NATROPHILITE, NaMn(PO₄), HAS ORDERED CATIONS

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Abstract

Natrophilite, $4NaMn(PO_4)$, a 10.523(5), b 4.987(2), c 6.312(3)Å, space group *Pnam,* has ordered cations, isostructural with triphylite, with Na $= M(1)$ and Mn $= M(2)$ referring to the octahedral site populations of the olivine structure type. $R(hkl) = 0.055$ based on atomic coordinate and isotropic thermal vibration parameter refinement utilizing 789 independent reflections. Average polyhedral Me—O distances are Na—O 2.374, Mn—O 2.211, and P—O 1.545 Å.

Natrophilite poses a paradox in olivine crystal chemistry: it is the only reported ordered structure where the $M(1)$ cation is larger than $M(2)$. The less charged and larger Na^+ cation seeks the site with maximum shared polyhedral edges to minimize cation–cation repulsion effects. However, an opposite effect, the tendency for a cation of smaller crystal radius to seek the site with maximum number of shared polyhedral edges, renders prediction of cation ordering based solely on electrostatic arguments uncertain.

It is suggested that natrophilite is a product of Na–metasomatic exchange reactions with lithiophilite and may potentially occur only when the Mn^{2+}-rich member of the lithiophilite–triphylite series is present. Members of the series rich in Fe^{2+} yield alluaudites as Na–metasomatic exchange products on account of the relative ease of Fe^{2+} oxidation and the apparent influence of Fe^{3+} on alluaudite stability.

Introduction

Recent interest in the crystal chemistry of transition metal phosphates of the alkalies necessitates detailed study of their atomic arrangements and cation distributions. Determination of the alluaudite structure by Moore (1971) assisted in interpreting its paragenesis and range of cation substitutions. Natrophilite, $NaMn(PO_4)$, is related in composition but possesses a simple structure which is evidently related to olivine.

Natrophilite was first described by Brush and Dana (1890) as a rare species associated with coarse primary lithiophilite crystals and their products of hydrothermal reaction from the famous Branchville pegmatite, Fairfield Co., Connecticut. The species replaces lithiophilite and, like lithiophilite, is followed by species of hydrothermal reworking such as hureaulite, reddingite, fairfieldite, dickinsonite, etc. The authors suggested that natrophilite formed from lithiophilite in a manner akin to the replacement of adjacent spodumene by "cymatolite" (= albite + muscovite). In other words, natrophilite is a metasomatic exchange product of lithiophilite, involving the addition of sodium and the removal of lithium. A parallel observation was noted

by Moore (1971) where alluaudite, *ca.* $Na_2Mn^{2+}Fe^{2+}Fe^{3+}(PO_4)_3$ usually replaces triphylite, $Li(Fe,Mn)(PO_4)$.

The atomic arrangement of natrophilite was investigated by Byström (1943) who concluded on the basis of trial structure factor calculations for disordered and ordered octahedral cations that the structure involves disordered $(Na_{0.5}Mn_{0.5})$ populations over the $M(1)$ and $M(2)$ sites of the olivine structure type. Triphylite, on the other hand, has been conclusively shown to possess ordered $Li = M(1)$ and $(Fe,Mn) = M(2)$ cations as a result of accurate three–dimensional atomic parameter refinement by Finger and Rapp (1970), despite the nearly identical crystal radii for Li^+ and Fe^{2+} in octahedral coordination by oxygen. Furthermore, the ordered nature of Li and Mn atoms in lithiophilite was established by Geller and Durand (1960). That Na^+ and Mn^{2+}, with crystal radii which differ by *ca.* 20 percent, would occur disordered is surprising.

I submit evidence that the Na^+ and Mn^{2+} cations are ordered in natrophilite, over the $M(1)$ and $M(2)$ sites respectively, and that the ordering scheme is consistent with simple electrostatic arguments involving cation–cation repulsion effects although *a priori* prediction of the correct ordering scheme is not obvious.

<div align="center">EXPERIMENTAL</div>

A single crystal was obtained from the sample investigated by Fisher (1965) which possesses the number "Yale, Brush No. 2363". A cleavage fragment, nearly a cube in shape, 90 microns on an edge, afforded superior single crystal data obtained from a PAILRED automated diffractometer with molybdenum radiation and graphite monochromator. The linear absorption coefficient, $\mu = 46.2$ cm^{-1}, only 5 percent maximum deviation from average for symmetry equivalent reflections of the type $I(hkl)$, $I(\bar{h}kl)$, and ω-scans with ± 6 percent deviation from the mean value, suggested that absorption correction was not necessary. 2033 reflections to $2\theta = 85°$ were collected from the $l = 0-$ through 9–levels. Background counting times of 20 seconds on each side of the individual peaks and 1.6° half-scans at a rate of 2.5°/min were applied. Symmetry equivalent reflections were averaged, leading to 789 non-zero independent $|F(obs)|$, 279 "zero" reflections (including systematic absences) and 106 rejected reflections (background differences in excess of 30 percent of the mean value). Only the non–zero data were used in the ensuing study.

A portion of the cleavage fragment was ground and rolled into a ball with rubber cement and the powder data obtained were unambiguously indexed using the single crystal data as a guide. Least–squares refinement of trial cell parameters resulted in the indexed powder data in Table 1 and the final cell parameters in Table 2. The cell parameters are in good agreement with previously reported results of Fisher (1965) and Byström (1943).

<div align="center">REFINEMENT AND OCTAHEDRAL ORDERING SCHEME</div>

Determination of the cationic distributions for natrophilite proceeded from the scattering tables of MacGillavry and Rieck (1962). Full–matrix least–squares

TABLE 1. NATROPHILITE. POWDER DATA.

(Fe/Mn radiation, 114.6 mm camera diameter, calibrated film)

I/Io	d(obs)	d(calc)	hkl	I/Io	d(obs)	d(calc)	hkl
3	5.241	5.262	200	2	1.438	1.439	710
6	4.498	4.507	110	2	1.416	1.416	232
6	4.045	4.042	201	2	1.401	1.403	711
3	3.904	3.913	011	2	1.398	1.399	621
5	3.656	3.668	111	2	1.384	1.383	314
1	3.610	3.619	210	2	1.372	1.372	423
5	3.154	3.156	002			1.372	431
8	2.863	2.869	310	1	1.356	1.356	332
2	2.702	2.706	202	3	1.348	1.347	603
10	2.604	2.612	311	2	1.334	1.333	024
10	2.583	2.585	112	2	1.306	1.304	033
3	2.487	2.494	020	1	1.246	1.247	040
4	2.424	2.428	401	2	1.223	1.223	333
		2.426	120	2	1.206	1.206	532
4	2.377	2.378	212	2	1.190	1.192	722
4	2.322	2.327	410	2	1.188	1.189	424
4	2.261	2.265	121			1.188	713
2	2.120	2.122	221			1.185	623
2	1.956	1.957	022	1	1.169	1.169	433
3	1.904	1.906	113	3	1.156	1.155	315
2	1.851	1.854	511	3	1.152	1.153	142
7	1.831	1.834	222	1	1.138	1.138	910
2	1.806	1.810	420	2	1.133	1.132	242
4	1.738	1.740	421	1	1.120	1.118	234
5	1.694	1.697	313	1	1.116	1.115	730
3	1.689	1.689	601	1	1.109	1.109	441
3	1.642	1.652	512	2	1.089	1.088	334
		1.643	403	4	1.072	1.071	912
1	1.606	1.608	031	2	1.065	1.063	714
2	1.586	1.589	131	2	1.058	1.058	541
3	1.578	1.578	004			1.058	515
3	1.533	1.533	602	2	1.053	1.052	10·0·0
1	1.501	1.502	330	2	1.037	1.035	425
3	1.460	1.461	331	4	1.026	1.025	605

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TABLE 2. NATROPHILITE. CRYSTAL CELL DATA.

	1	2	3
a	10.523(5) Å	10.53	10.52(1)
b	4.987(2)	5.00	4.97(1)
c	6.312(3)	6.29	6.32(1)
space group	Pnam	Pnam	Pnam
formula	$Na(Mn_{0.93}Fe_{0.07})(PO_4)$		
Z	4		
specific gravity	3.40, 3.42		
density (calc.)	3.47 gm/cm^3		

[1] This study. The Mn:Fe ratio and specific gravities were obtained from Brush and Dana (1890)

[2] Fisher (1965).

[3] Byström (1943), with b- and c-axes interchanged.

refinement of atomic multiplicities, coordinates, and isotropic temperature factors utilized a local modification of the familiar ORFLS program for IBM 7094 computer of Busing, Martin, and Levy (1962). The initial scattering curves applied included $(Mn^+ + Na^+)/2 = M(1) = M(2)$; $P^{3+} = P$ and $O^- = O(1) = O(2) = O(3)$. The following cycles in proper order were: scale factor; atomic coordinates; scale factor, atomic coordinates; $M(1)$, $M(2)$ multiplicities; scale factor, $M(1)$, $M(2)$ multiplicities and atomic coordinates; and scale factor, $M(1)$, $M(2)$ multiplicities, atomic coordinates, and isotropic thermal vibration parameters. In the first sequence, $R(hkl) = \Sigma \mid\mid F(obs) \mid - \mid F(calc) \mid\mid / \Sigma \mid F(obs)\mid = 0.058$, resulting in the $M(1)$, $M(2)$ multiplicities, atomic parameters and isotropic temperature factor convergences in Table 3. From the disparate multiplicities, it was obvious that a parallel refinement was necessary with $M(1) = Na^+$ and $M(2) = Mn^+$ substituted for the $(Na^+ + Mn^+)/2$ table. Convergence was assured at $R(hkl) = 0.055$ and the results in Table 3 clearly show that natrophilite is essentially an ordered crystal with $M(1) = Na$ and $M(2) = (Nn, Fe)$.

Several features are noteworthy in this study. First, convergence by atom multiplicity refinement quickly leads to an approximate estimate of site populations, provided that the individual curves and the combination of scattering curves are reasonably congruent over $\sin \theta/\lambda$. Second, both convergences in atom coordinates and isotropic thermal vibration parameters are close to the limits of error, adding confidence to the physical meaning of the thermal vibration parameters, provided that a rather complete $\mid F(obs)\mid$ data set is available. The isotropic temperature factors $Na^+ = 1.18$, $Mn^{2+} = 0.55$, $P^{5+} = 0.47$, and $O(1) =$

TABLE 3. NATROPHILITE. CELL SITE MULTIPLICITIES, ATOMIC COORDINATES AND
ISOTROPIC TEMPERATURE FACTORS. (Errors in parentheses refer to the last digit.)

	M	x	y	z	B($\AA^2$)
M(1) = $Na_{0.5}Mn_{0.5}$	2.30(4)	0	0	0	1.17(3)
M(2) = $Na_{0.5}Mn_{0.5}$	5.80(3)	0.28475(9)	-0.0065(2)	1/4	0.46(2)
[1]M(1) = $Na_{1.0}$	3.93(4)	0	0	0	1.18(4)
[1]M(2) = $Mn_{0.93}Fe_{0.07}$	4.00(2)	0.28469(8)	-0.0065(2)	1/4	0.55(1)
P	4.0	0.1068(1)	0.4400(3)	1/4	0.47(2)
O(1)	4.0	0.1131(4)	0.7471(9)	1/4	0.74(5)
O(2)	4.0	0.4687(4)	0.1605(9)	1/4	0.74(6)
O(3)	8.0	0.1755(3)	0.3114(6)	0.0568(5)	0.74(4)

[1] Correct site preference scheme of octahedral cations.

O(2) = O(3) = 0.74 Å² are typical values for these ions in a dense–packed arrangement. Since thermal vibration parameters are sensitive to the scattering powers applied when atomic site multiplicities are fixed, they add confidence to the conclusion that natrophilite has ordered cations.

We inquire why Byström (1943) was unable to derive the correct ordering scheme for natrophilite. Several explanations are possible. First, Byström notes "From the dimensions and space group of natrophilite, it could be assumed that the structure should be of the olivine type. It seemed thus as if the distribution was the same as lithiophilite with the Li–atoms substituted by Na–atoms. This could not, however, explain the difference in powder photographs and a preliminary calculation of the intensities showed the impossibility of this scheme". Unfortunately, Byström was apparently not aware of the very delicate balance between atomic coordinates and relative intensities—particularly at higher Bragg angles—for close-packed structures. Natrophilite is sufficiently distorted away from the lithiophilite geometry to contribute to considerable intensity differences, Na substitution for Li notwithstanding. Indeed, scale factor refinement using Byström's coordinates and the ordered distribution model led to $R(hkl) = 0.35$. His data set was too incomplete for accurate refinement. This leaves us with the sobering thought that all older site preference schemes involving hand calculations with limited data must be treated with some suspicion.

The final $|F(\text{obs})|-F(\text{calc})$ data appear in Table 4[1].

[1] To obtain a copy of Table 4, order NAPS Document 01859 from ASIS National Auxiliary Publications Service, c/o CCM Information Corporation, 866 Third Avenue, New York, N.Y. 10022; remitting $2.00 for microfiche or $5.00 for photocopies payable to CCMIC-NAPS.

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Fig. 1. Polyhedral interatomic O—O' and M—O distances in natrophilite, lithiophilite and triphylite shown as Schlegel diagrams. The M—O distances are given in parentheses. Shared edges are drawn bold. m = reflection, s = screw, i = inversion operations performed on coordinates arranged as in Table 3. Estimated standard errors for natrophilite are M—O ± 0.005 and O—O' ± 0.007 Å.
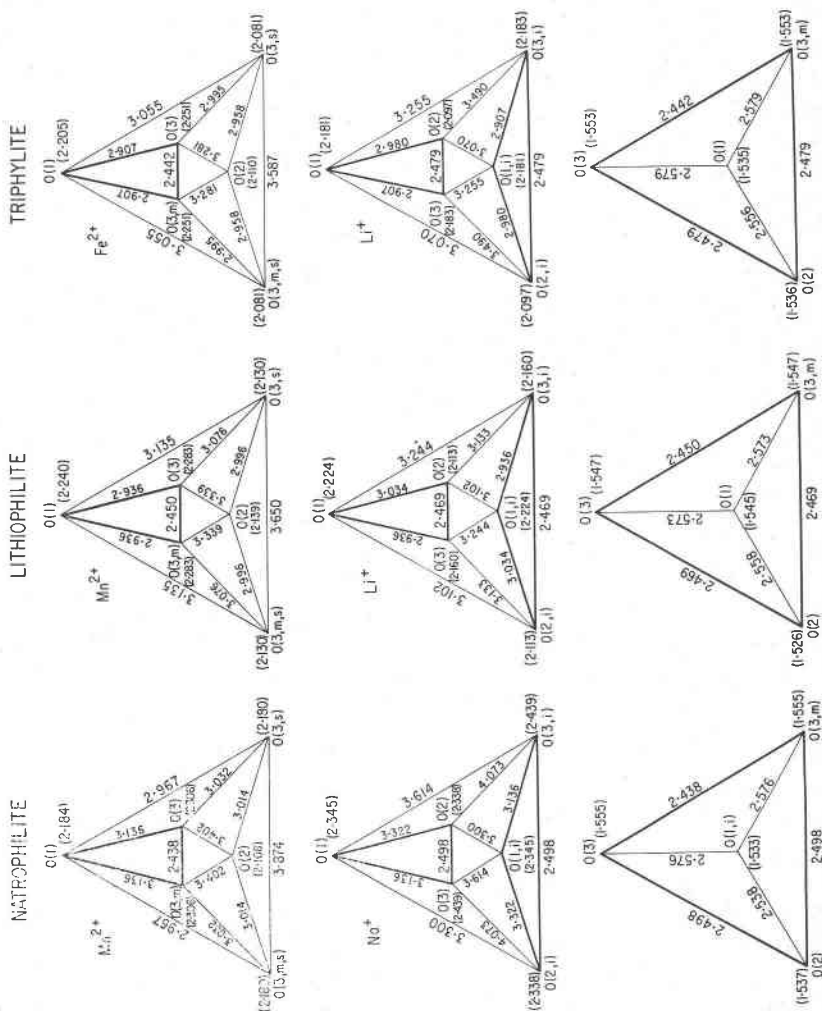
INTERATOMIC DISTANCES

Figure 1 presents Schlegel diagrams of the coordination polyhedra in natrophilite. Such diagrams have the advantage of direct comparison of polyhedral interatomic distances between different crystals; the diagrams have been discussed by Moore (1970). Included are the interatomic distances for lithiophilite, refined by Geller and Durand (1969), and for triphylite by Finger and Rapp (1970). In all three structures, the P–O distances are essentially the same and within the limits of experimental error. For natrophilite, the averages are P—O 1.545, Na—2.374, and Mn—O 2.211 Å.

A hierarchy of polyhedral distortions is evident. For all three structures, the corresponding O—O′ tetrahedral distances differ only within 3σ of each other and the tetrahedron exerts the greatest influence on the other polyhedra. The $M(2)$ polyhedral distances for lithiophilite are the dilated equivalents of triphylite on account of the larger crystal radius of Mn^{2+}. The $M(2)$ polyhedron in natrophilite departs from the geometrical similarity evident in the other two structures on account of the large Na^+ cation in $M(1)$. Although $O(1)$—$O(3)$, the shared edge between $M(1)$ and $M(2)$, is shorter than $O(1)$—$O(3,s)$ in the other structures, the reverse is true in natrophilite. In all three structures, the edge opposing the $P = O = M(2)$ shared edge evinces extreme compensation and is the largest edge for the $M(2)$ polyhedra. This is particularly noticeable in natrophilite where the $P = O = M(2)$ shared $O(3,m)$—$O(3)$ 2.438 Å is compensated by $O(3,m,s)$—$O(3,s)$ 3.874 Å.

The $M(1)$ polyhedron, on account of the cation of low charge, is most dependent on the geometry of the $M(2)$ and P polyhedra. Particularly noticeable are the $O(2,i)$–$O(3)$ edge distances on the equator which includes the pair of opposing $P = O = M(1)$ shared edges. Its distances are 3.13, 3.49, and 4.07 Å for lithiophilite, triphylite, and natrophilite respectively. The dilation from lithiophilite to triphylite indicates that the Coulombic repulsion between $M(1)$ and P is very sensitive to $M(1)$—P distances since this distance is shorter in triphylite. In natrophilite, the geometrical and Coulombic repulsion effects are additive, since the $O(2)$—$O(3)$ shared edges remain essentially invariant for all three structures and the large NaO_6 octahedron results in extreme dilation of $O(2,i)$—$O(3)$. This confirms the third rule of Baur (1970), that the *average* value of the distances within a coordination polyhedron is approximately constant. Thus, the compensatory effects between shared and opposing unshared polyhedral edges strive to approximate this invariance for a given coordination polyhedron and its ionic species.

Ordering of $M(1)$ and $M(2)$ In Natrophilite

For the classical ionic model involving non–equivalent sites of the same oxygen coordination, several qualitative predictions can be made as regards possible ordering of cations. The model introduced here is overly simplistic but, within the limitations of compounds belonging to the same structure type, should reveal at least trends when different charged species are considered. For cations of different charge but similar crystal radius in an identical anionic matrix, the high–charged cation will favor the site with the minimum overall nearest neighbor cation–cation repulsion. This can be stated in the following manner: define the coordination number of the nearest neighbor cations (K'), the charge of the nearest neighbor cations (Z_c'), the charge of the central cation (Z_c), its coordination number K, and the interatomic distance between the central cation and its i–th nearest neighbor cation, (d_i). As a normalizing factor, the bond strength of the i–th nearest neighbor cation, $(Z_c'/K')_i$, is introduced. The Coulombic repulsion is

$$Q = Z_c/K \sum_i (Z_c'/K')_i \, d_i^{-2}$$

To assess this term for the non–equivalent sites of a given structure type, consider Z_c' and Z_c of the same radius. The values of Q are then computed. Accordingly, the site with highest Q will accommodate the cation of lowest charge in the actual crystal, thus minimizing cation–cation repulsion effect.

In the olivine structure type, the $M(1)$ octahedron shares two edges with T (the tetrahedron), two edges with other $M(1)$ and two edges with $M(2)$; but $M(2)$ shares only one edge with T and two edges with $M(1)$. Thus, $M(1)$, with the higher Q–value, should accommodate the cation of lower charge, *providing the crystal radii of the cations in question are similar.*

Now consider the case for two cations of like charge but different crystal radius. Where will the larger cation go? Intuitively, it should go into the site with highest Q–value since the d_i^{-2} terms will be less, minimizing cation–cation repulsion effects. However, empirical evidence greatly favors the opposite effect: the smaller cation tends to preferentially occupy the site of maximum Q–value. My unpublished results on absolute volumes for 44 independent $[AlO_6]$ octahedra in well–refined oxide and silicate structures reveal that octahedral volume decreases with increase in the value of Q. The dependence of volume (V) upon Q is quite substantial: for example, in chrysoberyl, Al_2BeO_4, $Q = 3.2$ and $V = 8.85$ Å for $M(1)$ and 1.5 and 9.48 Å³ for $M(2)$, a volume difference of 7 percent. An extreme case of the preferential

occupancy of a small highly charged cation in positions with maximum shared edges occurs for $CdSb_2O_6$, which is based on hexagonal close-packed oxygen atoms. In this structure, the Sb^{5+} cations occur in the centers of octahedra which define a sheet of the $Al(OH)_3$ type, with each octahedron sharing three edges. The Cd^{2+} cation resides in an octahedron between sheets above the sheet voids and shares only corners with other polyhedra (Magnéli, 1941). In sapphirine, where eight non-equivalent octahedra occur in a cubic close–packed oxygen array (Moore, 1969), the Al–rich populations occur in the sites with most shared edges, whereas the Mg–rich populations appear at the positions with least shared edges. In the olivine structures, Mg^{2+} resides in $M(1)$ and Ca^{2+} in $M(2)$ for monticellite (Onken, 1965).

Thus, there are two competing effects which determine octahedral site preferences in the olivines: the electrostatic effect where cations of low charge tend toward the site of maximum Q–value, and the size or geometrical effect where the smaller cation tends toward the site of maximum Q–value. Table 5 lists olivine structures where structural refinements have afforded ordering schemes. For the ordered olivine structures with cations of same charge (monticellite and glaucochroite), the $M(1)$ position accommodates the smaller cation. For the cations of different charge, the smaller charged cation occurs at $M(1)$ (lithiophilite, triphylite, and natrophilite) with the exception of sinhalite. For sinhalite, the geometrical effect evidently is more important but there is accumulating evidence in this laboratory that Mg^{2+} and Al^{3+} are partly disordered in this crystal. In the forsterite-fayalite series

TABLE 5. COMPARISON OF IONIC RADII OF CATIONS IN M(1) AND M(2) SITES FOR OLIVINE STRUCTURES[1,2].

Compound	Formula	M(1)	M(2)	($\Delta r \times 100$)	$1 - \frac{ZM(1)}{ZM(2)}$
monticellite	$CaMg[SiO_4]$	Mg^{2+}	Ca^{2+}	+ 28%	0.00
sinhalite	$MgAl[BO_4]$	Al^{3+}	Mg^{2+}	+ 26	- .50
glaucochroite	$CaMn[SiO_4]$	Mn^{2+}	Ca^{2+}	+ 18	0.00
lithiophilite	$LiMn[PO_4]$	Li^+	Mn^{2+}	+ 10	+ .50
triphylite	$LiFe[PO_4]$	Li^+	Fe^{2+}	+ 4	+ .50
forsterite-fayalite	$(Mg,Fe)_2[SiO_4]$	Nearly statistical	distr.	$\pm$ 6	0.00
natrophilite	$NaMn[PO_4]$	Na^+	Mn^{2+}	- 19	+ .50

[1] $\Delta r = \frac{\text{ionic radius } (M(2) - M(1))}{\text{ionic radius } M(2)}$. The effective ionic radii (based on $r^{VI}O^{2-} = 1.40$ Å) are from Shannon and Prewitt (1969).

[2] $Z(M(1))$ and $Z(M(2))$ are the ionic charges on M(1) and M(2) respectively.

where both charge and ionic radius are similar, (Mg,Fe) disorder is extensive.

Natrophilite is of particular interest since it is the only compound of an ordered olivine structure type where the $M(1)$ cation is much larger than $M(2)$, with radius ratio $r_M(1):r_M(2) = 1.24$. It points out a "paradox": possible solid solution may occur only when the two effects "cross", that is, when the larger cation of low charge is potentially more stable in a solid solution with a smaller cation rather than another cation of identical radius. Solution would appear when the ratio in their ionic size is *exceeded* by some amount considerably greater than 1.0. In other words, $M(2)$ is predicted to potentially accommodate the larger cation of lower charge as well, as observed for sinhalite. Below this value, the electrostatic effect predominates, and at 1.0 and below the geometrical effect as well, the last two cases representing ordered olivine structures. This tempts the question: given the composition, say, $NaMg(PO_4)$ (providing it crystallizes with the olivine structure type), $r_{Na}+:r_{Mg}2+ = 1.41$, is the crystal ordered with $Na = M(1)$ or with $Na = M(2)$, or is it disordered?

THE NATROPHILITE PARAGENESIS

Natrophilite has been reported only from the Branchville pegmatite where it occurred replacing lithiophilite nodules associated with altered spodumene in a cleavelandite replacement unit. The altered spodumene consists of "β-spodumene", resulting from extensive replacement of Na for Li leading to a mixture of eucryptite and albite, and "cymatolite" which is a mixture of albite and muscovite. According to Brush and Dana (1890), natrophilite occurs in a paragenesis which parallels that of the metasomatically altered spodumene, suggesting that natrophilite is a Na-metasomatic exchange product of lithiophilite.

The Custer Mountain Lode, also called the Skookum Feldspar Mine, 1 1/2 miles east-southeast (SW 1/4, SE 1/4, sec. 30, T.3s) of Custer, South Dakota, reveals a replacement unit which in many respects is similar to the Branchville pegmatite. According to Fisher (1945) the lithiophilite, which is compositionally near the Branchville material, crystallized in the early hypothermal stage followed by spodumene with which it is closely associated. Cleavelandite in turn postdates both minerals. I have personally examined the main pit and the lithiophilite and spodumene occurring in place. As noted by Fisher, the spodumene associated with the lithiophilite is fresh and reveals no "cymatolite" alteration. Examination of several hundred lithiophilite specimens collected by myself and Fisher failed to reveal any natrophilite. Instead, the alkali–leached oxidized products sicklerite and purpurite

were found bordering fractures and rimming the lithiophilite. The deep green mineral noted by Fisher (1945) which occasionally replaces the lithiophilite in a paragenesis similar to natrophilite at Branchville is definitely a member of the alluaudite series on the basis of my X-ray studies.

Alluaudite is a very abundant and typical metasomatic reaction product of triphylite–lithiophilite at many pegmatites in the Black Hills. Too numerous to mention, the primary and secondary phosphate–bearing pegmatites are being presently studied in detail. According to Moore (1971), the alluaudite series at the iron–rich side can be written $NaCaMn^{2+}Fe_2^{2+}(PO_4)_3$–$NaNaMn^{2+}Fe^{2+}Fe^{3+}(PO_4)_3$–$Mn^{2+}Fe_2^{3+}(PO_4)_3$, and all examples studied so far involve some iron in the ferric state.

Why doesn't natrophilite occur at the Custer Mountain Lode? It appears that Na–metasomatic exchange of the lithiophilite and spodumene was not nearly as extensive as at Branchville. But more significant, all examples of Black Hills Na–metasomatism of triphylite–lithiophilite involve partial oxidation of Fe^{2+} which favors the stability of the alluaudite structure. Since no alluaudite has evidently been recorded from the Branchville pegmatite, it can be inferred that Na–metasomatic exchange occurred under conditions which did not lead to oxidation of the subordinate iron in solid solution. Postdating this exchange reaction at lower temperature were the oxidative alkali-leaching reactions leading to the formation of sicklerite and purpurite.

Since Mn^{2+} is more resistant than Fe^{2+} to oxidation in crystals and in solution, potential natrophilite occurrences should be found only where the lithiophilite member prevails. Such localities are few and the products are at least partially oxidized. At Varuträsk, Sweden, an alluaudite replaced the lithiophilite (Quensel, 1956) and at Pala, California, where lithiophilite nodules have suffered much hydrothermal attack, the secondary phosphates contain ferric iron.

Since primary pegmatite phosphates are highly susceptible to chemical exchange and reaction, they are indicative of the delicate reactions which postdate primary giant crystal formation and can reveal much information easily overlooked in studies on the far more resistant silicates. These observations on phosphates have not been appreciated: survey reports on the mineralogy of pegmatites are notoriously inaccurate in interpretation of the phosphate phases present and in cases where gross Na–metasomatic exchange results in alluaudite replacing triphylite–lithiophilite, a jig in the pegmatite puzzle has been overlooked. This part of the puzzle is necessary to our understanding of replacement units in pegmatites and when repeated from pegmatite

to pegmatite, as in the Black Hills, suggests that such phenomena are not unusual or very local but more general than previously suspected.

REFERENCES

BAUR, W. H. (1970) Bond length variation and distorted coordination polyhedra in inorganic crystals. *Trans. Amer. Crystallogr. Assoc.* **6**, 129–155.

BRUSH, G. J., AND E. S. DANA (1890) On the mineral locality at Branchville, Connecticut: Fifth paper. *Amer. J. Sci.* **39**, 201–216.

BUSING, W. R., K. O. MARTIN, AND H. A. LEVY (1962) ORFLS, a Fortran crystallographic least-squares program. *U.S. Oak Ridge Nat. Lab. (U.S. Clearinghouse Fed. Sci. Tech. Info.) Rep.* ORNL-TM-305.

BYSTRÖM, A. (1943) The structure of natrophilite, $NaMnPO_4$. *Ark. Kemi. Mineral. Geol.* **17B**, 1–4.

FINGER, L. W., AND G. R. RAPP, JR. (1970) Refinement of the crystal structure of triphylite. *Ann. Carnegie Inst. Wash. Year Book*, **68**, 290–292.

FISHER, D. J. (1945) Preliminary report on the mineralogy of some pegmatites near Custer. *S. Dakota Geol. Surv. Rep. Invest.* **50**, 37–56.

—— (1965) Natrophilite. *Amer. Mineral.* **50**, 1096–1097.

GELLER, S., AND J. L. DURAND (1960) Refinement of the structure of $LiMnPO_4$. *Acta Crystallogr.* **13**, 325–331.

MACGILLAVRY, C. H., AND G. D. RIECK (1962) *International Tables for X-ray Crystallography, Vol.* **3**, the Kynoch Press, Birmingham, England.

MAGNÉLI, A. (1941) The crystal structure of lead metantimonate and isomorphous compounds. *Ark. Kemi. Mineral. Geol.* **15B**, 1–6.

MOORE, P. B. (1969) The crystal structure of sapphirine. *Amer. Mineral.* **54**, 31–49.

—— (1971) Crystal chemistry of the alluaudite structure type: contribution to the paragenesis of pegmatite phosphate giant crystals. *Amer. Mineral.* **56**, 1955–1975.

ONKEN, H. (1965) Verfeinerung der Kristallstruktur von Monticellit. *Tschermak's Mineral. Petrogr. Mitt.* **10**, 34–44.

QUENSEL, P. (1956) The paragenesis of the Varuträsk pegmatite including a review of its mineral assemblage. *Ark. Mineral. Geol.* **2**, 9–83.