Canadian Mineralogist
Vol. 15, pp. 518-521 (1977)

THE CRYSTAL STRUCTURE OF THE NEW MINERAL MARICITE, $NaFePO_4$

YVON LE PAGE AND GABRIELLE DONNAY

Department of Geological Sciences, McGill University, Montreal, P.Q. H3A 2A7

ABSTRACT

Maricite from the Big Fish River area, Yukon Territory, has a chemical formula $Na_{1.00}(Fe_{0.90}Mn_{0.06}Mg_{0.03}Ca_{0.01})PO_4$. Its cell dimensions at 293K (λ Mo$K\alpha_1$=0.70930Å) are *a* 6.861(1), *b* 8.987(1), *c* 5.045(1)Å; space group *Pmnb*, $Z=4$; *D*(meas.) 3.64-3.68 g/cm^3, *D*(calc) 3.69 g/cm^3. From a crystal ground into a sphere, with crystal-monochromatized Mo$K\alpha$ radiation and stationary-crystal, stationary-counter procedure, we collected 520 diffracted intensities, 488 of which had $I>3_\sigma$. A trial structure of the high-temperature $CoSO_4$ type with Na added in 4*(c)* (¼, 0.851, 0.531) was refined by least squares with anisotropic temperature factors to an unweighted residual of 3.0%. Na is surrounded by ten oxygen atoms within 3Å, in irregular coordination. The distorted octahedron about Fe is of the (2+2+2) type; the phosphate tetrahedron is nearly regular. Half the oxygen atoms are coordinated to two Na^+, two Fe^{2+}, and one P^{5+} ions, and the other half to three Na^+, one Fe^{2+}, and one P^{5+} ions. The packing efficiency is 70%.

SOMMAIRE

La maricite de la région de la rivière Big Fish, Territoire du Yukon, a pour formule chimique: $Na_{1.00}(Fe_{0.90}Mn_{0.06}Mg_{0.03}Ca_{0.01})PO_4$. Ses paramètres cristallins à 293K (λMo$K\alpha_1$=0.70930Å) sont *a* 6.861(1), *b* 8.987(1), *c* 5.045(1)Å; son groupe d'espace est *Pmnb* avec $Z=4$; $D_{mes}=3.64\text{-}3.68$, $D_{calc}=3.69$. Nous avons mesuré sur un échantillon sphérique, par la méthode cristal fixe-détecteur fixe, 520 intensités dont 488 avaient $I>3\sigma(I)$ à l'aide de la radiation Mo$K\alpha$ monochromatisée par un cristal de graphite. Un modèle du type $CoSO_4$, forme haute température, avec un atome de Na ajouté en 4*(c)* (¼, 0.851, 0.531) s'est affiné par moindres carrés avec des facteurs d'agitation thermique anisotropes jusqu'à un résidu non pondéré de 3.0%. Le sodium est en coordinence irrégulière, lié à 10 atomes d'oxygène à moins de 3Å. L'octaèdre du fer a une distortion très prononcée du type (2+2+2). Le tétraèdre du phosphore est à peu près régulier. La moitié des atomes d'oxygène sont liées à deux ions Na^+, deux Fe^{2+} et un P^{5+}, l'autre moitié à trois Na^+, un Fe^{2+} et un P^{5+}. Le coefficient d'empilement est 70%.

INTRODUCTION

Despite its simple formula, sodium ferrous phosphate has not received much attention from chemists. It was reported in the chemical literature as a deposit in boiler pipes once in the last twenty years. Sturman *et al.* (1977) discovered this compound as a new mineral of hydrothermal origin in the Big Fish River area, Yukon Territory, and named it maricite. The sample utilized for structure determination had been analyzed on the electron microprobe by Dr. M. Corlett at Queen's University. Her analysis, recalculated to 4.00 oxygen atoms per formula unit, is given in Table 1.

CRYSTAL DATA

The crystals range from one to several mm in longest dimension, which is *a* in the orthorhombic cell (Table 1). Some of the crystals are clear and colorless, others are milky and grey. X-ray diffraction patterns of both types, however, are indistinguishable.

A clear grain selected for data collection was ground to a sphere 0.30 mm in diameter. The reported cell edges result from a least-squares refinement of 12 high-order reflections (Mo$K\alpha_1$ =0.70930Å) centered on an automated diffractometer. The space-group absences and lattice repeats were observed on precession, cone-axis, rotation, and Weissenberg films as follows: *h*0*l* absent for $h+l=2n+1$; *hk*0 absent for $k=2n+1$. They characterize diffraction aspect *P*nb*. Since

TABLE 1. CRYSTAL DATA

Space group *Pmnb*		Chemical formula:
a	6.861(1)Å	$Na_{1.00}(Fe_{0.90}Mn_{0.06}Mg_{0.03}Ca_{0.01})PO_4$
b	8.987(1)	$Z=4$
c	5.045(1)	$D_{meas}=3.64 - 3.68$ g/cm^3
T	293K	$D_{calc}=3.69$ g/cm^3
λ	Mo$K\alpha_1$	0.70930Å

Linear absorption coefficient for Mo$K\alpha$ 51.2 cm^{-1}
Observed forms: {011}, {020}, {012}, {032}; {021} is an unexplained anomalous absence.

TABLE 2. CRYSTAL-STRUCTURE PARAMETERS AFTER REFINEMENT†

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	1/4	0.8508(3)	0.5305(5)	1.6(1)	1.2(1)	1.1(1)	0	0	0.0(1)
Fe	0	0	0	0.87(4)	0.64(3)	0.82(4)	0.22(3)	-0.31(3)	-0.40(3)
P	1/4	0.1760(1)	0.4640(3)	0.64(1)	0.29(5)	0.37(6)	0	0	-0.01(5)
O(1)	1/4	0.1164(4)	0.7521(8)	1.4(2)	0.65(2)	0.71(2)	0	0	0.2(1)
O(2)	1/4	0.3492(4)	0.4557(8)	0.9(2)	0.3(2)	1.0(2)	0	0	0.1(1)
O(3)	0.0692(4)	0.1213(3)	0.3174(5)	0.8(1)	1.0(1)	1.0(1)	0.2(1)	-0.1(1)	-0.4(1)

†Thermal parameters (in Å^{2}x100) have the form $T=\exp -2\pi^2(h^2a^{*2}U_{11}+\ldots+2hka^*b^*U_{12}+\ldots)$

morphology did not show any forms such as $\{hkl\}$, $\{h0l\}$, $\{hk0\}$ or $\{100\}$ that could have established the space group uniquely, we first assumed a center of symmetry. This proved to be correct as the structure was found to belong to space group *Pmnb*.

EXPERIMENTAL PROCEDURE

Intensities were measured on an automated 4-circle Picker diffractometer, using graphite-monochromatized Mo*K*α radiation. The fixed-counter method of intensity measurement was used with a take-off angle of 9°. The reflections were intense enough for the tube to be operated at 30 kV, 10 mA during the entire procedure of data collection. We counted for 20 seconds on the peak, and 10 seconds at each of two points 1.5° away from the peak and on each side of it along the central lattice row. No attenuators were used. The intensities were corrected for counter dead time, the largest correction being approximately 5% of the accumulated counts. All the reflections in the hemisphere $h \geqslant 0$ were measured up to $2\theta=60°$. Three standard reflections chosen at high angles were measured after every 30 reflections; in no case did the variation from their mean intensity exceed 1.5%. Comparison of symmetrically related reflections showed a 2.1% mean deviation of the square root of the intensity, a value that compares favourably with the reproducibility routinely obtained from 2θ scan measurements. The standard deviation of intensities was evaluated from counting statistics allowing for an additional 2% "instrumental instability" (Stout & Jensen 1970). The number of symmetry-independent reflections stands at 520, 32 of which were less than 3σ and were considered unobserved. The intensities were reduced to F_{obs} values by the DATRDN program (Stewart *et al.* 1970).

DETERMINATION OF THE CRYSTAL STRUCTURE

We first looked for a promising trial structure in *Crystal Data* (Donnay *et al.* 1973) among compounds with similar axial ratios, the same space group, and similar chemistry. Many double-metal phosphates, such as natrophilite and triphylite, crystallize in *Pmnb* with an olivine-type structure. Their *a*/*b* axial ratios, however, cluster around 0.60, as compared to 0.76 for $NaFePO_4$. Around $a/b=0.78$ is another group of compounds, with the structure of high-temperature $CoSO_4$. Because these are single-metal sulfates, selenates, and $LiClO_4$, we carefully examined the isostructural $CuSO_4$ (Kokkoros & Rentzeperis 1958; Rama Roa 1961) for holes large enough to accommodate Na ions. Such a position exists on the (010) mirror, 4(*c*) : ¼, ~0.85,~0.53, where a sodium atom would be surrounded by ten oxygen atoms at acceptable distances of less than 3Å. The alkali ion would not come too close to other cations. A trial structure for $NaFePO_4$, making use of position 4(*c*) for Na and the atomic coordinates of high-temperature $CuSO_4$ for the remaining elements,

TABLE 4. BOND VALENCE SUMMATION

	${}^{x}Na$ (4 c)	${}^{vi}(Fe,Mn,Mg,Ca)$ (4 a)	${}^{iv}P$ (4 c)	$\Sigma_{C}\, v_A$
$v_{O(1)}$ (4 c)	2.636(5) Å 0.093 v.u. 2.375(5) Å 0.167 v.u.	^{2}2.367(3)^{2} 0.145	1.549(4) 1.220	1.77 v.u.
$v_{O(2)}$ (4 c)	2.592(5) 0.102 2.453(5) 0.140	^{2}2.197(2)^{2} 0.295	1.558(4) 1.192	2.02
$v_{O(3)}$ (8 a)	2.933(4)^{2} 0.037 2.334(3)^{2} 0.184 2.979(4)^{2} 0.029	1.995(3)^{2} 0.560	1.525(3)^{2} 1.294	2.10
$\bar{L}$	2.655	2.186	1.539	
L max	3.13	2.521	1.95	
v_L	0.10	0.333	1.25	
p	5.589	6.525	3.744	
N.F.	0.896	0.926	1.000	
$\Sigma_A v_C$	1.00	2.00	5.00	

*The superscript on the left of the bond distance indicates the multiplicity of the bond evaluated at the anion, on the right, at the cation.

TABLE 5. TETRAHEDRON AND OCTAHEDRON ANGLES

Phosphate tetrahedron		Iron octahedron	
O(1)-P-O(2)	111.8(2)°	O(1)-Fe-O(2)	76.2(1)°
O(1)-P-O(3)	110.1(1)°	O(1)-Fe-O(2)'	103.8(1)°
O(2)-P-O(3)	108.0(2)°	O(1)-Fe-O(3)	89.4(1)°
O(3)-P-O(3)'	108.8(2)°	O(1)-Fe-O(3)'	90.6(1)°
		O(2)-Fe-O(3)	86.0(1)°
		O(2)-Fe-O(3)'	94.0(1)°

gave a 38% initial residual. After four cycles of unweighted least-squares refinement, the last one performed with anisotropic temperature factors, the residual converged to 3.6%. The data were then corrected for secondary extinction, and the unweighted residual dropped to 3.0%, whereas the conventional weighted residual came to 4.0%. Atomic coordinates and anisotropic temperature factors are given in Table 2. Table 3, which lists F_{obs} and F_{calc} values, is available at nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada, K1A 0S2.

DESCRIPTION OF THE CRYSTAL STRUCTURE

The structure has a high packing efficiency of 70% as compared with 66% for the manganous analogue with olivine-type structure, natrophilite. The density of 3.69 g/cm^3 is significantly higher than that of natrophilite, 3.45 g/cm^3. The centrosymmetric Fe octahedron is distorted and of the (2+2+2) type (Table 4), in contrast to the Cu octahedron (4+2) in the high-temperature CuSO$_4$ structure (Rama Rao 1961). The angular deviations from 90° for the angles O-Fe-O (Table 5) extend to about 14°. The phosphate tetrahedron displays two short bonds and two longer ones, and its angles are close to tetrahedral angles ((Tables 4, 5). The coordination polyhedron about the sodium atom is irregular. The Na-O distances range from 2.33 to 2.93Å (Table 4).

Iron occupies the nodes of a pseudo-hexagonal lattice with orthohexagonal parameters $a_H = c \sim b/(2\cos 30°)$, $c_H = a$, obtained by matrix 001/010/$\bar{1}$00 (Fig. 1). Let the iron layers at heights $x = 0$ and $x = ½$ be called *A;* they are interleaved by a layer *B* of Na, P and both O(1) and O(2) at $x = ¼$ and by its centrosymmetric equivalent layer *C* (due to $\bar{1}$ at ½, ½, ½). In (100) projection, Na and P occupy the centers of the Fe triangles, giving a sequence of cations *ABACA* . . . so that the diffraction pattern shows *a*/2 as the pseudo-repeat. The pseudo-hexagonal structure explains the morphologically most important {011} and {020} since they become {10$\bar{1}$0}

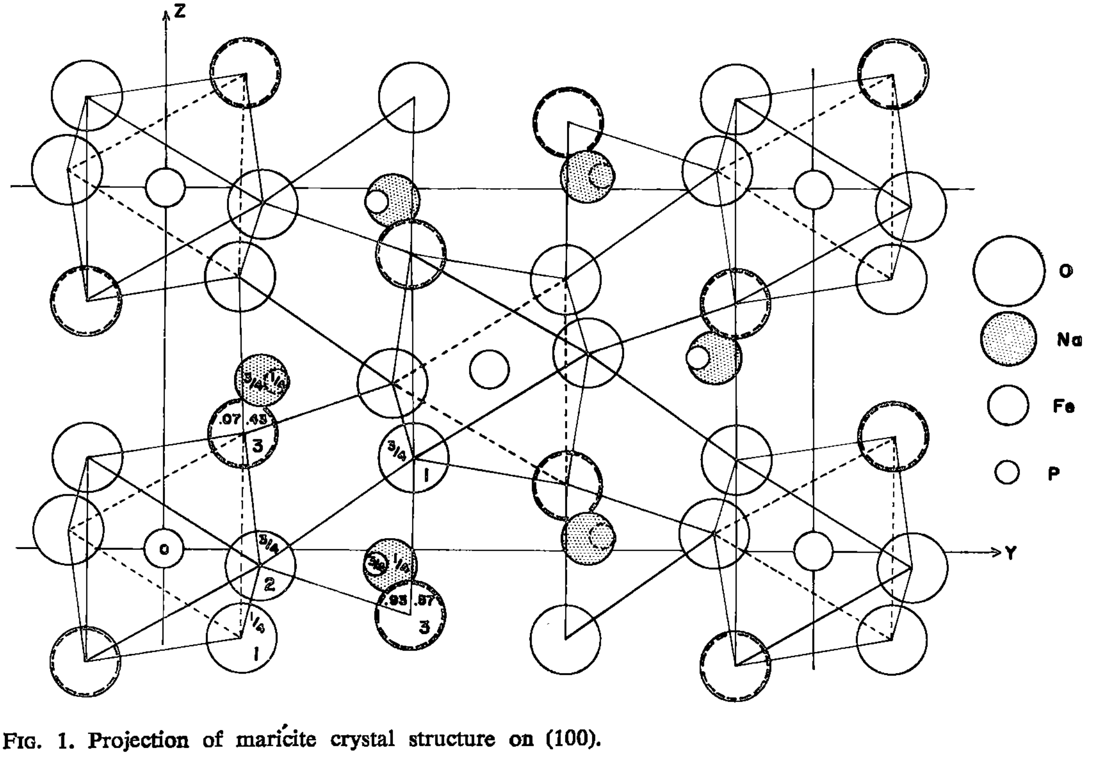

FIG. 1. Projection of maricite crystal structure on (100).

with reference to the hexagonal lattice. The observed habit, elongation along *a*, is due to the halving of *a*.

Half of the oxygen atoms are located in layers *B* and *C*, the other half are in a general position. Each oxygen atom is five-coordinated : oxygen atoms in the two special positions form corners of two Na, two Fe, and one P polyhedra whereas the general-position anions are shared by three Na, one Fe, and one P polyhedra. The bond-valence sums (Donnay & Allmann 1970) for O(2) and O(3) (Table 4) are acceptable; that for O(1) is not, since it is 0.23 v.u. too low, which is a larger deviation than has been found so far in any well-refined structure of a phosphate, sulfate, borate, or silicate. The possibility of partial replacement of O by OH or F can be ruled out because, in the nearly regular PO_4 tetrahedron, P^{5+} gives 1.25 v.u. to each anion and this is more than can be accepted by a fluorine ion or a hydroxyl group, which does not form a hydrogen bond. Hydrogen bonds are ruled out because they would have to lie along tetrahedral edges, an electrostatistically unfavorable arrangement that has never been observed. The O(1) atoms are thus in an energetically unfavorable placement which may play a role in making this crystal structure a metastable one. We note that this compound has not been synthesized.

ACKNOWLEDGEMENTS

We thank Mr. B. D. Sturman and Dr. J. A. Mandarino, who provided the sample used in this study. Professor J. D. H. Donnay critically read the manuscript. We thank the National Research Council of Canada for its financial support.

ADDENDUM

After the above manuscript was accepted for publication, Professor Erika Hermon joined our group to study the Fe Mössbauer spectrum of marićite. At the lowest and highest temperatures studied, namely 77±0.1 and 293±0.1K, the quadrupole splittings are 2.23 and 2.31 mm/sec.; the isomer shifts are 1.21 and 1.32 mm/sec. with respect to metallic iron; the line widths measure 0.36 and 0.40 mm/sec., respectively. The spectrum changes continuously on gradual lowering of temperature, indicating the absence of any transition. The temperature dependence of the quadrupole splitting, due to a Boltzman-type temperature dependence of the electric field gradient, appears normal. On heating marićite, the DTA curve shows a singularity at 410±1K corresponding to a second-order transition.

We thank Professor D. J. Simkin for the use of his Mössbauer equipment.

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Received March 1977; revised manuscript accepted May 1977.