

## SHORT COMMUNICATIONS

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### Ashcroftine is not a zeolite!

DURING systematic studies on zeolite chemistry, Hey and Bannister (1933) showed that 'kalithomsonite' of Gordon (1924) was not immediately related to any major zeolite group and was therefore a new species. Named *ashcroftine*, the species has been generally accepted as a highly complex zeolite, principally because of its structure cell data and chemical composition. Smith (1963) suggested that ashcroftine may be structurally related to paulingite on the basis of the similarity between their cell data.

Because of our interest in zeolites, we decided to study type ashcroftine in more detail. A vial of small pale pink needles from Gordon's type specimen was kindly provided by Mr. Paul E. Desautels of the U.S. National Museum (Washington, D.C.). No difficulty was encountered in obtaining a suitable single crystal for X-ray study, which gave  $a\ 24.044 \pm 0.004$ ,  $c\ 17.553 \pm 0.008$  Å. Indexed powder data, obtained from a diffractometer slide mount with Si ( $a\ 5.4301$  Å) as internal standard, and used for cell refinements, appear in table I. The X-ray data of Hey and Bannister compare well with ours, if their  $a$ -axis is divided by  $\sqrt{2}$ . On the basis of assorted rotation and Weissenberg photographs, we have found the space group to be  $I4/mmm$ ,  $I4mm$ ,  $I422$  or  $\bar{I}4m2$ , which differs from the tentative space group of Hey and Bannister. Thus their cell with [110] as the  $a$ -axis should be based on the  $F$ -centred cell.

We then collected a set of three-dimensional single crystal data as a step toward detailed crystal structure analysis. The Patterson synthesis could not be interpreted with the accepted composition of the mineral; accordingly, an ARL electron microprobe scan was performed. It was discovered that only trace quantities of aluminum were present and that the reported alumina is actually yttria with minor amounts of other rare-earth oxides. The other elements qualitatively agree with the analysis of Whitfield in Gordon and accordingly we accepted this analysis, but with yttria in place of alumina. Since the probe results were not corrected for absorption and atomic number effects, these data are not included herein.

The crystal cell computation appears in table II. It is not immediately reconcilable into any simple formula. Assuming that Nature's ways are simple, we have attempted to extract a reasonable formula based on an integral number of silicon atoms for the space group  $I4/mmm$ . The equipoint rank number must be some multiple of 8, since lower numbers cannot accommodate tetrahedral geometries. The analysis then suggests there must either be 12 or 13 coordinate-independent silicon atoms in the cell. A fair fit with whole numbers, in multiples of 4, can be obtained if we assume 12 independent silicon atoms or  $12 \times 8 = 96$  Si in the cell. Recomputing, we obtain the

TABLE I. *Ashcroftine, Narsarsuk, West Greenland. Powder data; spacings in Å*

<i>I</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>	<i>I</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>	<i>I</i>	<i>d</i> <sub>obs</sub>
100	17·027	17·002	110	25	4·252	4·250	440	10	2·575
10	14·209	14·177	101	10	4·127	4·124	530	10	2·563
90	12·043	12·022	200	15	4·006	4·007	600	10	2·534
15	8·514	8·501	220	15	3·826	3·825	442	10	2·437
60	7·615	7·603	310	20	3·672	3·672	541	10	2·407
25	7·098	7·088	202	25	3·542	3·544	404	5	2·314
20	6·108	6·106	222	10	3·485	3·488	622	5	2·282
30	6·014	6·011	400	15	3·402	3·400	710	10	2·126
15	5·666	5·667	330	15	3·209	3·212	514	15	2·061
35	5·379	5·376	420	50	3·114	3·117	642	5	1·8402
10	4·720	4·715	510	10	3·004	3·004	800	10	1·7571
10	4·639	4·638	501	15	2·959	2·959	604	10	1·7054
			431	10	2·939	2·940	811	10	1·6369
10	4·389	4·388	004	20	2·831	2·834	660		
5	4·324	4·327	521	50	2·687	2·687	840		

TABLE II. *Ashcroftine. Crystallochemical calculations*

	Wt. %*	Empirical cell contents†	Ratios to Si = 96	Theor. wt %‡	Gladstone-Dale calculations§
SiO <sub>2</sub>	38·09	Si 101·3	96·0	40·8	0·0846
Yt <sub>2</sub> O <sub>3</sub>	26·61	Yt 37·7	35·7	25·6	0·0368
MgO	0·87	Mg 3·4	3·3	—	—
CaO	5·72	Ca 16·3	15·4	6·3	0·0143
Na <sub>2</sub> O	3·62	Na 18·7	17·6	3·5	0·0064
K <sub>2</sub> O	5·65	K 19·2	18·1	5·3	0·0101
H <sub>2</sub> O <sup>+</sup>	12·00	OH 213·2	202·0	10·3	} 0·0624
H <sub>2</sub> O <sup>-</sup>	6·40	H <sub>2</sub> O 56·8	53·8	8·2	
MnO	0·79	Mn 1·8	1·7	—	k = 0·2146
	99·75			100·00	

\* Analysis of Whitfield in Gordon (1924) with Al<sub>2</sub>O<sub>3</sub> reckoned as Yt<sub>2</sub>O<sub>3</sub>.

† Based on *a* 24·044, *c* 17·553 Å, and the specific gravity of 2·61 reported by Hey and Bannister.

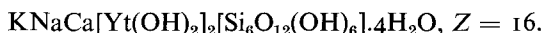
‡ For the formula KNaCaYt<sub>2</sub>Si<sub>6</sub>O<sub>12</sub>(OH)<sub>10</sub>·4H<sub>2</sub>O, M.W. = 882·55.

§ For proposed formula and  $n = (2\omega + \epsilon)/3 = 1·559$ . The optical data from Hey and Bannister were used.

approximate formula K<sub>16</sub>Na<sub>16</sub>Ca<sub>16</sub>Mg<sub>4</sub>Yt<sub>36</sub>Si<sub>196</sub>O<sub>192</sub>(OH)<sub>180</sub>·64H<sub>2</sub>O. This suggests a simpler formula, with  $Z = 16$ : KNaCaYt<sub>2</sub>Si<sub>6</sub>O<sub>12</sub>(OH)<sub>10</sub>·4H<sub>2</sub>O.

The formula requires less yttria; though we do not have quantitative analyses of the much denser lanthanides, they are nevertheless present, accounting for a higher weight-percentage of reported Yt<sub>2</sub>O<sub>3</sub>. We have also assumed that Mg may be present either as an impurity or as a substituent for other cations.

We suggest a tentative formula for ashcroftine:



This formula is akin to that of lovozerite, Na<sub>2</sub>Zr[Si<sub>6</sub>O<sub>12</sub>(OH)<sub>6</sub>], a rare mineral occurring

as a hydrothermally reworked product of eudialyte in nepheline syenites. Indeed, ashcroftine was found in vugs in augite-syenite at Narsarsuk, Greenland and for this reason the presence of yttria is not surprising. Finally, we have computed wt % for the proposed ashcroftine formula (table II) and these values are in fair agreement with the Whitfield analysis. The Gladstone-Dale calculation in table II yielded  $d = (n-1)/k = 2.51 \text{ g/cm}^3$  which, with the earlier discussion, suggests that the observed specific gravity of 2.61 reported by Hey and Bannister is too high.

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## Rankinite and kilchoanite from Tokatoka, New Zealand

Two polymorphs of tricalcium disilicate, rankinite and kilchoanite, have been discovered near Tokatoka, New Zealand.

The first record of high-temperature calc-silicates in the Tokatoka district was by Mason (1957) who described larnite, gehlenite, spurrite, and scawtite from a contact zone adjacent to a small dyke near Rehia, 2 miles SE. of Tokatoka. During a later survey the writer discovered several more localities of high-temperature calc-silicates; a study of the mineralogy and petrology of these occurrences is in progress.

Examination of one locality, a limestone/basalt contact, 1 mile NNW. of Tokatoka revealed the presence of rankinite and kilchoanite. Neither of these minerals has been recorded previously in the district.

Rankinite and kilchoanite occur with other high-temperature calc-silicates in a band, approximately 1 m wide, of dark-grey flinty rocks. These rocks are separated from the basalt by a narrow zone a few millimetres wide of wollastonite and grossular and from the unmetamorphosed country rocks by white coarsely crystalline wollastonite-, scawtite-, tobermorite-, and hydrogrossular-bearing limestones.

Thin section and X-ray diffraction study of the dark calc-silicate rocks show that they consist of essentially monomineralic lenses and bands of larnite, spurrite, and rankinite. The dark colour is due to finely disseminated iron ores; the only other