TWO YTTRIUM MINERALS: SPENCITE AND ROWLANDITE[1]

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ABSTRACT

Spencite is a new borate-silicate of calcium and yttrium,

$$(Ca, Fe)_2(Y, La)_3(B_3Si_{4.3}Al_{.7})_8(O, OH, F, Cl)_{20}$$

from a pegmatite in Cardiff township, Haliburton County, Ontario. Found as dark reddish brown to brownish black anhedral masses. Hardness 3½, specific gravity 3.05. Metamict; isotropic with *n* near 1.630. When the mineral is heated at 325° C the *n* increases to about 1.640 and the specific gravity to 3.20. At high temperatures the mineral decomposes before it recrystallizes and *x*-ray diffraction data cannot be obtained. Spencite is related chemically to the minerals of the Datolite Group and may be isostructural with them. It is named after the Canadian mineralogist Hugh S. Spence.

A re-examination of the little known mineral rowlandite from Baringer Hill, Texas, establishes it as a valid species. Composition near $(Y, Fe, Ce)_3(SiO_4)_2(F, OH)$. Metamict; with *n* 1.704. Hardness 5½, specific gravity 4.39; *x*-ray powder data are given for material recrystallized in nitrogen at 900° C (with mean *n* 1.76, specific gravity 4.55).

SPENCITE

This new mineral was collected by Hugh S. Spence in 1934 from a prospect pit in Cardiff township, lot 7, concession XX, Haliburton County, Ontario, and was tentatively identified as thalenite. It occurred as masses in a narrow pegmatite stringer in a vuggy pyroxenite, associated with calcite, red apatite crystals, diopside, purple fluorite, and wernerite, about 200 feet from an outcrop of normal reddish granite pegmatite. About 24 pounds of pure material were obtained, including a single mass weighing 8 pounds that apparently was a fragment of a single crystal. Cracks in the mineral are filmed by a fine-grained white carbonate that is high in yttrium.

Spencite is dark reddish brown to brownish black in colour, translucent in thin splinters, and has a weakly vitreous lustre. The powder is greenish grey. The mineral is metamict and isotropic. The index of refraction varies between 1.627 and 1.653 with the bulk near 1.630. The colour in transmitted light is pale olive-brown to yellowish brown. The hardness is 3½ and the measured specific gravity is 3.05. When heated in air at 325° C for 46 hours the average index of refraction increased to about 1.640 and the specific gravity to 3.20; the material was still isotropic and did not give a diffraction pattern.

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A quantitative chemical analysis, carried out in unusual detail by C. O. Ingamells, with supplementary determinations by others, is cited in Table 1. The analysis sample weighed 15 grams. It had been treated by heavy liquid and magnetic techniques, which removed traces of foreign matter, and under the microscope appeared homogeneous. The mineral does not afford a distinct *x*-ray powder diffraction pattern, either unheated or when heated near to the point of apparent chemical decomposition, and this has hindered the interpretation of the systematic crystallochemical relations.

TABLE 1. CHEMICAL ANALYSIS OF SPENCITE

		M.Q.	Atoms per 8(B, Si, Al, P, Ti)	
Na_2O	0.11	.0018	0.037	2.09
K_2O	0.01	.0001	0.002	
MgO	0.50	.0124	0.127	
CaO	7.81	.1393	1.424	
SrO	0.05	.0005	0.005	
Fe_2O_3*	3.22	.202	0.412	
MnO	0.60	.0084	0.086	
Y_2O_3†	28.20	.11249	2.554	3.00
Ce_2O_3	1.44	.0044	0.090	
La_2O_3‡	4.16	.0128	0.262	
ThO_2	2.44	.0092	0.094	
Al_2O_3§	3.87	.0380	0.777	8
TiO_2	0.27	.0034	0.035	
B_2O_3‖	10.04	.1442	2.949	
SiO_2	24.89	.4144	4.237	
P_2O_5	0.02	.0001	0.002	
Cl	0.45	.0127	0.130	
F	0.44	.0232	0.237	
H_2O+	9.82	Oxygen atoms = 20.7		
H_2O-	1.93	(H_2O, F, Cl excluded)		
Total	100.27			
Less O = F, Cl	0.28			
	99.99			

*Total iron reported as trivalent, but believed to be present in the non-metamict mineral as divalent and so treated in the derived formula.

†*X*-ray spectrographic analysis indicates that the other rare earths of the yttrium group are present only in very small amounts (chiefly Gd, Er, Ho).

‡*X*-ray spectrographic analysis indicates that other lanthanide elements are present only in small amounts (chiefly Nd).

§Includes BeO in undetermined but quite small amount.

‖A confirmatory quantitative spectrographic analysis by H. Bastrom of the U.S. Geological Survey gave 10.0 B_3O_3.

NOTE: Examination by optical and *x*-ray spectrographic methods shows the presence in trace amounts of U, Sn, Cu, Ni, Co, Pb, Zr, and Sc.

Basically, spencite is a borate-silicate of calcium and yttrium. Since the main cations are large in size, the analysis was calculated on the assumption that the subordinate small ions Al and Ti were part of the anionic framework together with Si and B. The trivalent rare earths together with Th, and the divalent cations together with iron as Fe^2 and Na were grouped separately. In this basis, virtually whole number ratios were obtained when the total of small ions (Si, B, Al, Ti), was taken as 8 (Table 1), and the formula may be written

$$(Ca_{1.36}Fe_{.39}Mg_{.12}Mn_{.09}Na_{.04})_2(Y_{2.56}Ce_{.09}La_{.26}Th_{.09})_3(Si_{4.24}B_{2.95}Al_{.78}Ti_{.03})_8 (O_{18.21}OH_{1.42}F_{.24}Cl_{.13})_{20}$$

In this formula the total of divalent cations has been adjusted to 2 from the calculated total of 2.09. The content of H_2O is uncertain. The analysis indicates $5H_2O$, but metamict minerals commonly contain much secondary water and the actual amount of essential H_2O present, doubtless is less than $5H_2O$ and may be nil. When heated at 325° C, the mineral loses 76.0 per cent of the total H_2O present (11.75 weight per cent). The irrational content of (F, Cl) indicates that (OH) must be present.

The composition suggests that the mineral may be structurally related to the Datolite Group (Table 2). In this group, the isostructural relation of datolite to herderite was recognized by Strunz (1936). The relation of datolite to bakerite and homilite was established by Frondel (1947) and later, with the inclusion of gadolinite, by Ito & Mori (1953). The structure of datolite as described by the latter authors is composed of complex sheets composed of interlinked (SiO_4) and (BO_3OH) tetrahedra with the composition $[B_2Si_2O_8(OH)_2]$. The sheets are bonded together by Ca ions coordinated with six oxygens and two (OH) groups. In herderite, Be replaces B and P replaces Si. In gadolinite, as shown by Ito & Mori (1953), Ca is replaced by Y, B by Be, (OH) by O, and in addition two Fe^2 ions enter the vacancies at 0, 0, 0 and 0, 1/2, 1/2 in the unit cell.

TABLE 2. MEMBERS OF THE DATOLITE GROUP

Name	Unit cell contents	a_0 (Å)	b_0	c_0	Beta (degrees)		Reference
Datolite	$Ca_4B_4(SiO_4)_4(OH)_4$	9.62	7.60	4.84	90	9	Ito & Mori (1953)
Bakerite	$Ca_4B_4(Si_3B_1)$ $(O_{15}(OH)_1)(OH)_4$						
Homilite	$Fe_2Ca_4B_4(SiO_4)_4O_4$	9.67	7.57	4.74	90	22	Tennyson, in Strunz (1957)
Herderite	$Ca_4Be_4(PO_4)_4(OH,F)_4$	9.82	7.70	4.81	90	6	Strunz (1936), Pavlov & Belov (1957)
Gadolinite	$Fe_2Y_4Be_4(SiO_4)_4O_4$	9.89	7.55	4.66	90	33	Brandenberger (1940)
Garrelsite	$Ba_4B_4(Si_2B_2)$ $(O_{14}(OH)_2)(OH)_4$						Christ (1959), Milton *et al.* (1955)
Spencite	$(Ca,Fe)_2Y_3(B,Si)_4(Si,$ $A10_4)_4(O,OH,F,Cl)_4$						

NOTE: Space group $P\ 2_1/a$

In bakerite, one of the four Si atoms in the cell is replaced by B, with a concomitant substitution of an (OH) for O in its coordination group. The composition of garrelsite has been discussed by Christ (1959), who also corrects the formula of bakerite as earlier written by Kramer & Allen (1956) and Frondel (1947). Garrelsite, however, is not isostructural with the Datolite Group although, like spencite, it is related chemically to the minerals of this group.

The formula of spencite can be recast in the structural form of the Datolite Group as follows

$$(Ca_{1.36}Fe_{.39}Mg_{.12}Mn_{.09}Na_{.04})_2(Y_{2.56}Ce_{.09}La_{.26}Th_{.09})_3(B_{2.95}Si_{1.02}Ti_{.03})_4 \\ ((Si_{3.22}Al_{.78})O_4)_4(O_{2.21}OH_{1.42}F_{.24}Cl_{.13})_4$$

This requires assigning $Si_{1.02}$ or $(Al_{.78}Si_{.24})$ to boron positions and leaves one of the cation positions vacant. The vacancy may be in the 8-coordinated Y positions, as written, or in a 6-coordinated Ca position (the Fe positions in gadolinite) with the two cation positions then occupied as $Ca(Y_3Ca)_4$.

Spencite differs significantly in composition and ratios from other known borate-silicates and in any case stands as a distinct chemical entity. Cappelenite, essentially a borate-silicate of barium and yttrium, has Y:B $\sim$ 1:1 and B:Si $\sim$ 2:1. It has a hexagonal morphology, and and *x*-ray powder pattern does not closely resemble either datolite or apatite. Melanocerite, caryocerite, and tritomite, all probably derivatives of the apatite structure, have Ce as the dominant rare-earth and are relatively low in B. Steenstrupine, a rhombohedral phosphate-silicate of (Ce, La), Ca and Na chiefly, lacks B but contains a small amount of Be. The yttrium silicates, thalenite, yttrialite, and rowlandite (redescribed beyond), are not related to spencite. Stillwellite, ideally $CeBSiO_5$, may be a cyclosilicate with the structural formula $Ce_3(B_3O_6)(Si_3O_9)$, as suggested by Strunz (1957). The mineral is hexagonal and its *x*-ray powder pattern (Gay, 1957) does not resemble that of datolite.

Unheated spencite does not give a distinguishable *x*-ray powder pattern. The metamict material is unstable thermally, and decomposes at a relatively low temperature, apparently in the range 450–550° C. Unfortunately this is below the range of temperature at which most metamict silicate minerals recrystallize at an appreciable rate, and it has not been possible to obtain useful *x*-ray powder patterns. Heated in nitrogen at 700 and 900° C a light-coloured, porous to slaggy mass is obtained; at 1050° C a yellowish white, sintered mass with a vitreous lustre is formed, that contains small bubbles. The *x*-ray pattern of the latter material is given in Table 3, and has not been identified.

TABLE 3. *X*-RAY POWDER SPACING DATA FOR ROWLANDITE AND HEATING PRODUCT OF SPENCITE

Rowlandite				Spencite product			
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
4.87	59	2.608	37	4.40	9	2.049	11
4.32	11	2.522	34	4.05	22	2.029	10
3.90	26	2.440	33	3.86	18	1.934	19
3.59	54	2.288	8	3.41	18	1.882	7
3.51	57	2.122	27	3.27	12	1.829	36
3.29	15	2.076	47	3.14	22	1.799	23
3.14	12	2.040	8	3.07	29	1.773	18
3.06	100	2.000	10	2.96	24	1.746	23
3.01	22	1.957	15	2.801	100	1.704	10
2.89	31	1.911	21	2.760	57		
2.840	15	1.803	13	2.708	34		
2.779	22	1.764	18	2.629	12		
2.656	20	1.720	42	2.254	10		

NOTE: Copper radiation, nickel filter, $\lambda = 1.5418$. Relative intensity in arbitrary chart units.

ROWLANDITE

The yttrium-silicate rowlandite was described in a note by W. E. Hidden in 1891 and no further information has been published, aside from a remark by F. L. Hess (1908) that it contains 5 per cent fluorine. The mineral was found as small irregular masses associated with yttrialite and gadolinite in the pegmatite at Baringer Hill, Llano County, Texas. Hidden stated that it was pale drab green in colour, transparent in thin splinters, with a specific gravity of 4.515. A partial chemical analysis gave (Y, etc.)$_2$O$_3$ 61.91, FeO 4.69, CaO 0.19, UO$_3$ 0.40, SiO$_2$ 25.98, ign. loss 2.01, total 95.18. The Baringer Hill pegmatite, in spite of the wealth of unusual minerals that it afforded, is very poorly represented by specimens in the leading reference collections. The type specimen here examined was preserved in the collection of the late O. I. Lee, a specialist in the rare earths, who obtained it from W. D. Niven, an associate of Hidden in the study and commercial development of the Baringer Hill pegmatite in the period 1887–1907. Summary accounts of the mineralogy of the pegmatite are given by Hess (1908) and by Landes (1932).

The mineral is metamict and isotropic, with n 1.704. Specific gravity 4.39, hardness 5½. It becomes crystalline when heated 1 hour in nitrogen at 900° C (mean index of refraction 1.76, specific gravity 4.55). The *x*-ray powder data are given in Table 3. It is not known whether these data refer to the original phase or to one or several recrystallization products. The data do not correspond to any known yttrium mineral.

Sufficient material is lacking for a chemical analysis. The presence of F in large amounts was confirmed, and this element probably makes up the bulk of the shortage in Hidden's analysis. The small ignition loss observed presumably is H$_2$O, usually present in metamict minerals, and may represent essential (OH) in part. Using an *x*-ray spectrograph with a LiF crystal and He path, borax fusions of the mineral were compared with borax standards containing known amounts of rare earths (together with Fe and Si in the same amount as in rowlandite). The large Y_2O_3 content was confirmed. Determinations of the minor constituents gave Ce and Nd in the range 1 to 5 per cent, with La, Mn, Th, U, Er, Lu, Dy, Ho, Gd, and Pr in amounts less than 1 per cent. An earlier optical spectrographic determination by K. E. Valentine of the U.S. Geological Survey gave Y and Si as the only major constituents with Ce and Nd as minor constituents. Boron and Be are present only in traces, and P is lacking. The formula of the mineral is conjectural on the basis of the existing analytical data. It may be near $(Y, Fe, Ca, Ce, etc.)_3(SiO_4)_2(F, OH)$. The crystalline phase obtained by heating Y_2O_3 with SiO_2 in the ratio 1:2 in air at 1000° C is neither identical with rowlandite nor isostructural with $Sc_2Si_2O_7$ (thortveitite) synthesized similarly from Sc_2O_3 and SiO_2. A few grains of an altering reddish brown mineral were observed veining the rowlandite. These gave an *x*-ray pattern closely resembling bastnaesite, but the mineral contains Y much in excess of Ce. Normal bastnaesite was identified in other specimens from Baringer Hill here examined.

Rowlandite was named by Hidden after the American physicist and spectrographer Henry A. Rowland (1849–1901), of Johns Hopkins University, who worked on the spectra of the rare earths.

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