KINGSMOUNTITE, A NEW MINERAL ISOSTRUCTURAL WITH MONTGOMERYITE

PETE J. DUNN

Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.

DONALD R. PEACOR

Department of Geology and Mineralogy, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

JOHN SAMPSON WHITE

Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.

ROBERT A. RAMIK

Department of Mineralogy and Geology, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario M5S 2C6

Abstract

Kingsmountite is a new mineral found at the Foote Mineral Company spodumene mine, near Kings Mountain in North Carolina, U.S.A. It is the ferroan analog of montgomervite and occurs as radiating bundles of subparallel fibres in white spherules associated with mitridatite and birnessite. Y is perpendicular to the fibre axis. Kingsmountite is monoclinic, space group (provisional) C2, a 10.029(6), b 24.46(1), c 6.258(4) Å, β 91.16(7)°. The average of three analyses gives MgO 0.2, CaO 14.9, MnO 8.1, FeO 4.1, Al₂O₃ 16.7, P₂O₅ 35.9%, with one water determination by TGA of 20.6%, sum = 100.5%, which corresponds to $(Ca_{3.15})$ $Mn_{0.85}$) (Fe²⁺_{0.56} $Mn_{0.50}Mg_{0.06}$) (Al_{3.88}Fe³⁺_{0.12}) (PO₄)₆ $(OH)_4 \cdot 11.6H_2O$, calculated on the basis of six phosphorus atoms. The idealized formula is Ca₄ $FeAl_4(PO_4)_6(OH)_4 \cdot 12H_2O$. Individual crystals are extremely small and highly imperfect. The density is 2.51 g/cm³(meas.); 2.58 g/cm³(calc.). The refractive indices are α 1.575(3), β 1.581(3) and γ 1.583(3).

Sommaire

Kingsmountite, nouveau minéral, provient de la mine de spodumène de la Foote Mineral Co., près de Kings Mountain, en Caroline du Nord, E.U.A. C'est l'analogue ferreux de la montgomeryite. Il se présente en faisceaux divergents de fibres subparallèles en sphérules blanches, accompagné de mitridatite et birnessite. Y est perpendiculaire à l'axe des fibres. Il est monoclinique, de groupe spatial C2 (à confirmer) avec maille de dimensions a 10.029(6), b 24.46(1), c 6.258(4) Å, β 91.16(7)°. La moyenne de trois analyses, MgO 0.2, CaO 14.9, MnO 8.1, FeO 4.1, Al₂O₃ 16.7, P₂O₅ 35.9%, combinée à une détermination de H₂O (20.6%) par ATG, donne un total de 100.5% et conduit à la formule $(Ca_{3.15}Mn_{0.85})$ $(Fe^{2+}_{0.56}Mn_{0.50}Mg_{0.06})$ $(Al_{3.88}Fe^{3+}_{0.12})$ $(PO_4)_6(OH)_4 \cdot 11.6H_2O$ quand on part de 6 atomes de phosphore, soit idéalement Ca_4FeAl_4 - $(PO_4)_6(OH)_4 \cdot 12H_2O$. Les cristaux isolés sont extrêmement petits et fort imparfaits; les valeurs de la densité sont Dm 2.51, Dx = 2.58. Les indices de réfraction sont α 1.575(3), β 1.581(3), γ 1.583(3).

(Traduit par la Rédaction)

INTRODUCTION

During an investigation of some secondary phosphate minerals, a sample of a mineral from near Kings Mountain in North Carolina, whose X-ray powder pattern was similar to that of montgomeryite $Ca_4MgAl_4(PO_4)_6(OH)_{4^*}12H_2O$, was noted to have no appreciable magnesium. According to Moore & Araki (1974) magnesium is essential to montgomeryite, and our analyses (unpubl. data) of montgomeryite from near Fairfield, Utah have confirmed the presence of magnesium. We therefore proceeded on the assumption that we had a new analog of montgomeryite, and the results of this investigation are described herein.

The new mineral kingsmountite is named for the town near which it occurs. The complete name of the locality is the Foote Mineral Company spodumene mine, near the town of Kings Mountain, Cleveland County, North Carolina. Holotype material is preserved in the Smithsonian Institution collections under catalog numbers NMNH 120972 and 120973. The new mineral and the name were approved by the Commission on New Minerals and Mineral Names, I. M. A., prior to publication.

PHYSICAL AND OPTICAL PROPERTIES

Kingsmountite occurs in white to very light brown hemispherules up to 2.0 mm in diameter; these are composed of tightly packed radiating arrays of crystals on the type specimens. The hemispherules are flat-topped, suggesting that they extended across very thin seams in the rock. The streak of kingsmountite is white and the lustre is pearly to fibrous on fresh fracture surfaces. The Mohs hardness is approximately 21/2. The occurrence of cleavages could not be determined due to the extremely small crystal size and the imperfect nature of the crystals. The density, determined by flotation in heavy liquids, is 2.51(3) g/cm³. The disparity between this and the calculated value of 2.58 g/cm³ is likely due to the presence of air or water between the fibrous crystals.

Kingsmountite is optically biaxial (-) with $2V = 62(5)^{\circ}$. The refractive indices are α 1.575(3), β 1.581(3), γ 1.583(3). The orientation, given relative to the lath-like habit of fragments, is: Y perpendicular to the lath, Z and Xare parallel to the lath; Z intercepts the direction of elongation at 35(5)°. The optical data are in good agreement with the theoretical values obtained using the Gladstone-Dale relationship and the constants of Mandarino (1976). The value of K_c obtained using the chemical analysis is 0.222, which compares very well with the value obtained from the refractive indices and the calculated density, $K_P = 0.225$. The compatibility of the data $(1.000 - K_P/K_c)$ is 0.013, giving superior agreement (Mandarino 1979). Kingsmountite does not fluoresce in ultraviolet radiation.

MORPHOLOGY

Crystals of kingsmountite were too small for goniometric study. However, the surface of the spherules comprises thousands of terminations of very small kingsmountite crystals. Several of these were photographed using a scanning electron-microscope and a photomicrograph of some crystals of kingsmountite is shown as Figure 1. The bladed habit of the crystals is immediately apparent and the striking resemblance to the morphological appearance of montgomeryite further supports the relationship proposed for these two species.

COMPOSITION

Kingsmountite was chemically analyzed with an ARL-SEMQ electron microprobe using an



FIG. 1. Scanning-electron-microscope photomicrograph of kingsmountite NMNH # 120973 (395x).

operating voltage of 15 kV and a sample current of 0.15 μ A. The data were corrected using Bence-Albee factors. The standards used were manganite for manganese, hornblende for iron, and montgomeryite for aluminum, magnesium, calcium and phosphorus. A wavelength-dispersive scan indicated the absence of any elements with atomic number greater than nine, except those reported herein. Microchemical tests revealed a strong reaction for Fe²⁺ and a very weak one for Fe³⁺, suggesting that most of the iron is divalent.

Water was determined by simultaneous thermogravimetric-evolved gas analysis, using a Mettler TA-1 Thermoanalyzer coupled with an Inficon 1Q 200 mass spectrometer. A sample weighing 11.294 mg, in equilibrium with a moderate atmospheric humidity, lost 3.79% water by weight when subjected to a vacuum of 10^{-7} torr for 70 h at 25°C in the thermoanalyzer. Upon heating in vacuum, a further 16.77% was lost between 55 and 634°C, totalling 20.6% H₂O by weight. This loss occurred in two major steps, indicated by water-vapor pressure maxima at 297 and 343°C (ascribed to dehydration and to dehydroxylation, respectively).

The resultant analyses are presented in Table 1. An examination of the analytical data in-

TABLE 1. CHEMICAL ANALYSES OF KINGSMOUNTITE

	#1	#2	# 3	Average
MgO	0.2	0.2	0.2	0.2
CaO	15.1	15.0	14.5	14.9
MnO	8.2	7.8	8.3	8.1
Fe0*	4.2	4.2	3.9	4.1
A1203	16.5	16.8	16.7	16.7
P205	36.0	35.9	35.9	35.9
H ₂ 0				20.6
Total				100.5

* Iron was determined as total iron and was calculated here as FeO.

****** Water determined by one DTA/TGA analysis. Accuracy of data: $\pm 3\%$ of the amount present.

dicates that the composition of kingsmountite varies only slightly among the three spherules analyzed. Based on six phosphorus atoms and four hydroxyl groups, the average analysis gives a calculated formula of $(Ca_{3.15}Mn_{0.85})$ $(Fe^{2+}_{0.56}Mn_{0.50}Mg_{0.06})$ $(Al_{3.88}Fe^{3+}_{0.12})$ $(PO_4)_{6.00}$ $(OH)_4$ • 11.6H₂O, which corresponds to the ideal formula Ca₄FeAl₄(PO₄)₆(OH)₄• 12H₂O, the ferroan analog of montgomeryite Ca₄MgAl₄(PO₄)₆ $(OH)_4 •$ 12H₂O.

The formula of kingsmountite is subject to some ambiguity involving the assignment of Mn and Fe^{2+} to the various sites. We have assigned Mn^{2+} rather than Fe^{2+} to the calcium sites in order to account for the deficiency of calcium, because Mn^{2+} has an ionic radius much nearer that of calcium than that of Fe^{2+} . In kingsmountite, the sites equivalent to those containing magnesium in montgomeryite have the cation content of $(Fe^{2+}_{0.56}Mn_{0.50}Mg_{0.06})$; kingsmountite is thus the ferroan analog of montgomeryite. However, it is possible that some Fe^{2+} may be substituting for calcium.

X-RAY CRYSTALLOGRAPHY

Attempts were made to obtain a specimen suitable for single-crystal X-ray analysis. Spherules of fibrous material separate into elongate fibres but even the smallest of these gave uninterpretable results. However, powder-diffraction patterns of montgomeryite and kingsmountite are very similar, and because other data indicated an isostructural relationship, we assumed that the lattice parameters of kingsmountite should be similar to those of montgomeryite. Table 2 contains a listing of d values obtained using a polycrystalline sample in a Gandolfi camera with Si as an internal standard. Initial indexing was accomplished using lattice parameters of montgomeryite. Least-squares refinelattice parameters ment vielded the а 10.029(6), b 24.46(1), c 6.258(4) Å and β 91.16(7)°. Final indexing of the powder data (Table 2) was satisfactorily accomplished assuming that the cell is C-centred, as for montgomervite. The low standard errors in the lattice parameters confirm their validity, despite the absence of single-crystal data.

Moore & Araki (1974) determined that the space group of montgomeryite is C2/c. Fanfani *et al.* (1976) subsequently determined that the

d _{obs}	^d calc	hkl	I/I ₀	d _{obs}	^d calc	hkl	1/10				
12.28	12.23	020	50	2.751	2.752	331	ı				
9.30	9.28	110	20		2.747	081					
6.33	6.33	130	30	2.679	2.679	202	10				
6.11	6.12	040	5	2.624	2.624	190	60				
5.57	5.57	021	20	2.416	2.418	281 242	5				
5.15	5.14	111	100		2.416	370					
4 42	4.42	131	20		2.415	191					
3 89	3,88	240	10		-						
3 60	F 3.61	151	.2	2.317	2.320	440	2				
5.00	3.58	151	-	2.258	2.263	172 312	5				
2 21	F 3 32	241	30	2,182	-		2				
3.51	3 31	310		1.971			1				
	3 30	170		1.889			2				
2 16	3.16	260	10								
3.15	2 12	002		1.846			5				
	L 31.13	002		1.779			2				
3 00	2.00	220	Б	1.747			10				
3.09	2.05	330	40	1.659			1				
2.900	2.901	177	20	1.565			5				
2.910	5 2 910	122	30	11000							
2.012	2.019	261		1.547			2				
	L 2.009	201		1.487			2				
				1.463			2				
				1.358			Ī				

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR KINGSMOUNTITE

Data obtained using a polycrystalline sample in a 114.6 ${\rm mm}$ diameter Gandolfi camera with Cu Xa X radiation and N.B.S. silicon as an internal standard. Intensities are estimated visually.

true space group is of lower symmetry than this, as indicated by the presence of some very weak intensities for diffraction planes h0l, l odd. They obtained a satisfactory structure-determination with space group C2. The isostructural relation between montgomeryite and kingsmountite indicated by our data therefore suggests that kingsmountite also has space group C2. The powder data are consistent with this suggestion, but single-crystal data will be required to confirm it.

OCCURRENCE

The geology of the Foote Mineral Company spodumene mine, near Kings Mountain, North Carolina, has been described by Kesler (1961). One of the authors (JSW) has made an extensive study of the complex suite of minerals found there; it was during one of many collecting trips to the locality that the kingsmountite specimens were found in the spring of 1968. There are three type specimens, all having once been part of a continuous surface. Kingsmountite is sparsely scattered over the surface of these specimens.

Three distinct parageneses have been established at the Foote mine: (1) primary, (2) late hydrothermal, and (3) supergene.

The primary minerals

The only primary phosphate mineral is manganoan apatite, present as very dark green anhedral crystals embedded in coarse-grained microcline, quartz and spodumene. It is widely distributed throughout the pegmatite, and moderately abundant. Presumably this apatite, when attacked by late hydrothermal solutions, provided most if not all of the phosphorus for the minerals of the late hydrothermal and supergene stages. There are large areas of pegmatite which are extensively leached, with vugs usually lined with very small albite and quartz crystals. All of the primary apatite has been removed from these parts of the pegmatite.

The late hydrothermal minerals

The secondary (late hydrothermal) suite consists, in part, of apatite, autunite, fairfieldite, collinsite, messelite, eosphorite, lithiophilite, lithiophosphate, a roscherite polymorph, and switzerite. These minerals are essentially limited in their occurrence to broad, flat fissure-surfaces or heavily brecciated zones which seem to have been conduits for hydrothermal solutions. Eucryptite seems to occur only in these zones. Secondary apatite is found throughout the quarry in a remarkable variety of crystal habits and colors (light pink to mauve is dominant).

The supergene minerals

The tertiary (supergene) suite is found in the upper levels of the quarry in a zone that extends some 7 to 12 m down from the soil zone; it is clearly delineated by a brownish stain caused by descending surface waters. The great variety of phosphate species found in the partly decomposed pegmatite in this zone is remarkable. The more common tertiary minerals include beraunite, ferrisicklerite, frondelite, hureaulite, kingsmountite, mitridatite, paravauxite, phosphosiderite, rockbridgeite, strengite, strunzite, triploidite, vivianite and jahnsite. Non-phosphate minerals found in this zone are birnessite, gypsum and siderite.

Kingsmountite is known to occur only on somewhat irregular fissure surfaces, the narrowness of which has restricted the development of what would have been hemispherical crystal clusters, causing the flat-topped appearance of the type specimens. The mineralogy is simple, associated species being only mitridatite, birnessite and an unidentified manganese aluminum phosphate mineral. The mitridatite has the appearance of a thin film of yellow-green to olive-green paint covering the rock surface. Where the film is thicker and mitridatite more coarsely crystalline, the color becomes dark reddish brown. Irregular botryoidal masses of birnessite no larger than 2 mm are scattered randomly on the mitridatite films. Kingsmountite is also scattered randomly on the mitridatite films, and is among the last minerals to form.

References

- FANFANI, L., NUNZI, A., ZANAZZI, P.F. & ZANZARI, A.R. (1976): Additional data on the crystal structure of montgomeryite. *Amer. Mineral.* 61, 12-14.
- KESLER, T.L. (1961): Exploration of the Kings Mountain pegmatites. *Mining Eng.* 13, 1063-1068.
- MANDARINO, J.A. (1976): The Gladstone-Dale relationship — I: Derivation of new constants. Can. Mineral. 14, 498-502.
- (1979): The Gladstone-Dale relationship. III. Some general applications. Can. Mineral. 17, 71-76.
- MOORE, P.B. & ARAKI, T. (1974): Montgomeryite, $Ca_4Mg(H_2O)_{12}[Al_4(OH)_4(PO_4)_6]$: its crystal structure and relation to vauxite, $Fe^{2+}_2(H_2O)_4$ $[Al_4(OH)_4(H_2O)_4(PO_4)_4] \cdot 4H_2O$. Amer. Mineral. 59, 843-850.
- Received March 1979; revised manuscript accepted June 1979.