Abukumalite, a New Yttrium Mineral.

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As reported in the previous communications,⁽¹⁾ several species of rare minerals have been found in the pegmatite dykes at Iisaka Village, Fukushima Prefecture, towards the end of 1936. In the present paper is described a newly discovered mineral named "abukumalite" having the chemical composition of a phosphosilicate of yttrium and calcium, and no mineral having such a chemical composition has hitherto been found to occur anywhere other than in this district.

The mineral is, however, very scarce in the locality, being found embedded in the dark reddish or greenish feldspar neighbouring to biotite layers, and intimately associated with yttrialite, thorogummite, tengerite, and also with allanite. It occurs usually in massive forms of dark reddish brown colour, measuring about 1~2 cm in diameter. Rarely it exists in short prismatic crystals, probably of hexagonal system, formed by the faces x and m. The largest specimen secured as a good crystal measures about 3 cm in diameter. The outer part of the mineral is always altered into earthy substance of yellowish white or sometimes yellowish brown colour. Cleavage is seen imperfectly parallel to the faces c and m. Fracture uneven to splintery. It is brittle having the hardness of 6·0. Specific gravity measured by a pycnometer is 4·35 at 19°C. The lustre observed on splinters is usually resinous and sometimes dull. The streak is of faint brown, and the colour of thin section is yellowish brown. When examined under microscope, it is optically uniaxial, birefringence being very low. Refractive indices determined by immersion method are $\omega=1{\cdot}750$ $\varepsilon=1{\cdot}752$. It is optically positive. The extinction is parallel to cleavage. The magnetic property examined by using a powerful electromagnet is weaker than allanite and greater than yttrialite and xenotime. In fine powder it is readily dissolved in cold dilute mineral acids. When measured by an α-ray electroscope it shows a weak radioactivity,

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(1) S. IIMORI and S. HATA: *Sc. Pap. I.P.C.R.*, **34** (1938), 447, 504; S. HATA: *Ibid.*, **34** (1938), 445, 619; T. IIMORI: *Ibid.*, **34** (1938), 832.

being about one fifth of that shown by the Ceylon monazite containing 9·26% ThO_2.(2) The X-ray examination of this mineral by Debye-Scherrer method was carried out by Mr. H. Inuzuka, who verified from the X-ray spectrograms that the specimen is not a mixture of different species of minerals and that the mineral should be of hexagonal system with the axial ratio $a : c = 1 : 0{\cdot}7$ and the lattice dimension $a_0 = 5{\cdot}7$ Å.

TABLE I. Outline of analytical scheme.

0·5 g of finely pulverized sample was digested with strong HCl, evaporated to dryness and leached out with diluted HCl.

R_1: Combined with R_2, ignited, and weighed. Treated with $HF + H_2SO_4$, and SiO_2 determined from the loss in weight. The residue fused with $Na_2S_2O_7$ and leached out with water, added to F_2.

F_1: Repeatedly evaporated to dryness, treated with HCl.

R_2: Added to R_1.

F_2: Saturated with H_2S to precipitate insoluble sulphides.

R_3: Ignited to oxides of heavy metals.

F_3: Boiled and oxidized with Br water, and precipitated with NH_4OH, after the addition of NH_4Cl.

R_4: Dissolved in conc. HCl and neutralized with NH_4OH. An excess of oxalic acid was added.

F_4: Freshly prepared $(NH_4)_2S$ was added.

R_6: Ignited and weighed as Mn_3O_4.

F_6: Ca and Mg were determined by usual methods.

R_5: Ignited, and dissolved in strong HNO_3, evaporated, extracted with NH_4NO_3 solution, and H_2O_2 was added.

F_5: Tartaric acid was added, saturated with H_2S after being made ammoniacal.

R_7: Ignited to ThO_2.

F_7: Precipitated by NH_4OH.

R_9: Dissolved in HNO_3 and treated with saturated solution of K_2SO_4 to separate Ce group from Y group.

F_9: Discarded.

R_8: Dissolved in a mixture of HNO_3 and H_2SO_4, boiled to destroy the organic matter and precipitated by NH_4OH. The precipitate was ignited to Fe_2O_3.

F_8: Acidified and boiled to expel H_2S. TiO_2 and ZrO_2 were tested by cupferron. Organic matter was decomposed by $HNO_3 + H_2SO_4$, and ammonium molybdate and NH_4NO_3 were added.

R_{10}: Dissolved in NH_4OH and reprecipitated by the Mg mixture. The precipitate was ignited to $Mg_2P_2O_7$.

F_{10}: After the removal of Mo by H_2S, Al and U were determined in this solution.

In Table I the symbols, R and F denote residue and filtrate, respectively.

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(2) S. IIMORI: *Sc. Pap. I. P. C. R.*, **10** (1929), 230.

A good specimen of the mineral was selected, pulverized and employed for the chemical analysis, a small quantity of any inclusions and altered portions being removed by means of an electromagnet. The method is outlined in Table I and some constituents such as F, CO_2, and H_2O were determined by other proper methods using separate samples.

The quantitative analyses were three times repeatedly carried out, twice on dark brown crystals with resinous lustre and once on the portions of dull lustre, as the preliminary analysis proved that the mineral had a singular chemical composition. No conspicuous difference was found among these three analyses, in Table II is, therefore, given the result obtained on an apparently fresh specimen of the mineral.

TABLE II. The analysis of abukumalite.

Constituents	Per cent	Molecular ratio		Constituents	Per cent	Molecular ratio	
BeO	0·00	0·00	26·30	B_2O_3	0·00	0·00	38·84
MgO	0·22	0·55		SiO_2	20·84	34·73	
CaO	13·53	24·16		TiO_2, ZrO_2	0·00	0·00	
MnO	1·13	1·59		Ta_2O_5, Nb_2O_5	0·00	0·00	
Fe_2O_3	2·10	1·31	21·96	P_2O_5	5·84	4·11	
Al_2O_3	1·05	1·03		H_2O (−)	0·16	——	
Cerium earths	6·45	19·28*		H_2O (+)	0·57	——	
Yttrium earths	45·98			CO_2	0·08	——	
ThO_2	0·90	0·34		F	0·45	——	
UO_2	0·00	0·00		Total	99·30		

* The mean molecular weight of this fraction was determined to be 272.

The analysis of the mineral shows that its main constituents consist of calcium oxide, rare earths, phosphorus pentoxide, and silica. The mean atomic weight of the rare-earth elements separated was calculated to be 112 from the weight of oxide and anhydrous sulphate of the fraction. This value, which almost coincides with that of yttrialite(3) coexisting with this mineral, indicates that the most part of the rare earths of this mineral is yttrium and the rest is considered to consist of gadolinium, dysprosium, erbium, etc., as infera-

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(3) The mean atomic weight of rare-earth elements of yttrialite from Iisaka was determined to be 110. Cf., S. HATA: *Sc. Pap. I. P. C. R.*, **34** (1938), 455.

ble from the case of yttrialite.

Regarding H_2O, CO_2, and F as non-essential, we obtain the empirical formula for this mineral to be R^{II}_{263} R^{III}_{440} Si_{347} P_{82} O_{1819}, which, by representing P in its equivalent quantity of Si, becomes R^{II}_{263} R^{III}_{440} $(Si, P)_{450}$ O_{1819} or $R^{II}_{263\times 1}$ $R^{III}_{220\times 2}$ $(Si, P)_{225\times 2}$ $O_{227\times 8}$. Hence, the chemical formula of the mineral should be R^{II} R^{III}_2 $(Si, P)_2O_8$, where $R^{II} = Ca$, $R^{III} = Y$, Gd, Dy, Er, etc., and the atomic ratio Si: P is nearly 4: 1.

The oxygen ratio of all the bases to acid radicals is exactly 1: 1, which indicates that the mineral is of the orthosilicate type. The mineral, therefore, is a calcium-yttrium orthosilicate, a part of silicium being replaced by phosphorus. Thus, this is rather a particular mineral, as there have been reported up to the present, only a few species of phosphosilicate minerals as well as calcium yttrium silicate minerals.

We quote here, in Table III, eleven minerals resembling in some respects to the mineral in question, the minerals being cited from sixty seven minerals of rare-earths silicate shown in Dana's *Textbook of Mineralogy* (1932) and seven new minerals reported in *Mineralogical Abstracts* up to 1938. In the table, the minerals containing phosphorus are included in the first group, those containing calcium in the second, and yttriumsilicate minerals in the third, abukumalite being shown as a mineral of the fourth group. The contents of each constituents are represented in per cent, and the oxygen ratio is thoroughly calculated taking the oxygen number of acid radicals as 6·0.

Among the minerals belonging to the group I shown in Table III, britholite resembles closely to the mineral in question in the oxygen ratio as well as in the chemical constitution, excepting the clear difference of the composition of rare earths contained. The physical characters of the both minerals also coincide almost with each other, for instance, especially in the colour, density, and the crystal system, the britholite from Greenland(4) being hexagonal with the axial ratio 1·000 : 0·724 7. The marked difference between both minerals lies in the composition of rare earths, *viz.*, cerium earths are predominating in britholite, while yttrium earths are so in the mineral from Iisaka.

Erikite, whose constitution is not as yet definitely known, is a cerium mineral containing much alumina and alkalis. Nagatelite and yamagutilite are varieties of allanite and zircon respectively. These

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(4) O. B. BÖGGILD: *Z. Kryst.*, **50** (1912), 435.

TABLE III.

Group	Minerals	Content (per cent) of					Other constituents contained over 3%	Oxygen ratios of base to acid
		CaO	Ce-earths	Y-earths	SiO_2	P_2O_5		
I	Britholite(5)	11	61	0	17	6		6: 6
	Erikite(6)	2	41	0	15	18	H_2O, Na_2O, Al_2O_3, ThO_2	9: 6
	Nagatelite(7)	10	22	5	25	6	FeO, Al_2O_3	6·5: 6
	Yamagutilite(8)	1	16		21	4	H_2O, ZrO_2, ThO_2	6: 6
II	Cenosite(9)	16	0	38	35		H_2O, CO_2	3: 6
	Lessingite(10)	12	59	3	20	1		8: 6
	Beckelite(11)	15	60	3	17		ZrO_2	9: 6
	Hellandite(12)	10	40		24		H_2O, MnO, Fe_2O_3, Al_2O_3	8: 6
	Bodenite(13)	6	28	17	26		H_2O, Fe_2O_3, Al_2O_3	5: 6
III	Yttrialite(14)	1	6	45	30		Fe_2O_3, ThO_2, UO_2	4·5: 6
	Thalenite(15)	0	5	62	29			4·5: 6
IV	Abukumalite	14	6	46	21	6		6: 6

three minerals are, therefore, quite different from abukumalite. The comparison with minerals of the group II shows that abukumalite can not be derived from either of these five minerals, as they all differ in oxygen ratio. Further, they contain generally certain bases which are wanting in abukumalite. Lastly, yttrialite and thalenite in the group III are diorthosilicate minerals and belong to entirely different species of minerals.

Thus, it is obviously concluded that the present mineral from Iisaka can not be comprised in any species ever known, and should be considered to belong to a new species of the britholite group, but

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(5) CHR. WINTHER: *Z. Kryst.*, **34** (1901), 686.
(6) O. B. BÖGGILD: *Z. Kryst.*, **41** (1906), 426.
(7) S. IIMORI, J. YOSHIMURA, and S. HATA: *Sc. Pap. I.P.C.R.*, **15** (1931), 83.
(8) K. KIMURA and Y. HIRONAKA: *J. Chem. Soc. Japan*, **57** (1936), 1195.
(9) R. MAUZELIUS and HJ. SJÖGREN: *Z. Kryst.*, **45** (1908), 102.
(10) V. SILBERMINZ: *Min. Abst.*, **4** (1929~1931), 150.
(11) C. DOELTER: "*Handbuch der Mineralchem.*," II **2** (1917), 182.
(12) W. C. BRÖGGER: *Z. Kryst.*, **42** (1906), 417.
(13) E. S. DANA: "*System of Min.*," (1914), 526.
(14) S. HATA: *Sc. Pap. I. P. C. R.*, **34** (1938), 455.
(15) C. B. BENEDICKS: *Z. Kryst.*, **32** (1900), 614.

being quite different from britholite itself in containing a preponderant amount of yttrium. Dr. S. Iimori suggested to name this mineral "abukumalite" after the Abukuma Range where the mineral was first discovered.

In conclusion I wish to express my heartfelt thanks to Dr. S. Iimori for his kind advices and to Messrs. N. Katayama and H. Inuzuka for their kindness shown in investigating this mineral by X-ray examination. Thanks are also due to Messrs. T. Iimori and O. Nagashima for their aids in collecting the mineral.