

The crystal structure of tetranatrolite from Mont Saint-Hilaire, Québec, and its chemical and structural relationship to paranatrolite and gonnardite

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ABSTRACT

The structure of tetranatrolite from Mont Saint-Hilaire, Québec (U.S. National Museum sample R1830) with $a = 13.197(7)$ Å, $c = 6.630(9)$ Å, and space group $I\bar{4}2d$, was refined using single-crystal X-ray data. A representative formula of tetranatrolite determined from electron microprobe analysis is $\text{Na}_{12.50}\text{K}_{0.01}\text{Ca}_{2.93}\text{Sr}_{0.11}\text{Al}_{19.09}\text{Si}_{20.91}\text{O}_{79.74}\cdot n\text{H}_2\text{O}$. The structure has the basic natrolite Si-Al-O framework configuration with Na, Ca, Sr, and K residing within inter-framework cages. Aluminum is disordered over the T1 and T2 tetrahedral sites, with $T2 > T1$. Water molecules O4 and O5 coordinate the intercage atoms and have high displacement parameters, indicating disorder within the cages. The Mont Saint-Hilaire tetranatrolite structure is compared to four previously determined structures, two tetranatrolite samples from Khibiny and Lovozero, Russia and two “gonnardite” samples from Tvedalen, Norway and Gignat, France. Observations are given to indicate that the Norwegian sample deduced to be tetranatrolite rather than gonnardite. Although the crystal structures of tetranatrolite and gonnardite are very similar, it is shown that the tetranatrolite compositions differ significantly from those of gonnardite. The tetranatrolite composition series varies along the join $\text{Na}_{16}\text{Al}_{16}\text{Si}_{24}\text{O}_{80}\text{--}\text{Na}_{12}\text{Ca}_4\text{Al}_{20}\text{Si}_{20}\text{O}_{80}$, and is represented by the formula $\text{Na}_{16-x}\text{Ca}_x\text{Al}_{16+x}\text{Si}_{24-x}\text{O}_{80}\cdot n\text{H}_2\text{O}$, where x extends from approximately 2.4 to 3.9. In contrast, gonnardites from Arkansas and Austria have compositions that vary along the join $\text{Na}_{16}\text{Al}_{16}\text{Si}_{24}\text{O}_{80}\text{--}\text{Na}_4\text{Ca}_8\text{Al}_{20}\text{Si}_{20}\text{O}_{80}$, which are represented by the formula $\square_x\text{Na}_{16-3x}\text{Ca}_{2x}\text{Al}_{16+x}\text{Si}_{24-x}\text{O}_{80}\cdot n\text{H}_2\text{O}$ and where \square indicates vacant intercage cation sites and x varies from approximately 0.3 to 3.2. Tetranatrolite is a dehydration product of paranatrolite and probably does not have a true stability field.

INTRODUCTION

There is still controversy concerning the true nature of three of the natrolite group minerals: paranatrolite, tetranatrolite, and gonnardite. The present paper: (1) presents a new crystal structure analysis of tetranatrolite from Mont Saint-Hilaire, Canada, (2) compares the Mont Saint-Hilaire tetranatrolite structure to three previous structure studies of tetranatrolite and one study of gonnardite, (3) establishes that tetranatrolite is a dehydration product of paranatrolite, (4) presents chemical, morphologic, and petrologic data to show that dehydrated paranatrolite (tetranatrolite) is chemically distinct from gonnardite, and (5) makes additional interpretations on the paragenetic, chemical, and structural relationships of tetranatrolite, gonnardite, and paranatrolite.

MINERALOGICAL REVIEW

Tetranatrolite and paranatrolite

Tetranatrolite was first described by Anderson et al. (1969), occurring as prismatic crystals in hydrothermal veins within

the Ilimaussaq alkaline massif of Greenland. They found the mineral to be tetragonal, $I\bar{4}2d$, $a = 13.043(1)$, $c = 6.619(1)$ Å, with the composition (based on Al + Si = 40) $\text{Na}_{14.28}\text{K}_{0.01}\text{Ca}_{0.37}\text{Al}_{15.37}\text{Si}_{24.63}\text{O}_{80}\cdot 16.30\text{H}_2\text{O}$.

Chen and Chao (1980) reported a second occurrence of tetranatrolite from an alkaline gabbro-syenite complex at Mont Saint-Hilaire, Québec, Canada. This tetranatrolite appears as epitactic overgrowths on natrolite. Single-crystal X-ray photographs of a composite natrolite-tetranatrolite crystal showed that this tetranatrolite has tetragonal symmetry, $I\bar{4}2d$ or $I4,md$, with $a = 13.098(2)$, $c = 6.635(2)$ Å. Recalculation of the chemical composition of tetranatrolite from previous electron microprobe (EPMA) chemical analysis (Chen and Chao 1980, Table 3) gives the chemical composition as: $\text{Na}_{14.09}\text{K}_{0.74}\text{Ca}_{0.83}(\text{Fe},\text{Ti})_{0.07}\text{Al}_{15.66}\text{Si}_{24.34}\text{O}_{80.51}\cdot 16.58\text{H}_2\text{O}$. They also suggested that tetranatrolite is a dehydration product of another phase.

Further understanding of the paragenesis of tetranatrolite was given by Chao (1980). He found that the overgrowths on some of the Mont Saint-Hilaire natrolite crystals were not tetranatrolite but rather a more hydrated form which he named paranatrolite, having the composition $\text{Na}_{14.00}\text{Ca}_{0.80}\text{K}_{0.72}\text{Fe}_{0.08}\text{Al}_{15.60}\text{Si}_{24.16}\text{O}_{80}\cdot 24\text{H}_2\text{O}$ and pseudo-orthorhombic symmetry with $a = 19.07(1)$, $b = 19.13(1)$, $c = 6.580(3)$ Å. These Mont Saint-Hilaire specimens were collected from a very moist environment and preserved in water, thus preventing dehydration of

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the paranatrolite overgrowths. When the natrolite-paranatrolite crystals were removed from an aqueous environment it was found that paranatrolite overgrowths rapidly dehydrated to tetranatrolite.

Khomyakov et al. (1987) described two occurrences of a tetranatrolite-paranatrolite assemblage from the Lovozero and Khibiny alkaline massifs of the Kola Peninsula. (These occurrences are very similar geologically to those described from the alkali massifs in Greenland and Canada). They too found that the paranatrolite crystals dehydrated to tetranatrolite when removed from an aqueous environment. Mikheeva et al. (1986) reported tetranatrolite from Khibiny massif as tetragonal, $I\bar{4}2d$, $a = 13.141(8)$, $c = 6.638(2)$ Å, with the composition $\text{Na}_{16.40}\text{K}_{1.76}\text{Ca}_{0.16}\text{Al}_{18.00}\text{Si}_{22.00}\text{O}_{80}\cdot 16\text{H}_2\text{O}$. Rastsvetaeva (1995) reported the Lovozero tetranatrolite as tetragonal, $I\bar{4}2d$, $a = 13.070(9)$, $c = 6.580(6)$ Å; she assumed for crystal-structure analysis the ideal composition $\text{Na}_{16}\text{Al}_{16}\text{Si}_{24}\text{O}_{80}\cdot 16\text{H}_2\text{O}$.

Ross et al. (1992) reexamined the natrolite-tetranatrolite-paranatrolite specimens from Mont Saint-Hilaire (U.S. National Museum R18930). In addition, they reported on a new occurrence of tetranatrolite from an alkaline igneous complex, Magnet Cove, Arkansas. In complete agreement with the observations of Chen and Chao (1980), Chao (1980), and Khomyakov et al. (1987), they observed that when the natrolite crystals with paranatrolite overgrowths were removed from the water-filled specimen container, the previously clear and transparent paranatrolite became cloudy-white and opaque, indicating dehydration from a more hydrated phase. The natrolite portions of the prismatic crystals remained clear and colorless (Ross et al. 1992, their Fig. 1c). The clear and cloudy portions of the crystals were easily separated from one another and were identified, using X-ray single-crystal and powder methods, as natrolite and tetranatrolite, respectively. Several electron microprobe analyses were made of the tetranatrolite overgrowths. Two representative analyses gave chemical compositions of $\text{Na}_{12.50}\text{K}_{0.01}\text{Ca}_{2.93}\text{Sr}_{0.11}\text{Al}_{19.09}\text{Si}_{20.91}\text{O}_{79.74}\cdot n\text{H}_2\text{O}$ and $\text{Na}_{12.99}\text{K}_{0.01}\text{Ca}_{2.13}\text{Sr}_{0.34}\text{Fe}_{0.02}\text{Al}_{18.51}\text{Si}_{21.49}\text{O}_{79.75}\cdot n\text{H}_2\text{O}$ (Ross et al. 1992, their Table 5). To obtain a better understanding of the complexities of tetranatrolite, a crystal fragment from Mont Saint-Hilaire sample R18930, composed entirely of tetranatrolite, was selected for crystal structure analysis and is described in this paper.

Crystals very similar in morphology to those from Mont Saint-Hilaire were found by Ross et al. (1992, Tables 5 and 6) in U.S. National Museum sample R16517 from Puy-de-Dôme, Gignat, France. Sample R16517 is mostly composed of large, clear colorless crystals of natrolite as shown by single-crystal and powder XRD. However, overgrowths of a second phase appear on the prism faces of some of the natrolite crystals. The overgrowth areas in R16517 have a distinctive appearance in that they are cloudy-white in color and contain numerous cracks and inclusions. These defects are absent in the clear natrolite cores (see Fig. 1D, Ross et al. 1992). Both the clear natrolite and the cloudy-white overgrowths have very similar compositions, close to the ideal natrolite composition $\text{Na}_{16}\text{Al}_{16}\text{Si}_{24}\text{O}_{80}\cdot n\text{H}_2\text{O}$. The cloudy material, however, has detectable calcium whereas no calcium was detected in the clear part of the sample.

Numerous probe analyses of tetranatrolite samples from Magnet Cove Arkansas (86-53A), Mont St. Hilaire (R18930) and Puy De Dôme, France (R16517) show that tetranatrolite compositions plot along the join $\text{Na}_{16}\text{Al}_{16}\text{Si}_{24}\text{O}_{80}\text{--}\text{Na}_{12}\text{Ca}_4\text{Al}_{20}\text{Si}_{20}\text{O}_{80}$. These compositions can thus be represented by the formula $\text{Na}_{16-x}\text{Ca}_x\text{Al}_{16+x}\text{Si}_{24-x}\text{O}_{80}\cdot n\text{H}_2\text{O}$, where x extends from 0.2 to 3.9 (see Table 5 and Fig. 5 of Ross et al. 1992). This composition trend line is disputed by Artioli and Galli (1999); however we will give chemical evidence to reject their conjecture.

Gonnardite

With but one exception, the studies of gonnardite presently reviewed describe the mineral as occurring as spherules or rosettes, often with intergrowths and/or overgrowths of thomsonite. Gottardi and Galli (1985, p. 71) state that gonnardite "occurs always as aggregates of microcrystalline fibers." Ross et al. (1992, Table 3) gave electron microprobe analyses of three gonnardite samples, two from Styria, Austria, and one from Magnet Cove, Arkansas. These show that the chemical composition of this mineral varies along the join $\text{Na}_{16}\text{Al}_{16}\text{Si}_{24}\text{O}_{80}\text{--}\text{Na}_4\text{Ca}_8\text{Al}_{20}\text{Si}_{20}\text{O}_{80}$ and is represented by the formula $\square_x\text{Na}_{16-3x}\text{Ca}_{2x}\text{Al}_{16+x}\text{Si}_{24-x}\text{O}_{80}\cdot n\text{H}_2\text{O}$, where \square indicates vacant cation sites within the intra-framework channels and x varies from approximately 0.3 to 3.2 (Ross et al. 1992, Figs. 2 and 4, trend line I). This series (possibly polysomatic in nature) appears to extend toward, but not to, the end-member thomsonite composition, $\text{Na}_4\text{Ca}_8\text{Al}_{20}\text{Si}_{20}\text{O}_{80}\cdot 24\text{H}_2\text{O}$. However, analyses such as those of gonnardite from Puy de Dôme, France, indicate a composition varies along a somewhat different trend line toward a less aluminous and more sodic thomsonite (Ross et al. 1992, see their Fig. 22).

Mazzi et al. (1986) described the crystal structure of "gonnardite" from an alkaline syenite massif (larvikite) located in the Vevja quarry, Tvedalen, Norway. They report the composition as: $\text{Na}_{12.84}\text{K}_{0.02}\text{Ca}_{3.00}\text{Al}_{18.44}\text{Si}_{21.46}\text{O}_{80}\cdot 24.74\text{H}_2\text{O}$ (Table 1, study 3). However, this composition plots close to the natrolite-tetranatrolite join described above. In addition, the sample does not crystallize as spherules typical of gonnardite, but rather as bundles of prismatic crystals (Mazzi et al. 1986, see their Fig. 1), a habit characteristic of previously described paranatrolite-tetranatrolite assemblages. On the basis of chemistry and morphology we propose that the "gonnardite" from Tvedalen, Norway is tetranatrolite and will treat it as such in this study.

Artioli and Galli (1999) described the crystal structure of gonnardite from Puy de Dôme, Gignat, France. The sample studied was composed of spherules of acicular gonnardite with rims of thomsonite. The structure determination was accomplished on a powdered sample using the Rietveld X-ray method.

We found both natrolite-tetranatrolite (USNM 16517) and gonnardite (USNM 157727) specimens from the Puy De Dôme locality, each with a distinctive chemical composition and crystal habit and (Fig. 1D and E, respectively, Ross et al. 1992). The natrolite-tetranatrolite specimens show a distinctive platy habit, the exterior overgrowth portions of the platelets contain cracks but the interior portions are homogeneous. In contrast, the gonnardite specimens occur as spherules, the cores of which

are composed of acicular gonnardite crystallites. Thomsonite overgrowths appear on the rims of the spherules. The crystal habit and chemical compositions described by Ross et al. (1992) and Artioli and Galli (1999) for gonnardite specimens from Puy De Dôme gonnardite specimens are very similar. The chemical composition (Table 1, study 5; see also Artioli and Galli 1999, Table 1 and Fig. 1) plots somewhat off the gonnardite solid-solution series (trend line I described above) but very close to the Puy de Dôme gonnardite compositions presented in Figure 22 of Ross et al. (1992).

THE CRYSTAL STRUCTURE OF TETRANATROLITE FROM MONT SAINT-HILAIRE

Structure refinement

The tetranatrolite single crystal chosen from Mont Saint-Hilaire sample R18930 for structure analysis (Table 1) is pale yellow-white in color and has a somewhat opaque and porous texture. It has a roughly octahedral shape with dimensions $0.16 \times 0.30 \times 0.46 \text{ mm}^3$. It was mounted with the tetragonal c -axis approximately parallel to the ϕ -axis. The unit-cell parameters were determined with 13 strong reflections ($\pm 4, \pm 4, 0$; $0, 0, 4$; $\pm 8, 0, 2$; $0, \pm 8, 2$; $\pm 5, \pm 5, 2$) in the range $18\text{--}28^\circ 2\theta$. The peak profiles (2θ scans) were somewhat irregular, but were well defined within an angular range of 0.5° . Averaging of the redundant reflections yielded an independent set of 302 intensity data and the final independent data set contained 255 I values. Using the structure parameters for tetranatrolite given by Rastsvetaeva (1995), refinement was commenced using the XTAL2.4 system of Hall and Stewart (1985). With isotropic thermal displacement parameters the reliability factor reached $R = 0.072$. With all atoms in anisotropic displacement mode, R

was reduced to 0.064, based on 252 |F| values and 40 parameters.

At this point a difference electron density map showed a smooth background varying between -0.5 and $1.0 \text{ e}/\text{\AA}^3$, with one exception—a distinct peak of $2.5 \text{ e}/\text{\AA}^3$ situated on the twofold axis at $x, y, z = 0.87, 0.25, 0.125$, located 2.4 \AA from Na, and more than 2.62 \AA from all oxygen atoms. When an oxygen atom of a water molecule was added at this position (O5) and given an isotropic temperature parameter, the structure refined to $R = 0.057$, with an occupancy factor of 0.36(2) for O5 and a large displacement parameter normal to the twofold axis at an angle of 30° to the c -axis direction. We concluded that the added atom was split between two close-lying sites. Refinement with isotropic thermal parameters for O5 then proceeded normally with a population factor of 0.18(1) at each split site, the two O5 sites being separated by a distance of 0.8 \AA (Fig. 1). When O5 was assigned anisotropic displacement parameters the two sites tended strongly to return to the twofold axis. Nevertheless, electron density at the O5 site strongly suggested that the split-atom model was the most appropriate one. Artioli and Galli (1999), as well as Mazzi et al. (1986), also found such an “extra” atom and assumed that it was slightly separated from the symmetrical position.

The question of Ca replacement at the Na site was addressed next. Refinement of the Na population factor led to a 10 percent increase over unity, indicating the presence of a small amount of Ca. This hypothesis was studied by refining the structure by iteration. The final occupancy values for Na = 0.85 and Ca = 0.15 corresponds to 6.8 Na and 1.2 Ca atoms per unit cell with an estimated uncertainty of 6.8 ± 0.4 and 1.2 ± 0.04 , respectively. The X-ray analysis compares favorably to the two electron probe analyses previously mentioned in which

TABLE 1. Chemical formula and crystallographic data for tetranatrolite and gonnardite crystal structures

Study Mineral	1a Tetra-natrolite*	1b Tetra-natrolite†	1c Tetra-natrolite‡	2 Tetra-natrolite‡	3 Gonnardite†,§	4 Tetra-natrolite#	5 Gonnardite†
Reference	This study	This study	This study	Mikheeva et al. (1986)	Mazzi et al. (1986)	Rastsvetaeva (1995)	Artioli and Galli (1999)
Atoms per unit cell							
Si	11.3	10.45	10.75	11.00	10.73	12	11.50
Al	8.7	9.55	9.25	9.00	9.22	8	8.59
Na	6.8	6.25	6.50	8.20	6.42	8	4.51
Ca	1.2	1.47	1.07	0.08	1.50		1.84
Fe ³⁺							0.006
Mg							0.004
Sr		0.05	0.17				0.002
Ba							0.002
K		0.01	0.001	0.88	0.01	8	0.007
H ₂ O	10.9			8	12.37		12.61
Locality		Mont Saint-Hilaire		Khibiny, Kola Pen.	Tvedalen, Norway	Lovozero, Kola Pen.	Gignat, France
Unit cells							
Space group	$\bar{4}2d$			$\bar{4}2d$	$\bar{4}2d$	$\bar{4}2d$	$\bar{4}2d$
$a \text{ \AA}$	13.197(7)			13.141(8)	13.21(1)	13.070(9)	13.2670(4)
$c \text{ \AA}$	6.630(9)			6.638(2)	6.622(4)	6.580(6)	6.6023(6)
$V \text{ \AA}^3$	1154(1)			1146.3	1156	1124.0	1162.09

* Composition from X-ray structure analysis.

† Composition from EMPA analysis.

‡ Composition from wet chemical analysis.

Composition assumed.

§ The structure was described as “gonnardite” but morphological and chemical evidence indicates that the sample is actually tetranatrolite.

TABLE 2. Crystallographic and experimental data for the structure determination of tetranatrolite from Mont Saint-Hilaire, Québec

Chemical formula	$\text{Na}_{6.8}\text{Ca}_{1.2}\text{Al}_{8.7}\text{Si}_{11.3}\text{O}_{40.2} \cdot 10.9\text{H}_2\text{O}$
Formula weight	320.9
Cell dimensions	$a = 13.197 \text{ \AA}$, $c = 6.630 \text{ \AA}$, $V = 1154 \text{ \AA}^3$
Z	1
Space group	$I\bar{4}2d$
Density	2.23 g/cm^3 (X-ray)
Equipment	Nonius CAD4
Radiation	$\text{MoK}\alpha$, $\lambda = 0.7107 \text{ \AA}$
Scan mode	ω - θ
2 θ range	50°
No. standard reflect.	220 (measured every hour)
No. recorded reflect.	2122
No. independent reflect.	302
No. obs. reflect. ($I > 4\sigma$)	255
No. obs. reflect. $ F > 2\sigma F$	252
R (merge)	0.041
Absorption coefficient (μ)	7.9 cm^{-1} (Gaussian quadrature method)
Transmission range	0.79–0.83
No. refined parameters	50
$R = \sum \Delta F / \sum F_o $	0.053
$R_w = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$	0.054
$w = 1/\sigma(F_o)$	

(Na+K):(Ca+Sr) is 6.26:1.52 and 6.51:1.24 (Table 1). Details on the crystal and reflection data are given in Table 2.

Selected bond lengths and final structure parameters are given in Tables 3 and 4, respectively. A list of observed and calculated structure factors is on deposit as Table 5¹. A general view of the Mont St. Hilaire tetranatrolite structure is shown in Figure 2.

Structural characteristics

The average T-O distances (T = Si,Al) are similar: for T1 = 1.663 \AA , for T2 = 1.680 \AA . Several precise studies of normal distances for Si and Al tetrahedra in natrolite-type structures have been made (natrolite, Artioli et al. 1984; edingtonite, Kvik and Smith 1983; scolecite, Kvik et al. 1985; thomsonite, Pluth et al. 1985). The average T-O distances in the fully ordered scolecite structure were found to be $1.621(1) \text{ \AA}$ for Si-O, and $1.747(1) \text{ \AA}$ for Al-O, with a span of $0.126(2) \text{ \AA}$ (Kvik et al. 1985). Using these data as a basis, the Al and Si unit-cell occupancy in the present structure is found to be 8.68 and 11.32 atoms, respectively, indicating a small excess of Al and deficiency of Si over the ideal ratio of 8:12. The excess of Al found by X-ray analysis (0.68 atoms) and chemical analysis (1.55 and 1.25 atoms) is partly balanced by replacement of Na with Ca and Sr. All interatomic distances lie within expected limits, except O4-O5 which is 2.49 \AA , less than a normal H_2O -O bond distance of $\sim 2.7 \text{ \AA}$. This close approach of the water molecules O4 and O5 is unexpected, but both atoms have rather high displacement parameters ($\sim 0.2 \text{ \AA}$).

¹For a copy of deposit Table 5, Document item AM-00-057, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the *American Mineralogist* web site at <http://www.minsocam.org>.

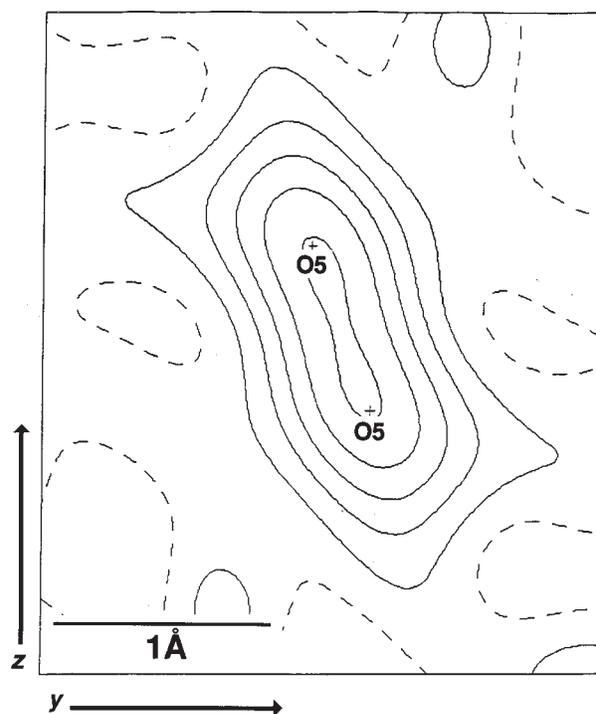


FIGURE 1. Electron density section normal to the a -axis around O5 near the twofold axis at $x, 1/4, 1/8$. Contours are plotted at intervals of 0.5 e/\AA^3 . Zero contours are dashed.

Comparison with previous structure studies

In addition to the present study, two structure determinations of minerals described as tetranatrolite (Mikheeva et al. 1986 and Rastsvetaeva 1995) and two determinations of minerals described as gonnardite (Mazzi et al. 1986 and Artioli and Galli 1999) from four different localities have been reported. Mazzi et al. (1986) identified the crystal they examined as “gonnardite,” but as discussed above, we believe that this “gonnardite” from Tvedalen, Norway is actually tetranatrolite. All four crystal structures have similar cell dimensions, were refined in space group $I\bar{4}2d$, and contain varying amounts of calcium and other cations. The unit-cell and chemical information for these four are compared to our own in Table 1. Tables 3 and 4 give selected interatomic distances and structure parameters, respectively, for the five determinations (the structure parameters of these four previous structure determinations are transformed to our setting from which the interatomic distances were recalculated). Many of the interatomic distances given in the original reports were substantially different from those listed in Table 3. Crystal structure data for tetranatrolite were also reported by Pechar (1989) and he gives unit-cell dimensions analogous to those given in Table 1. However, the coordinates listed by that author cannot be reconciled with the space group $I\bar{4}2d$; therefore his results are not presented.

Corresponding parameters of the five crystal structures listed in Tables 1, 3, and 4 are similar but show considerable differ-

ences in detail, presumably owing to variations in cation content (Si-Al; Na-Ca-Sr-K; and H₂O). The crystal used for our structure determination was not analyzed with the electron-microprobe; thus the composition shown in Table 1 (study 1a) is based on X-ray analysis only, but it is compared to two electron microprobe analyses of other crystals from the same sample (Table 1, study 1b, 1c). This variation in chemical composition may reflect crystal zoning.

Using mean T-O bond lengths to estimate the Si:Al ratio, we make the following observations. Our tetranatrolite structure and those of Mikheeva et al. (1986) and Mazzi et al. (1986) are found to have Al completely or nearly completely disordered over T1 and T2, whereas that of Rastsvetaeva (1995) shows Al is confined to T2. The Si-O and Al-O bond lengths (Table 3) calculated from the atomic parameters of Artioli and Galli (1999, their Table 2) indicate that in their gonnardite structure Al is concentrated in the 4-fold T1 site rather than the 16-fold T2 site, in contradiction to the statement that there is complete Al-Si disorder (Artioli and Galli 1999, p. 1448).

SUMMARY: THE CHEMICAL, MORPHOLOGICAL, STRUCTURAL, AND PETROGENIC NATURE OF PARANATROLITE, TETRANATROLITE, AND GONNARDITE

Chemical composition and morphology

The range in composition of paranatrolite and tetranatrolite (based on electron microprobe analyses of Ross et al. 1992) is described by the formula: Na_{16-x}Ca_xAl_{16+x}Si_{24-x}O₈₀nH₂O, where n = 24 and 16 for paranatrolite and tetranatrolite, respectively. In contrast to gonnardite, there appear to be few if any intercharge cation vacancies in these two minerals. The amount of calcium+strontium replacing sodium (x) varies from as little as 0.2 to 3.9 atoms per formula unit. The water content of paranatrolite and tetranatrolite, though indirectly determined, appears to be correct based on unit-cell volume and symmetry requirements. We note that tetranatrolite is dehydrated paranatrolite and thus inherits the chemical composition, with the exception of water content.

Artioli and Galli (1999, p. 1448, Fig. 1) take exception to this chemical description. They state that tetranatrolite compositions taken from various literature sources, when plotted in the ternary system SiO₂-Na₁₀Al₁₀Si₁₀O₄₀-Ca₅Al₁₀Si₁₀O₄₀, show significant scatter from our proposed natrolite-tetranatrolite join. Because of this apparent scatter they state that tetranatrolite and gonnardite compositions cannot be distinguished from one another. Of the 13 tetranatrolite analyses plotted in their Figure 1, five analyses are clearly of unacceptable quality for they do not meet the required chemical and structural criteria of the natrolite group, that is Al ≥ 16 and Na + Ca + Sr ≤ 16. The Al content is significantly less than 16 in analyses 1, 3, and 13 and Na + Ca + Sr is significantly greater than 16 in analyses 2 and 5. Their three low-calcium tetranatrolites analyses (Nos. 4, 6, and 7) plot close to both the natrolite-tetranatrolite and natrolite-gonnardite joins, but since both joins converge to the ideal natrolite composition one needs to examine high-calcium tetranatrolites to distinguish between these two series. The five other tetranatrolite analyses (Nos. 8-12) presented in their Fig-

ure 1 are from Ross et al. (1992). In addition, Ross et al. (1992, their Fig. 5) give 17 additional tetranatrolite analysis that conform to the proposed series Na_{16-x}Ca_xAl_{16+x}Si_{24-x}O₈₀nH₂O. This is especially evident when (Ca + Sr) is plotted vs. Al. The plotting method of Artioli and Galli (1999) completely disguises the relationship between Na and (Ca + Sr) vs. Al, and number of vacancies within the framework cages. In conclusion, Ross et al. (1992) give 23 analyses (22 are new electron-microprobe analyses) that refute the contention that tetranatrolite is not chemically distinguishable from gonnardite, whereas Artioli and Galli give only three analyses that weakly support this contention.

Artioli and Galli (1999, p. 1449) state: "almost all gonnardite and tetranatrolite minerals reported in the literature can be considered the same mineral." This cannot be true; the natrolite-paranatrolite-tetranatrolite association is distinct from the gonnardite-thomsonite association. Tetranatrolite may be distinguished from gonnardite by: (1) the chemical composition as discussed above, (2) distinctive differences in habit between the two minerals; gonnardite always crystallizing as spherules or rosettes, paranatrolite-tetranatrolite as overgrowths on natrolite prism faces, (3) universal association of the gonnardite spherules with intergrowths and/or overgrowths of thomsonite, and (4) formation of tetranatrolite by dehydration of paranatrolite.

Artioli and Galli (1999, p. 1445) state that gonnardite "has a large chemical variability, and its chemical composition broadly covers the join between natrolite and thomsonite" (p. 1445). This is the join first proposed by Ross et al. (1992) based on 200 electron-microprobe (EPMA) chemical analyses. The remarkable linear compositional trends of gonnardite discussed by Ross et al. (1992) beg for a better explanation of the chemical nature of this mineral. One hypothesis to explain such a composition trend is to assume that "gonnardite" is but a mixture of varying amounts of natrolite and thomsonite. This supposition cannot be correct, for the gonnardite samples we have studied give a distinctive X-ray power pattern. The gonnardite powder patterns never indicate the presence of natrolite, however weak powder lines of thomsonite are usually present except in carefully hand-picked samples.

Crystal structure

In this study we confirm the general structural relationships of three tetranatrolite samples and one gonnardite sample described in the literature. All of these structures were refined in space group *I*4̄2*d*. Various degrees of disorder have been found within the assumed symmetry, with Al varying from totally disordered over T1 and T2, to ordered on T2. The interstitial cation content is variable and found to charge compensate the Al content within the accuracy of the structure determinations. Water content is also variable with an additional fraction located in a second site (O5). We note, however, that these relationships are based on the refinement of what may be subcell or pseudocell crystal structures. The structure of tetranatrolite is that of a "collapsed" paranatrolite, the unit-cell of tetranatrolite probably corresponding to a sub-cell of paranatrolite.

The crystal structures of the members of the natrolite min-

TABLE 3. Interatomic distances (Å) in published structures of tetranatrolite and gonnardite

Mineral Reference	Tetranatrolite This work	Tetranatrolite Mikheeva et al. (1986)	"Gonnardite"* Mazzi et al. (1986)	Tetranatrolite Rastsveteeva (1995)	Gonnardite Artioli and Galli (1999)
T1-O3, ×4	1.663 (7)	1.662 (11)	1.672 (1)	1.600 (9)	1.700 (7)
T2-O1	1.685 (4)	1.660 (5)	1.686 (5)	1.678 (6)	1.672 (5)
T2-O2	1.674 (8)	1.662 (11)	1.684 (2)	1.681 (10)	1.624 (8)
T2-O2'	1.688 (7)	1.656 (11)	1.687 (2)	1.686 (10)	1.661 (8)
T2-O3	1.674 (7)	1.687 (14)	1.674 (2)	1.703 (10)	1.656 (8)
Average	1.680	1.666	1.683	1.687	1.653
Na-O1, ×2	2.640 (6)	2.664 (6)	2.667 (1)	2.564 (3)	2.726 (7)
Na-O2, ×2	2.399 (8)	2.402 (11)	2.411 (2)	2.366 (8)	2.520 (8)
Na-O4, ×2	2.388 (8)	2.414 (9)	2.383 (2)	2.390 (1)	2.312 (5)
Na-O5	2.38 (3)		2.442 (13)		
Average	2.48	2.49	2.48	2.44	2.53
O4-O1, ×2	3.331 (2)	3.339 (2)	3.339 (4)	3.300 (1)	3.357 (2)
O4-O1'	3.444 (15)	3.492 (15)	3.447 (3)	3.343 (2)	3.585 (2)
O4-O2, ×2	3.417 (8)	3.468 (11)	3.414 (2)	3.452 (11)	3.399 (2)
O4-O5	2.49		2.468		2.27, 3.09 (3)
	3.08 (4)		3.127 (13)		
O5-O3	2.59		2.665		2.59, 2.92 (3)
	2.82 (5)		2.809 (13)		
O5-O5	0.80†		0.959 (19)		1.06 (5)

* From chemical and morphological evidence this "gonnardite" from Tvedalen, Norway is assumed to be a tetranatrolite.

† Separation of split O5 water molecule sites.

TABLE 4. Comparison of published structure parameters of tetranatrolite and gonnardite

Mineral Reference	Tetranatrolite This work	Tetranatrolite Mikheeva et al. (1986)	"Gonnardite"* Mazzi et al. (1986)	Tetranatrolite Rastsveteeva (1995)	Gonnardite Artioli and Galli (1999)
Framework atoms					
T1 U_{eq}	0.0225 (22)	0.015 (1)	0.0106 (1)	0.009 (1)	0.025 (3)
T2 x	0.0554 (2)	0.0543 (3)	0.0536	0.0576 (2)	0.0512 (3)
T2 y	0.1330 (2)	0.1336 (3)	0.1332	0.1338 (2)	0.1319 (3)
T2 z	0.6214 (5)	0.6210 (6)	0.6211 (1)	0.6209 (6)	0.6155 (8)
T2 U_{eq}	0.0214 (22)	0.0157 (5)	0.0099 (1)	0.009 (1)	0.029 (1)
O1 x	0.3944 (6)	0.3967 (6)	0.3963 (1)	0.3878 (9)	0.4051 (5)
O1 U_{eq}	0.022 (5)	0.019 (3)	0.0297 (8)	0.015 (2)	0.031 (9)
O2 x	0.1333 (5)	0.1345 (7)	0.1325 (1)	0.1381 (8)	0.1279 (5)
O2 y	0.0627 (5)	0.0598 (7)	0.0631 (1)	0.0589 (7)	0.0627 (5)
O2 z	0.4813 (15)	0.487 (2)	0.4790 (4)	0.487 (2)	0.474 (1)
O2 U_{eq}	0.032 (4)	0.027 (3)	0.0208 (4)	0.024 (2)	0.027 (3)
O3 x	0.0506 (5)	0.0475 (7)	0.0503 (1)	0.0448 (7)	0.0522 (5)
O3 y	0.0918 (5)	0.0931 (7)	0.0917 (1)	0.0910 (6)	0.0903 (5)
O3 z	0.8603 (10)	0.862 (2)	0.8594 (2)	0.864 (2)	0.851 (1)
O3 U_{eq}	0.015 (3)	0.024 (3)	0.0216 (4)	0.020 (2)	0.029 (3)
Interstitial atoms					
Na, Ca x	0.6914 (4)	0.6867 (6)	0.6916 (1)	0.6895 (5)	0.6995 (5)
Na, Ca U_{eq}	0.032 (3)	0.027 (1)	0.0297 (4)	0.027 (1)	0.013 (4)
Occ.† (Na)	0.85 (1)	1	0.816	1	0.58 (2)
Occ.† (Ca)	0.15		0.184		0.23
O4(w) x	0.1334 (10)	0.131 (1)	0.1348 (1)	0.132 (1)	0.1349 (9)
O4(w) U_{eq}	0.047 (6)	0.030 (4)	0.0425 (9)	0.032 (3)	0.046 (4)
O5(w) x	0.872 (3)		0.872 (1)		0.861 (2)
O5(w) y	0.260 (4)		0.257 (1)		0.265 (2)
O5(w) z	0.182 (6)		0.196 (2)		0.199 (5)
O5(w) U_{eq}	0.033 (10)		0.076 (6)		0.037 (5)
Occ.† (w)	0.18 (1) (x2)		0.25		0.35 (2)

* From chemical and morphological evidence this "gonnardite" from Tvedalen, Norway, is assumed to be a tetranatrolite.

† Occupancy.

eral subgroup can be described as having a subcell, with $a = 13.2$, $c = 6.6$ Å. The fact that tetranatrolite and gonnardite have very similar subcells does not prove that they are identical minerals. Electron diffraction examination of gonnardite from Klöch, Styria, Austria (Ross et al. 1992, Fig. 20) suggests that the true cell is more complex than indicated by Artioli and Galli (1999). However, because the high-energy electron beam may have possibly altered the crystal structure we cannot be sure of the significance of the electron-diffraction patterns. Hey and Bannister (1932, p. 118) noted that extra layer lines appear on the X-ray fiber diffraction patterns of gonnardite from Gignat, Puy De Dôme, France, indicating an apparent doubling of the c dimension to 13.3 Å. The X-ray powder measurements used by Artioli and Galli to refine the crystal structure cannot be expected to resolve weak superlattice reflections (or even weak reflections that may violate the assumed $I42d$ space group symmetry). Therefore, we must conclude that the true symmetry and full nature of the crystal structure of gonnardite is still unknown. The X-ray and electron-microprobe methods have taken this problem about as far as they can; further understanding must await analysis with a state of the art analytical electron-microscope equipped with a low energy electron beam and a cold stage.

We suggest that the compositional variation in gonnardite might be explained if the crystal structure is composed of mixed domains of a natrolite-type framework and a thomsonite-like or edingtonite-like framework (see Ross et al. 1992, Fig. 21). Such "polysomatic" series are common in rock-forming silicate minerals, for example, mixed single, double, triple-width chain structures found in the pyroxene and amphibole mineral groups (for example, see Veblen 1992).

Paragenetic reactions

We propose the following paragenetic reactions for the crystallization of these minerals:

(1) **Natrolite-paranatrolite.** Calcium-free natrolite first crystallizes from aqueous solutions in the lower temperature range (probably at temperatures much less than 200 °C). As temperature decreases and humidity remains high a more hydrated phase, paranatrolite, becomes the stable phase and begins to crystallize epitaxially on the prism faces of the precursor natrolite. The change in composition of Si^{4+} , Al^{3+} , Ca^{2+} , and Na^+ in the crystallizing solutions during cooling is reflected by change in the composition of paranatrolite crystals through the coupled substitution (NaSi) for (CaAl) and expressed by the formula $\text{Na}_{16-x}\text{Ca}_x\text{Al}_{16+x}\text{Si}_{24-x}\text{O}_{80}\cdot n\text{H}_2\text{O}$.

(2) **Paranatrolite-tetranatrolite.** Paranatrolite is stable in the presence of a low temperature-high humidity environment. On removal from such an environment, such as to open air, paranatrolite will dehydrate to metastable tetranatrolite. There is no evidence that tetranatrolite will rehydrate to paranatrolite when immersed in aqueous solutions. A much better understanding of the nature of tetranatrolite must await the solution of the paranatrolite crystal structure. Museum samples of paranatrolite crystals that have been preserved in water-filled containers are readily available for crystal structure analysis. Dehydration during X-ray analysis may be prevented by passing a stream of air through ice water and then on to the crystal.

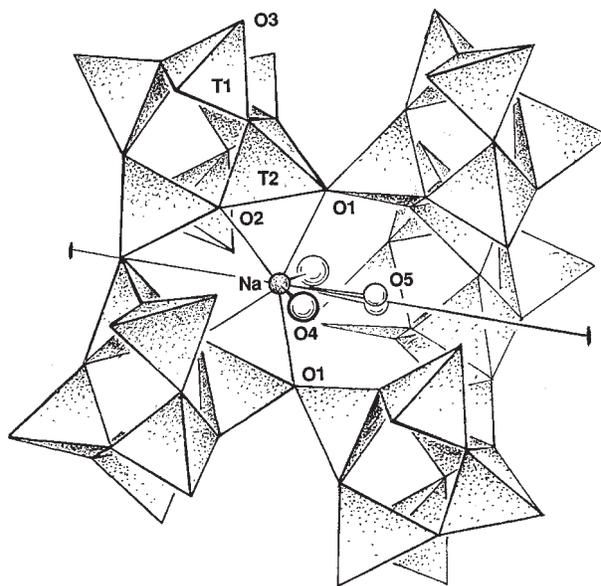


FIGURE 2. View of the crystal structure of tetranatrolite showing the location of the sodium atoms and the O4 and O5 water molecules within the Si-Al-O framework. A twofold symmetry axis, passing through O1 and Na, is shown.

(3) **Gonnardite-thomsonite.** Gonnardite crystallizes from solutions at moderately low temperatures (<200 °C). As fractional crystallization proceeds, both the solutions and the solid phases become more calcium-rich. One possible substitution mechanism for gonnardite is (Ca_4Al_2) for (Na_6Si_2) , as expressed by:

$\square_x\text{Na}_{16-3x}\text{Ca}_{2x}\text{Al}_{16+x}\text{Si}_{24-x}\text{O}_{80}\cdot n\text{H}_2\text{O}$, where \square denotes inter-cage vacancies. As the crystallizing solutions become even more concentrated in calcium ion, thomsonite begins to crystallize, often on the outer surface of the gonnardite spherules. The chemical composition of the Puy de Dôme gonnardite shows a somewhat different compositional trend from that given above, the trend being between the ideal natrolite composition and a less aluminous more sodic thomsonite composition [compare gray circles in Fig. 1 of Artioli and Galli (1999) to open squares in Fig. 22 of Ross et al., (1992)].

Nomenclature

The Zeolite Nomenclature Committee (Coombs et al. 1997) place tetranatrolite and paranatrolite in "doubtful status," but did not recommend discarding the names. Joel D. Grice, Chairman of the International Mineralogical Association Committee on New Minerals and New Mineral Names (personal communication, April 14, 2000), stated that "tetranatrolite is recognized as a valid species by the Commission." We also suggest that the name "tetranatrolite" be retained, with the caveat that it apparently forms only by dehydration of paranatrolite. This reaction appears to be irreversible, thus tetranatrolite probably does not have a true stability field. All chemical analyses of tetranatrolite (with the exception of water content) should be considered to also represent the compo-

sition of the precursor paranatrolite. We believe the name paranatrolite should also be retained for it appears to be a stable phase, crystallizing within a particular temperature and humidity range. Paranatrolite has a chemical composition and crystal structure that is distinctly different from that of natrolite, thus it cannot be considered just a higher hydrate of natrolite.

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