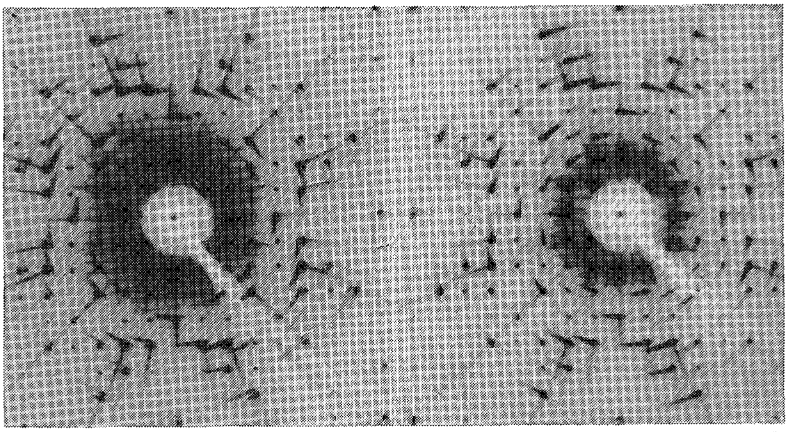

FIG. 1. Precession photograph (c axis) of a composite fragment mounted in a water-filled capillary, showing the epitactic relationship between paranatrolite (diffuse reflections) and natrolite (sharp reflections). Mo $K\alpha$ radiation. Note the relative positions of the paranatrolite and natrolite reflections.

FIG. 2. Precession photograph (c axis) of the same composite fragment as in Figure 1 taken 24 hours after the removal of the capillary seal, showing that paranatrolite had completely changed to tetranatrolite (diffuse reflections). Mo $K\alpha$ radiation. Note the relative positions of the tetranatrolite and natrolite reflections.

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Received August 1979, revised manuscript accepted October 1979.