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SPENCITE, THE YTTRIUM ANALOGUE OF TRITOMITE FROM SUSSEX COUNTY, NEW JERSEY

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ABSTRACT

Spencite, the yttrium analogue of tritomite, is a metamict boro-silicate of yttrium, thorium, and calcium. It occurs as anhedral grains and masses in pegmatite near Cranberry Lake, Sussex County, New Jersey. The metamict phase is black; luster is vitreous to resinous, and fracture is conchoidal. It is pale green in transmitted light, isotropic, $n=1.670$, $G=3.40$, $H=6.5$. When heated to 1000° C., in air, it crystallizes to an amber, vesicular mixture of a rare earth boro-silicate-apatite and glass. The crystalline phase is hexagonal; $a=9.32$ Å, $c=6.84$ Å; mean $n=1.770$; birefringence is low. The estimated composition is $[Y_3{}^{3+}(Ce, Pr, Th)^{4+}Ca](Si_2B)O_{12}O$.

INTRODUCTION

Tritomite, a rare, metamict boro-silicate of the cerium earths, calcium, and thorium, is known only from the nepheline syenite pegmatites of Låven, Brevik, and Barkevik, in the Langesundsfjord district of southern Norway. Recently, a new metamict yttrium analogue of tritomite was identified by the authors in granite pegmatite dikes associated with magnetite-rich rock and gneisses in the Precambrian complex of northern New Jersey. The specimen studied came from pegmatite near Cranberry Lake, in Sussex County, approximately twelve miles northwest of Dover. Coincidentally, a very similar metamict mineral was identified by Frondel (1961) from a pegmatite in Haliburton, Ontario, and named spencite, after Hugh S. Spence who collected the material. When heated to 1000° C., both the Ontario and New Jersey minerals recrystallize, in part, to a phase which yields an *x*-ray diffraction pattern identical with that of heated tritomite from Langesundsfjord. A further comparison of the optical properties and chemical analyses of unheated, metamict spencite from Ontario and New Jersey have lead Drs. Michael Fleischer, Clifford Frondel, and the authors to conclude that both minerals are the same.

Tritomite was originally found by Weibye (1849) at Låven, in the Langesundsfjord district, and was named from the Greek, *τpiτoμos*, meaning "cut in three parts," in allusion to the triangular and pseudo-tetrahedral crystal outline. Brögger (1890), in his classic monograph on the pegmatites of southern Norway, concluded that tritomite was hexagonal, on the basis of goniometric measurements. Six chemical analyses were made of tritomite during the period, 1849 to 1877, and none has appeared since then. The analyses were published by Berlin (1849), Forbes (1855), Möller (1861), and Engstrom (1877). Of the six analyses, only the two made by Engstrom appear to be valid, inasmuch as the earlier analyses did not include determinations of either boron or fluorine. Brögger (1890) assumed that the specimens with a triangular outline were crystalline, and that the massive material was amorphous due to hydration. Recent data by Neumann *et al.* (1957) on Langesundsfjord material, by Frondel (1961) on Ontario material, and by the authors on New Jersey material, indicate that tritomite and spencite are completely metamict and give no trace of an *x*-ray diffraction pattern in the natural state. When heated in air to temperatures ranging from 600° C. – 1000° C., both tritomite and spencite recrystallize to an apatite structure + an amorphous phase, presumably a calcium borosilicate glass.

OCCURRENCE

Spencite from New Jersey occurs in a granite pegmatite composed of microcline, quartz, oligoclase, magnetite, black zircon, clinopyroxene, soda amphibole, fergusonite, sphene (var. keilhauite), apatite, tourmaline, biotite, fluorite, and galena. It is intimately associated with magnetite, black zircon, apatite, and fergusonite, although it contains no niobium or tantalum and only traces of zirconium or phosphorus. The area lies approximately nine miles to the northwest of the Dover magnetite district in which is the Scrub Oak mine described by Sims (1953) and Klemic, *et al.* (1959). The Scrub Oak mine contains magnetite deposits associated with gneiss, skarn, albite-oligoclase granite, and granite pegmatite. The pegmatitic phase is enriched in yttrium, and the occurrence of such minerals as xenotime and doverite, the yttrium analogue of synchisite, has been described by Smith, *et al.* (1955, 1960). Although spencite has not been reported from the Scrub Oak mine, the unusual black zircon is abundant. Zircon found in Precambrian rocks is usually brown, red, or hyacinth in color; it is rarely black. It would appear that this part of the New Jersey highlands is an yttrium-rich as well as a magnetite-rich province, and that both pegmatites have had a common origin. Thus, spencite, rather than tritomite, was formed in the pegmatites of this area which carry rare earths predominantly of the yttrium group. The Langesundsfjord pegmatites, which contain tritomite, are enriched in rare earths predominantly of the cerium group (Brögger, 1890).

MINERALOGY

Physical and Optical Properties

Spencite from New Jersey occurs as anhedral grains and irregular masses up to one inch in size. The sample on which detailed studies were made was an essentially homogeneous mass, approximately one inch in diameter. The only impurity observed was calcite which formed less than

2 per cent of the specimen. Calcite was identified microscopically and verified by an analytical determination of 0.84 per cent CO_2, equivalent to 1.91 per cent calcite. This amount was not sufficient to register on the *x*-ray diffraction pattern which yielded a complete blank on unheated material.

Spencite from New Jersey is dark, greenish black, with a resinous to vitreous luster, a conchoidal fracture, and a hardness of 6.5. It is decomposed by hydrochloric acid with separation of gelatinous silica. In transmitted light, it is very pale green, completely isotropic, and has an index of refraction of 1.670 ± 0.002; in a few grains n varies from 1.668 to 1.673. The density measured with the Berman microbalance, and toluene, is 3.40 at 23.5° C., the average of measurements made on three different fragments which yielded values of 3.40, 3.37, and 3.44. Spencite from Ontario (Frondel, 1961) has an index of refraction of 1.630, with some variation in the range, 1.627 to 1.653. The hardness is 3.5, and the measured density, 3.05. Ford (1932) and Winchell (1951) give a value of 4.2 for the density of Langesundsfjord tritomite. Brögger (1890) concluded that 4.25–4.45 was the most representative density range of the Langesundsfjord material, although earlier workers reported 4.16–4.66 (Berlin, 1849), 3.91 (Forbes, 1855), 4.26 (Möller, 1861), and 4.05–4.18 (Engström, 1877). The index of refraction of tritomite from Langesundsfjord is even more variable, ranging from 1.650 to 1.757, for two samples measured by Larsen and Berman (1934). Unfortunately, no index of refraction or density measurement of tritomite is tied to a specific chemical analysis. Large variations in the index of refraction of metamict minerals are well-known and have been reported for chevkinite by Kauffman and Jaffe (1946) and Jaffe *et al.* (1956), and for zircon by Gottfried *et al.* (1959). In the present investigation of spencite from New Jersey, the index of refraction, density, and chemical analysis were obtained on a single sample, and their relation will be discussed later.

X-ray Diffraction Data

Neumann *et al.* (1957) who have published a large number of schematic *x*-ray diffraction patterns, heated Langesundfjord tritomite both in air and under water pressure to temperatures of 600° to 1000° C., and observed that it crystallized to a low temperature modification, tritomite-A, with a pattern similar to that of apatite, and a high temperature modification, tritomite-B, with a pattern similar to that of uraninite. They state that the transition temperature varies with the specimen. No optical data are given that would indicate whether all or part of the heated material was crystallized. Upon heating New Jersey spencite from 800° to 1000° C. in air at intervals of 2 to 24 hours, the writers were

TABLE I. *X*-RAY POWDER DIFFRACTION PATTERNS OF HEATED SPENCITE, TRITOMITE-A AND FLUORAPATITE, FeKα RADIATION ($\lambda = 1.93597$ Å), Mn FILTER, 57.3 MM. CAMERA

SPENCITE New Jersey (1000° C./3 hrs./air)				SPENCITE Ontario (1050° C./N)		FLUORAPATITE Montana		TRITOMITE-A Langesundsfjord (600°–1000° C.)	
hkl	*d*(calc.)	*d*(meas.)	I	*d*(meas.)*	I	*d*(meas.)	I	*d*(meas.)	I
200	4.03	4.02	50	4.05	22	4.04	10	4.05	20
111	3.85	3.83	40	3.86	18	3.85	10	3.89	20
002	3.42	3.42	30	3.41	18	3.44	60	3.44	40
102	3.15	3.13	50	3.14	22	3.17	10	3.16	20
120	3.05	3.05	40	3.07	29	3.07	10	3.08	30
121	2.79	2.78	100	2.80	100	2.80	100	2.81	100
112	2.76	2.76	40	2.76	57	2.78	50	2.78	20
300	2.69	2.69	30	2.71	34	2.71	60	2.70	30
202	2.61	—	—	2.63	12	2.62	50	—	—
130	2.24	2.25	10	2.25	10	2.24	30	2.25	10
221	2.20	—	—			—	—	2.22	10
131	2.13	2.14	5			2.14	10	2.14	5
113	2.05	2.04	30	2.05	11	—	—	2.07	5
400	2.02	—	—	2.03	10	2.04	10	2.04	10
222	1.925	1.930	40	1.934	19	1.933	60	1.94	30
132	1.872	1.874	30	1.882	7	1.885	20	1.89	20
123	1.825	1.824	40	1.829	36	1.834	60	1.84	40
231	1.787	1.794	20	1.799	23	1.797	20	1.80	20
140	1.761	1.770	10	1.773	18	1.770	20	1.77	20
402	1.738	1.740	30	1.746	23	1.747	20	1.74	30
004	1.709	1.709	30	1.704	10	1.720	30	1.72	5
232	1.628	1.629	5			1.639	30	1.63	5
133	1.597	—	—			—	—	—	—
142	1.566	1.571	5			—	—	1.57	5
240	1.525	1.530	5			1.531	10	1.53	5
331	1.520	—	—			—	—	—	—
124	1.491	1.498	20			1.500	10	1.51	5
502	1.459	1.468	20			1.467	40	1.49	20
304	1.443	1.448	30			1.451	30	1.45	30
233	1.437	—	—			—	—	1.43	20
151	1.418	1.423	20			1.426	20	1.41	20
115	1.312	1.311	20			1.311	10	1.32	5
251	1.270	1.278	20			1.276	20	1.28	30
602	1.251	1.251	30			1.255	20	1.26	20
160	1.231	1.230	30			1.233	30	1.24	40
161	1.211	1.217	40			1.217	40	1.22	30

* The following additional lines were observed: (CuKα radiation, Ni filter) $d=4.40$, $I=9$, $d=3.27$, $I=12$, and $d=2.96$, $I=24$. These do not occur in the patterns of spencite, tritomite, or fluorapatite from other localities.

TABLE I—(*continued*)

Spencite New Jersey (1000° C./3 hrs./air)				Spencite Ontario (1050° C./N)		Fluorapatite Montana		Tritomite-A Langesundsfjord (600°–1000° C.)	
hkl	*d*(calc.)	*d*(meas.)	I	*d*(meas.)*	I	*d*(meas.)	I	*d*(meas.)	I
504	1.173	1.174	10			1.170	5	1.18	20
350	1.153	—	—			1.155	30	1.15	10
343	1.141	1.143	20			1.145	30	1.14	10
106	1.128	1.130	30			1.132	5	1.12	20
154	1.106	1.111	50			1.114	40	1.12	20
261	1.104	1.103	50			1.107	5	1.11	10
702	1.092	1.091	10			1.099	50	—	—
		1.077	5			1.076	10	—	—
		1.029	5			1.037	5	1.04	10
		—	—			1.028	5	—	
		1.020	5			1.022	5	—	
		—	—			1.012	10	—	
		1.006	10			1.006	30	—	
		—	—			1.001	20	—	
		0.997	5			0.999	10	—	
						0.981	50	—	
						0.979	10	—	

able to obtain only the low temperature modification identical with tritomite-A.

When heated in air to a temperature of 800° C., spencite forms a mass of small buff globules in a fine matrix, resembling a conglomerate on a microscopic scale. From material heated to this temperature, a very feeble apatite-type *x*-ray diffraction pattern is obtained. When heated to 1000° C., in air, for periods of 2 to 24 hours, spencite fuses to a light amber, vesicular, mass of crystals and glass, with a ratio of crystals to glass estimated to be 60:40. *X*-ray diffraction and microscopic data, obtained on this material agree closely with that of tritomite-A from Langesundsfjord and common fluorapatite (Table I and Figure 1). Most of the crystals are exceedingly small and are not readily resolved by petrographic microscopic examination. Scattered larger crystals, however, reveal several of the optical properties of apatite. These include: a crystal habit of short laths and rare basal plates, low birefringence, parallel extinction, and a length fast or negative elongation. The glass is colorless, whereas the crystals have a pale buff color. Precise indices of refraction were not obtained because of the difficulty in getting a clear crystal edge in contact with the immersion liquids. The crystals have a mean index of

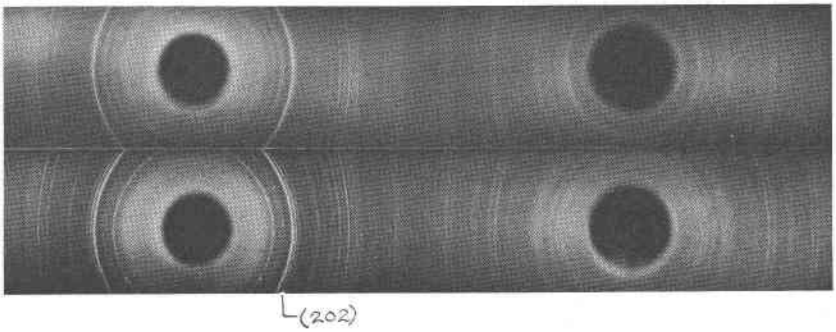

Fig. 1. *X*-ray powder diffraction photographs of heated spencite, New Jersey (upper) and fluorapatite, Montana (lower). FeKα radiation, Mn filter, 57.3 mm. camera.

refraction of 1.770, and low birefringence, whereas the glass has an index of refraction of 1.650. Electron micrographs of heated spencite (Fig. 2) reveal a characteristic hexagonal, apatite-like morphology of the crystals not readily resolved in the petrographic microscope. The electron micrographs were taken with a Siemens electron microscope, at a magnification of 20,000.

The *x*-ray powder diffraction pattern of heated spencite was obtained with a Norelco-Phillips basic unit, using a 57.3 mm. diameter camera, FeKα radiation ($\lambda = 1.93597$ Å), and a Mn filter. Hexagonal unit cell dimensions of $a_0 = 9.32$ Å and $c_0 = 6.84$ Å were calculated from $d_{(300)} = 2.69$ Å, $d_{(002)} = 3.42$ Å, and $d_{(004)} = 1.709$ Å, by analogy with the apatite struc-

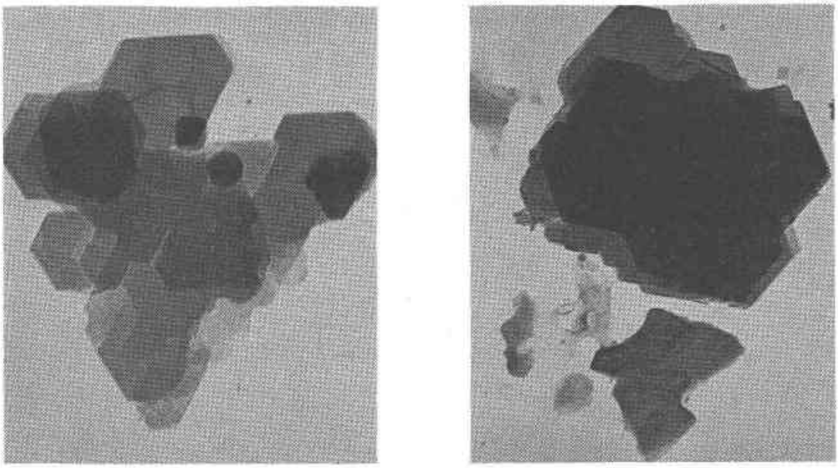

Fig. 2. Electron micrographs of hexagonal plates of heated spencite. Siemens Electron Microscope, 20,000×.

TABLE II. UNIT CELL DATA FOR HEATED SPENCITE, TRITOMITE-A, FLUORAPATITE, AND RELATED NATURAL AND SYNTHETIC RARE EARTH SILICATE APATITES

	a	c
1. Heated spencite, New Jersey	9.32	6.84
2. Tritomite-A, Langesundsfjord	9.35	6.88
3. Fluorapatite, Ontario	9.36	6.88
4. Britholite, Greenland	9.61	7.02
5. Lessingite, Russia	9.67	7.08
6. Ca-Y-abukumalite, synthetic	9.31	6.58
7. Na-Ca-Nd-britholite, synthetic	9.55	6.83
8. Na-Ca-La-britholite, synthetic	9.65	6.84

1., 2. New data, calculated from *x*-ray diffraction pattern.
3. McConnell (1938)
4. Hägele and Machatschki (1939), Gay (1937).
5. Gay (1957).
6., 7., 8. Trömel and Eitel (1957).

ture. From these data, all of the interplanar spacings down to $d = 1.091$ Å were indexed, indicating that heated spencite has the apatite structure (Table I). The patterns of both the heated spencite and Langesundsfjord tritomite-A show close correspondence to that of apatite; the principal difference is the absence of the fairly strong (202) reflection characteristic of fluorapatite (Fig. 1). This reflection is present in the *x*-ray pattern of analyzed fluorapatite from Ontario (McConnell, 1938). Data for unanalyzed fluorapatite from Montana are used in Table I and Figure 1 because they were obtained under the same conditions as that of heated spencite. Fluorapatite from Montana (Table I and Fig. 1) has the optical properties of normal fluorapatite, $n_\omega = 1.633$, $n_\epsilon = 1.630$, uniaxial negative. The unit cell dimensions of spencite, tritomite-A, related rare earth apatites, and fluorapatite are compared in Table II. Heated spencite has the smaller unit cell dimensions, which apparently result from the substitution of B^{3+} ions (I.R. = 0.23 Å) for the larger P^{5+} ions (I.R. = 0.35 Å), in tetrahedral sites. Both lessingite and britholite, cerium earth silicate apatites, have unit cell dimensions larger than fluorapatite, partly due to the substitution of Si^{4+} (I.R. = 0.42 Å) for P^{5+} ions. The ionic radii of the larger cations Y^{3+}(0.92 Å), Ca^{2+}(0.99 Å), and Ce^{3+}(1.07 Å), (all cation radii are from Ahrens, 1952), are also in accord with an increasing unit cell size going from heated spencite through tritomite-A, and fluorapatite, to britholite and lessingite, the cerium-rich apatites. The expansion of the unit cell with the increasing size of substituted rare earth cations, Y^{3+}, Nd^{3+}, and La^{3+} (0.92, 1.04, and 1.14 Å, respectively) has also been demonstrated by Trömel and Eitel (1957) for a series of synthetic rare earth silicate apatites (Table II).

CHEMISTRY

A complete chemical analysis of New Jersey spencite made by the junior author is presented in Table III. Also included for comparison are analyses of spencite from Ontario, two tritomites from Langesundsfjord, and other rare earth silicate apatites, lessingite, britholite, and abukamulite. Although spencite and tritomite are metamict, and of variable

TABLE III. ANALYSES OF SPENCITE, TRITOMITE AND RARE EARTH SILICATE APATITES

	1	1a	2	3	4	5	6	7
SiO_2	24.12	24.66	24.89	13.54	13.59	20.84	19.85	16.77
P_2O_5	<0.1		0.02			5.84	1.13	6.48
B_2O_3	10.88	11.12	10.04	7.31	8.37			
BeO	0.22	0.23						
Ta_2O_5				1.15	1.11			
TiO_2	0.22	0.23	0.27					
ZrO_2	<0.1			1.09	1.03			
Al_2O_3	6.08	6.21	3.87	1.18	0.88	1.05	0.26	
Fe_2O_3			3.22	1.67	1.55	2.10	0.65	0.43
FeO	3.39	3.47						
MnO	0.44	0.45	0.60	0.67	0.34	1.13	0.88	
MgO	0.20	0.20	0.50			0.22	0.17	0.13
CaO	17.32	16.61	7.81	7.04	6.97	13.53	11.71	11.28
SrO			0.05					
BaO								
PbO	0.11	0.11						
Ce_2O_3	2.79	2.85	1.44	10.65	8.14	6.45	22.48	60.54
CeO_2				11.69	11.26			
La_2O_3*	5.60	5.72	4.16	21.88	26.32		36.65	
Y_2O_3*	19.60	20.03	28.20	2.97	2.58	45.98	3.42	
ThO_2	2.78	2.84	2.44	9.51	8.58	0.90		
UO_3	0.90	0.92						
Na_2O	0.08	0.08	0.11	1.40	0.71		0.08	
K_2O			0.01					1.85
CO_2	0.84					0.08	0.35	
H_2O	3.60	3.68	11.75	6.40	6.48	0.73	1.94	1.27
F	1.00	1.02	0.44	4.29	3.15	0.45	0.54	1.35
Cl			0.45					
	100.16	100.43	100.27	102.44	101.06	99.30	100.11	100.08
Less=O=F, Cl	0.42	0.43	0.28	1.81	1.33	0.19	0.23	0.56
Total	99.74	100.00	99.99	100.63	99.73	99.11	99.88	99.52
Density	3.40		3.05	4.2	4.2	4.35	4.69	4.45

chemical composition, formulas were calculated from the analyses on the basis of 13[O,(OH),F,Cl] for comparison with the apatite structure to which it recrystallizes on heating. These calculations were made in order to indicate the degree of departure of the composition of metamict spencite and tritomite from that required by the apatite structure, $A_5B_3[O,(OH),F,Cl]_{13}$. The formulas calculated from Table III are given below. Assignment of cations to the A-group or B-group was made essentially on a basis of ionic size. Be^{2+}, present in spencite from New Jersey, was assigned to the B-group of small cations, along with P^{5+}, Si^{4+}, and B^{3+}. Be^{2+} has an ionic radius of 0.35 Å (Ahrens, 1952), exactly that of P^{5+} and should be in tetrahedral coordination.

Spencites from New Jersey and Ontario and tritomites from the Langesundsfjord localities (Brevik and Barkevik), give no *x*-ray diffraction patterns in the metamict state and show a large departure from stoichiometry. Lessingite, originally described by Zilbermintz (1929) gives an apatite-type *x*-ray diffraction pattern which Gay (1957) could index on the basis of the hexagonal unit cell dimensions cited in Table II.

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* La_2O_3 includes other cerium group rare earth oxides.
* Y_2O_3 includes other yttrium group rare earth oxides.
Loss on ignition at 1000° C. = 4.60% for analysis 1.

1. Spencite, Cranberry Lake, Sussex Co., N. J.
1a. Spencite, recalculated to 100% after deduction of 0.84% CO_2 and 1.07% CaO equivalent to 1.91% calcite.
2. Spencite, Haliburton, Ontario, Frondel (1961).
3. Tritomite, Brevik, Langesundsfjord, Norway, Engstrom (1877).
4. Tritomite, Barkevik, Langesundsfjord, Norway, Engstrom (1877).
5. Abukumalite, Abukuma Range, Iisaka, Japan, Hata (1938).
6. Lessingite, Kyshtym district, Urals, Russia, Zilbermintz (1929).
7. Britholite, Naujakasik, Julianehaab, Greenland, Winter, (1901).

Spectrographic analysis of spencite, N. J., showed: >10% Y, Si, Ca, B, 1.–10.%: Fe, 0.7–7.%: Nd, Th, Er, Yb, 0.3–3.%: Ce, La, Pr, Sm, Dy, Mn, 0.2–2.%: Na, Zr, Gd, Tm, 0.1–1.%: Mg, Be, Pb, <0.1%: Ho, U, Eu, Tb, Cu, Ti

Mineral	*Cations on a basis of* 13[*O*, (*OH*), *F*]	
Apatite	$Ca_{5\cdot00}$	$P_{3\cdot00}$
Spencite, N. J.	$(Y, Ca, Ce, La, Th, Al, Fe, Mn, U, Ti, Mg, Na)_{3\cdot83}$	$(Si, B, Be)_{3\cdot91}$
Spencite, Ontario	$(Y, Ca, Ce, La, Th, Al, Fe, Mn, Ti, Mg, Na, K)_{2\cdot76}$	$(Si, B, P)_{3\cdot36}$
Tritomite, Brevik	$(Ce, La, Ca, Y, Th, Zr, Ta, Mn, Al, Fe, Na)_{3\cdot69}$	$(Si, B)_{2\cdot83}$
Tritomite, Barkevik	$(Ce, La, Ca, Y, Th, Zr, Ta, Mn, Fe, Al, Na)_{3\cdot48}$	$(Si, B)_{3\cdot04}$
Abukumalite, Japan	$(Y, Ca, Ce, La, Th, Fe, Mn, Mg)_{4\cdot90}$	$(Si, P, Al)_{2\cdot98}$
Lessingite, Russia	$(Ce, La, Ca, Y, Fe, Mn, Mg)_{4\cdot91}$	$(Si, P, Al)_{2\cdot76}$
Britholite, Greenland	$(Ce, La, Ca, Na, Fe, Mg)_{4\cdot92}$	$(Si, P)_{2\cdot85}$

Although lessingite and britholite are optically biaxial, this may be an anomalous property inasmuch as x-ray measurements by Hägele and Machatschki (1939) showed that britholite has a hexagonal unit cell of the dimensions listed in Table II.

Frondel (1961) has considered the possibility that spencite from Ontario may be related to the datolite group. This suggestion was offered wholly on chemical data. By considering that the major part of the water (Table III, anal. 2) is unessential, Frondel calculated the following formula for Ontario spencite, suggesting a possible relation to the datolite group:

Spencite, Ontario	$(Ca, Fe)_2Y_3(B, Si)_4(Si, AlO_4)_4(O, OH, F, Cl)_4$
Datolite	$Ca_4B_4(SiO_4)_4(OH)_4$

Calculation of a formula for New Jersey spencite (Table III, anal. 1a), on this basis, yields:

$$(Ca, Y, La, Ce\ Th, U, Fe, Mn, Na, Mg)_5(B, Al, Ti)_3(Si, B, BeO_4)_4(O, OH, F)_4$$

In this calculation all of the water was considered to be essential, as there is no way of determining how much is unessential. Drs. Fleischer, Frondel, and the authors have compared the data for spencites from New Jersey and Ontario, and discussed their formulation, at length. All parties agree that the relation of spencite to the datolite group is uncertain, although possible. Inasmuch as both samples of spencite, as well as Langesundsfjord tritomite crystallize, in part, when heated to yield the same apatite-group x-ray diffraction pattern, the tritomite-A of Neumann *et al.* (1957), Fleischer (priv. comm., 1961), and the authors prefer to relate the formulation of spencite to the apatite, rather than the datolite group. Metamict minerals are difficult to classify because one never knows how much of the original material is represented by the x-ray identification of the phase obtained on heat-treated material.

As has been previously noted, metamict spencite, upon heating to 1000° C., changes to a mixture of crystals with the apatite structure (Tables I and II), and an amorphous phase, presumably a calcium borosilicate glass. Inasmuch as the crystals could not be physically separated from the glass matrix it was not possible to determine their composition. An evaluation of all of the laboratory data, however, suggests that the composition of the crystals is represented by one of two possible formulas analogous to apatite, $Ca_5P_3O_{12}[F,(OH),Cl]$. These are:

$$\underbrace{[Y_4^{3+}(Ce, Pr, Th)^{4+}]}_{5}\ \underbrace{(Si_2B)}_{3}O_{12}(BO_3), \quad \text{and} \quad \underbrace{[Y_3^{3+}(Ce, Pr, Th)^{4+}Ca]}_{5}\ \underbrace{(Si_2B)}_{3}O_{12}O.$$

Inasmuch as the crystalline phase of heated spencite forms at 800°–

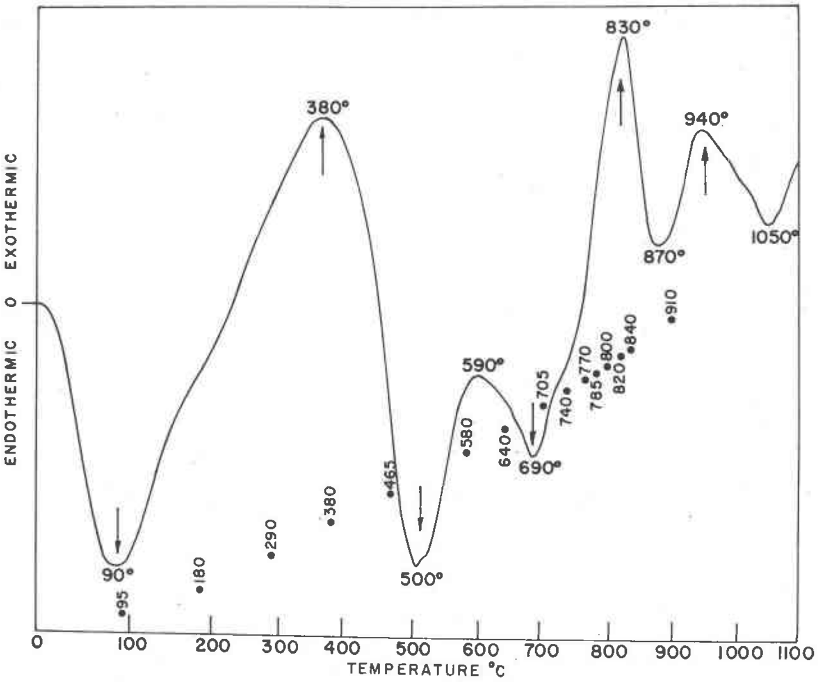

FIG. 3. Differential thermal analysis curve for spencite, Sussex Co., N. J. Sensitivity: 1/6 Cr/Al; inert-calcined kaolin; temp. incr.: 10° C./min.

1000° C., at which temperature, all of the water and fluorine are lost, the structural positions normally occupied by $(OH)^-$ or F^-, in apatites, must be proxied for by either $(BO_3)^{3-}$ or O^{2-}, the only anions available. Loss of water, fluorine, and the small amount of carbon dioxide present is indicated by the differential thermal analysis curve for tritomite (Fig. 3). This shows three endothermic reactions: one at 90° C., loss of unessential water; and two at 500° C., and 690° C., indicating loss of water, fluorine, and carbon dioxide. No additional endothermic reactions occur beyond 690° C. The broad exothermic reaction at 380° C. represents the oxidation of Fe^{2+}, Mn^{2+}, Ce^{3+}, and Pr^{3+} to Fe^{3+}, Mn^{4+}, Ce^{4+} and Pr^{4+}. The two exothermic peaks at 830° and 940° C. represent the formation of the crystals and glass. *X*-ray diffraction studies indicate that a small amount of the same crystalline phase forms at 800° C. At 1000° C., the sample contains about 60 per cent crystals and 40 per cent glass. A material balance was calculated, from the analysis of spencite (Table III, col. 1), to compare the net loss on ignition with the value determined by the analyst. The amount of Pr_2O_3 present was taken as $\frac{1}{3}$ of the value determined for La_2O_3 (Table III, col. 1), which includes cerium rare earth oxides other than Ce_2O_3. The calculated net loss on ignition agrees favorably with the determined value, as indicated below:

inferred loss on ignition:		
H_2O		3.60%
F		1.00%
CO_2		0.84%
Total		5.44%
gain through oxidation:		
Ce_2O_3-CeO_2		0.13%
Pr_2O_3-PrO_2		0.08%
MnO-MnO_2		0.10%
FeO-Fe_2O_3		0.39%
Total		0.70%
net loss on ignition (calculated):	4.74%	
loss on ignition (determined):	4.60%	

Inasmuch as hydroxyl and hydrogen bonding are readily detectable by their infrared absorption spectra in the wavelength region of 2.5 to 3.5 microns, an analysis was made of heated spencite to further verify the ignition loss data. Heated spencite was pelletized with KBr and an infrared absorption pattern was obtained with a Perkin-Elmer model 221 spectrophotometer. No evidence of either hydroxyl bonding or absorbed water was observed.

If all of the water and fluorine are lost at 1000° C., as indicated, the only anions available to occupy F^- or $(OH)^-$ positions are $(BO_3)^{3-}$ or O^{2-}. This brings to mind the carbonate-apatite and oxy-apatite problems which have been discussed extensively by Gruner and McConnell (1937), McConnell (1938, 1960), and Wyckoff (1960). All of these investigators reject the idea that F^- can be replaced by the larger $(CO_3)^{2-}$ anion. Pauling (1948) and Zachariesen (1934) give characteristic C–O and B–O distances and 1.31 Å and 1.35 Å, respectively, for threefold or triangular coordination of O^{2-} (I.R. = 1.40 Å, Pauling, 1948) around C^{4+} (I.R. = 0.16 Å, Ahrens, 1952) and B^{3+} (I.R. = 0.23 Å, Ahrens, 1952). Although the effective radius of O^{2-} is considerably reduced, by partial double-bonding in $(CO_3)^{2-}$ and $(BO_3)^{3-}$, the radii of these anions must be appreciably larger than 1.31 Å and 1.35 Å, cited in some tables as ionic radii. Some investigators of carbonate-apatite have assumed that $(CO_3)^{2-}$ groups are located on hexagonal screw axes, either in F^- positions or halfway between two F^- positions. Gruner and McConnell (1937), however, reject this idea because such a substitution would expand the *a* unit cell dimension, whereas, a slight contraction of *a* occurs in carbonate-apatite. Wyckoff

(1960) also suggests that the hole between two F^- anions, on hexagonal screw axes, would be too small to accommodate $(CO_3)^{2-}$ groups. The *a* unit cell dimensions of heated spencite from New Jersey and Norway are both slightly smaller than that of fluorapatite (Table II) and it is therefore unlikely that $(BO_3)^{3-}$ would occupy F^- positions, or lie halfway between F^- anions. This leaves oxygen as the only anion available to substitute for fluorine. Inasmuch as O^{2-} and F^- anions are essentially of the same size, no change in the unit cell dimensions would be expected to result from this substitution. Heated spencite from New Jersey would be expected to have a slightly smaller unit cell than normal fluorapatite because of the substitution of Y^{3+}(0.92 Å) for Ca^{2+}(0.99 Å), and B^{3+}(0.23 Å) for P^{5+}(0.35 Å), (ionic radii from Ahrens, 1952). This is confirmed by the *x*-ray data (Table II) which show $a = 9.32$ Å and $c = 6.84$ Å for heated spencite compared with values $a = 9.36$ Å and $c = 6.88$ Å for fluorapatite. These data suggest that the crystalline phase of heated spencite is an oxyapatite, in which O^{2-} proxies for F^-; rare earths replace most of the calcium; and Si^{4+} and B^{3+} replace all of the P^{5+}. This phase, formed from the metamict, yttrium-dominant spencite from New Jersey, and tritomite-A, formed from the metamict cerium-dominant tritomite from Langesundsfjord, may be represented by the following hypothetical formulas:

heated spencite, New Jersey: $\underbrace{[Y_3^{3+}(Ce, Pr, Th)^{4+}Ca]}_{5}\ \underbrace{(Si_2B)}_{3}O_{12}O$

tritomite-A, Langesundsfjord: $\underbrace{[(La, Nd)^{3+}(Ce, Pr, Th)_2^{4+}Ca_2]}_{5}\ \underbrace{(Si_2B)}_{3}O_{12}O$

Although carbonate- and silicate-apatites are known to occur naturally (Winchell, 1951, Palache, *et al.* 1951), boron-apatites have not been reported. Carbonate-apatites were reportedly synthesized by Eitel (1924). These and other synthetic apatites are recorded in an extensive survey of the literature made by Jaffe (1951). A lead boro-silicate apatite prepared by Moore and Eitel (1957) has been further described by Trömel and Eitel (1957) as a defect structure produced because of the high polarizability of the Pb^{2+} ion.

Relation between chemical composition, density and index of refraction

Application of the rule of Gladstone and Dale, $(n-1)/d = K$, to the evaluation of analytical, density, and optical data obtained on minerals has been suggested by Larsen and Berman (1936) and Jaffe (1956). Using the chemical analysis (Table III, col. 1a), the measured density, 3.40, and the specific refractive energy values (k) of Larsen and Berman, and Jaffe, a calculated index of refraction of 1.671 was obtained for metamict

TABLE IV. COMPARISON OF MEASURED INDEX OF REFRACTION WITH THAT CALCULATED FROM THE RULE OF GLADSTONE AND DALE, $n-1/d=K$, FOR SPENCITE FROM NEW JERSEY

Oxide	Wt. %	k†	Wt. %x k
SiO_2	24.66	.207	.051046
B_2O_3	11.12	.220	.024464
BeO	0.23	.238	.000547
TiO_2	0.23	.397	.000913
Al_2O_3	6.21	.193	.011985
FeO	3.47	.187	.006489
MgO	0.20	.200	.000400
MnO	0.45	.191	.000859
CaO	16.61	.225	.037373
PbO	0.11	.137	.000151
Ce_2O_3	2.85	.149	.004246
La_2O_3*	5.72	.140	.008008
Y_2O_3	20.03	.170	.034051
ThO_2	2.84	.120	.003408
UO_3	0.92	.134	.001232
Na_2O	0.08	.181	.000145
H_2O	3.68	.340	.012512
F	1.02	.043	.000439
	100.43		.198268
Less O=F	0.43	.203	.000873
Total	100.00		.197395=K
			3.40 =d
		n calc.	1.671 =dK+1
		n obs.	1.670

* Includes Nd_2O_3, Pr_2O_3, and other cerium group rare earth oxides.

† k = specific refractive energy values:

Ce_2O_3, La_2O_3 and Y_2O_3 values from Jaffe (1956).

All other values from Larsen and Berman (1934).

spencite. The measured value, previously cited, is 1.670. The specific refractive energy values used, and the Gladstone and Dale calculation, are given in Table IV.

A density was not determined for the heated material as it was a mixture of crystals and glass, and, in addition, was vesicular. An x-ray density was calculated for the hypothetical composition, $[Y_3{}^{3+}(Ce,Pr,Th)^{4+}Ca]\ (Si_2B)O_{12}O$, believed to represent heated spencite crystallized from the New Jersey material. Assuming that $z=2$, as in apatite, the calculated density is 4.21. This is in the same range as the values 4.35, 4.69, and 4.45, determined for the rare earth silicate apatites, abukumalite, lessingite, and britholite, respectively (Table III).

Age Calculation

Inasmuch as Th and U had been determined by both conventional wet chemical methods, as well as by gamma ray spectrometry, a quantitative spectrographic determination was made for Pb in order to determine whether spencite might be useful as an age mineral. Using these data: Pb=1020 ppm, U=7700 ppm, Th=24960 ppm, and the formula of Keevil (1939), as cited by Gottfried, Jaffe, and Senftle (1959); t (age in millions of years) $=7.18\times10^3$ Pb/U+0.312 Th, a total lead age of 470 million years was obtained. This apparent age is too low as the pegmatites associated with the magnetite deposits in the New Jersey highlands are of Precambrian age. It would appear that spencite has lost lead, presumably during a metamorphic event. A lead-alpha age determination made by Jaffe, *et al.* (1959), on black zircon from the Scrub Oaks mine at Dover, gave a value of 620 million years. The same black zircon occurs at Cranberry Lake, associated with spencite, and both pegmatites are undoubtedly of the same age. Jaffe, *et al.* (1959) also determined lead alpha ages of 640 and 660 million years for zircon in hedenbergite quartz syenites from elsewhere in the New Jersey highlands. This age may also be low if lead has been lost from zircon during metamorphism. In any event, the Dover and Cranberry Lake pegmatites, are 600 million years old, or greater, and are hence, Precambrian.

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