X-RAY INVESTIGATION OF FERRIERITE, A ZEOLITE

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ABSTRACT

Ferrierite was named and described in 1918 by R. P. D. Graham. The Kamloops Lake locality is its only reported occurrence. An x-ray study of the mineral indicates cell dimensions: $a_0 = 19.12 \pm 0.06$ Å, $b_0 = 14.14 \pm 0.03$ Å, $c_0 = 7.48 \pm 0.02$ Å and an orthorhombic body centered lattice. The choice of axes is Graham's and departs from the conventional orthorhombic orientation in which $c < a < b$. The following space groups are compatible with the x-ray observations: $Immm$, $I222$, $Imm2$, $I2_1I2_1I2_1$. Tests for piezoelectricity in liquid nitrogen were negative or inconclusive. From the cell content calculation a general formula of $(Na, K)_4Mg_2(Si_{30}Al_6)O_{72}(OH)_2 18H_2O$ is indicated. Although ferrierite, because of its high magnesium content, is unusual among zeolites, rehydration and other tests point to a tectosilicate framework structure rather than a sheet structure, and consequently it is considered to be a true zeolite.

INTRODUCTION

Ferrierite was described by R. P. D. Graham in 1918 and named in honor of the late W. F. Ferrier of the Canadian Geological Survey. To date, the only locality from which ferrierite has been reported is the north shore of Kamloops Lake in British Columbia where it occurs as spherical aggregates of radiating blades enclosed in chalcedony. This chalcedony fills seams in basalt flows of the Kamloops Volcanic Group of lower Miocene age, according to Graham (1918). A complete description of the petrology of the area and the occurrence of ferrierite is given in Graham's paper.

The presence of almost 3% magnesia in ferrierite makes it unusual among zeolites. Likewise of interest is the high silica content which is over 69%. Silica-rich heulandite (clinoptilolite) and mordenite approach ferrierite in silica content, but most zeolites only contain silica in the range between 40% and 60%. The high content of magnesia, together with the platy structure of ferrierite, raises some doubt as to whether or not the mineral is a zeolite. This problem was considered in the present investigation.

ACKNOWLEDGMENTS

The first material used for x-ray and optical study was obtained from the Geological Museum of Harvard University through the kindness of C. Frondel. Later, additional material was given by R. P. D. Graham. The x-ray work was carried on in the Mineralogical Laboratory of the University of California, Berkeley. Professor A. Pabst contributed a great deal to the study, not only in making valuable suggestions but in actually assisting in much of the x-ray work.

PHYSICAL PROPERTIES

In the present study, in addition to a re-examination of the recorded data on ferrierite, additional information was obtained using x-ray methods. Graham's earlier work, without benefit of x-rays, proved to be accurate and very satisfactory.

Graham measured two of the indices of refraction by total reflection, and also the size of the obtuse optic axial angle. From these he calculated the size of the acute optic axial angle and the third index of refraction. The indices determined in immersion liquids during the present investigation were within 0.002 of Graham's, which is within the usual limit of error.

Graham oriented the crystals with a-axis$=\alpha$, b-axis$=\beta$, c-axis$=\gamma$. He notes, "in each case compensation takes place when the quartz wedge is inserted normal to the length." For this to be true his quartz wedge must have been cut from the less usual position with its length parallel to the c-axis of the quartz crystal. Graham states that crystals are tabular parallel to (100) and elongated parallel to the c-axis. This orientation is most common, but it is also true that some crystals are tabular parallel to (100) but elongated parallel to the b-axis. This difference in elongation aided in the x-ray work.

In regard to the orientation of the crystals, Graham's orientation has been followed. This leads to $c<b<a$ rather than the conventional $c<a<b$ for the orthorhombic system.

Graham determined the specific gravity to be 2.150, but he did not state the method used in making the determination. A precise determination is difficult; air spaces between the tabular crystals tend to give values too low, and included chalcedony raises the values. Occasionally opal is present along with the chalcedony. Westphal balance determinations made on small grains carefully selected under the microscope gave the best results and indicates the specific gravity of 2.15, suggested by Graham as acceptable.

Correlation with morphology. Graham reported the angle $100\wedge101=67°47'$, obtained by measuring 2 or 3 crystals with minute (101) faces yielding only faint images. This corresponds to $c:a=0.4084$. X-ray measurements lead to a ratio of $c_0:a_0=0.3922$, which would require that the angle $100\wedge101$ be $68°35'$.

X-RAY DATA

Powder photographs taken with copper radiation and a nickel filter gave sharp lines and led to the data in Table 1. Lines with d_{hkl} less than 2.5 Å were not indexed. Seven Weissenberg and precession patterns were fully indexed over this range to aid in obtaining the powder pattern indexing.

TABLE 1. INDEXED PORTION OF POWDER PATTERN OF FERRIERITE

hkl	$d_{calc.}$	$d_{meas.}$	$I_{obs.}$	hkl	$d_{calc.}$	$d_{meas.}$	$I_{obs.}$
110	11.38	11.33	2	501	3.41	3.42	2
200	9.56	9.61	10	240	3.32	3.31	2
020	7.07	7.00	3	600	3.19	3.20	1
101	6.97			141	3.15	3.15	3
011	6.61	6.61	2	312	3.14		
310	5.81	5.84	5	222	3.12		
220	5.68			521	3.07	3.07	3
211	5.44			431	3.06		
121	4.96	4.96	1−	530	2.97	2.97	3
301	4.85	4.80	1−	402	2.95		
400	4.78			620	2.905	2.90	2
130	4.57	4.58	1−	132	2.896		
321	4.00	3.99	9	611	2.871		
031	3.99			341	2.857		
420	3.96			440	2.842		
411	3.87	3.88	1	150	2.798		
330	3.79	3.79	2	422	2.719	2.72	2
002	3.74			710	2.682		
510	3.69	3.69	5	332	2.662		
231	3.68			051	2.645	2.64	2
112	3.55	3.54	8	512	2.627		
040	3.53			350	2.585	2.58	3
202	3.48	3.49	8	042	2.569		
				701	2.566		
				251	2.549		

Additional lines, not indexed:

2	2.49	2	2.11	4	1.78	1−	1.55	2	1.37
2	2.43	2	2.04	1−	1.72	2	1.50	1	1.34
4	2.37	3	2.00	2	1.65	2	1.47	1	1.27
1−	2.32	B3	1.94	B2	1.63	3	1.43	2	1.25
1−	2.26	3	1.87	2	1.60	1−	1.41		

Lines marked B are broad.

CELL DIMENSIONS AND SPACE GROUPS

From Weissenberg and precession patterns, using copper and molybdenum radiation and correcting for shrinkage, the cell dimensions obtained were:

$$a_0 = 19.12\ \text{Å} \pm 0.06\ \text{Å}$$
$$b_0 = 14.14\ \text{Å} \pm 0.03\ \text{Å}$$
$$c_0 = 7.48\ \text{Å} \pm 0.02\ \text{Å}$$

A study of the Weissenberg and precession patterns leads to the conclusion that the only systematic extinction occurs for *hkl* when $h+k+l$

is even. This is also evident from indexing of powder patterns and fulfills the requirements for a body-centered lattice. No additional extinctions indicating glide planes could be established and consequently the following space groups are consistent with the x-ray data: $Immm$; $I222$; $I2_12_12_1$, $Imm2$.

Robert M. Douglass and Edward Clark, then graduate students at the University of California, kindly assisted in carrying out tests for piezoelectricity in liquid nitrogen on five selected crystals. Results of repeated trials on all five crystals were negative or inconclusive. A positive result would have been an indication for the group $Imm2$, but lacking evidence of this it is not possible to select any one uniquely.

CELL CONTENT OF FERRIERITE

Because of the lack of sufficient pure material, no new chemical analyses have been made, and the cell content determined here is based on Graham's analysis.

Cell volume: 19.12 Å×14.14 Å×7.48 Å = 2022.26 Å^3
Density: 2.15
Cell weight: 4347.86×10^{-24} grs.

Graham's Analysis		Number of Atoms in Cell	
SiO_2	69.13 wt. %	Si	30.15
Al_2O_3	11.44	Al	5.88
CaO	none	Mg	1.895
MgO	2.92	Na	3.35
Na_2O	3.97	K	0.20
K_2O	0.36	H	37.94
H_2O	13.05	O	91.76
	100.87		

The number of atoms in the cell was determined using a weight for the unit of atomic weight of 1.6602×10^{-24}grs.

As will be noted, the sum of Si+Al is near 36 and the number O−H/2 is near 72, so O/(Si+Al) is close to 2/1, a ratio characteristic of the zeolites. Based on a general formula

$$(Na, K)_x(Mg_{1+(y/2)}, Al_{z/3})(Si_{36-(x+y+z)}, Al_{(x+y+z)})O_{72}(OH)_2 18H_2O$$

a possible formula close to the actual one would be

$$(Na, K)_{3.35}(Mg_{1.98}, Al_{0.18})(Si_{30.15}, Al_{5.85})O_{72}(OH)_2 18H_2O.$$

The actual formula based on Graham's analysis is

$$(Na, K)_{3.55}(Mg_{1.895}, Al_{0.03})(Si_{30.15}, Al_{5.85})O_{71.82}(OH)_{1.94} 18H_2O$$

which is close to the theoretical formula. Rounded off with simple subscripts, this would suggest the formula for ferrierite:

$$(Na, K)_4Mg_2(Si_{30}, Al_6)O_{72}(OH)_2 18H_2O.$$

In the generalized formula suggested first above there is no guide as to the range of values for x, y, z, as no comparison with other members of a series can be made, and there is no definite knowledge of the structure. Consequently, no limits of variation for x, y, z, are given, although they undoubtedly exist.

STRUCTURE

The formula suggested requires a framework structure of linked (Si, Al) O_4 tetrahedra sharing all corners with 2 additional negative ions (OH) for every 36 linked tetrahedra. An example of this type of structure in which anions are added to the framework is shown by scapolite and cancrinite, although a specific example of added (OH) ions is not known.

The single eminent cleavage of ferrierite *a*(100) and the long spacing normal to this cleavage ($a_0 = 19.12$ Å) might be considered to indicate a sheet structure. However, rehydration experiments indicate most of the water is not firmly bound and hence probably not involved in the sheet structure. Ferrierite heated at 125° for 30 minutes lost 2.73% H_2O and on standing 2 days regained almost all (98.8%) of the lost water. Heating at 250° for 30 minutes caused a loss of 6.21% of which almost all (97.7%) was regained in 24 hours. This high degree of rehydration indicates that a tectosilicate structure is most probable and that the mineral is a true zeolite.

REFERENCE

GRAHAM, R. P. D. (1918), On ferrierite, a new zeolitic mineral, from British Columbia; with notes on some other Canadian minerals: *Royal Society of Canada, Proc. & Trans.*, 3rd Ser., **12**, Sect IV, 185–190.