BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 925—928 (1966)

Chemical Studies of Minerals Containing Rarer Elements from the Far East District. LX.*,1) Thalenite from Suishoyama, Kawamata-machi, Fukushima Prefecture, Japan

By Kozo NAGASHIMA**

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

and Akira KATO

Department of Geology, National Science Museum, Ueno Park, Taito-ku, Tokyo

(Received September 10, 1965)

Chemical studies of thanlenite from Suishoyama pegmatite, Fukushima Prefecture, showed its composition to be very close to the ideal formula, $Y_2Si_2O_7$, and to a selective distribution pattern of rare earths belonging to the thortveitite-type as defined by Goldschmidt and Thomassen. The X-ray powder studies disclosed a metamict state hitherto unknown in this species, and the original state could be recovered by thermal treatment. Optical and other properties: color, colorless to light gray; luster, resinous; optical properties, $\alpha=1.709\pm0.002$, $\beta=1.716\pm0.002$, $\gamma=1.723\pm0.002$, $(-)2V\sim70^\circ$, $\rho<v$; specific gravity, 4.16, hardness; $6^1/_2$. Chemical analysis: SiO_2, 30.68%; Al_2O_3, 0.10%; Fe_2O_3, 0.17%; $\sum Y_2O_3$, 64.89%; UO_2, 1.12%; ThO_2, 0.20%; CaO, 0.35%; MnO, 0.38%; MgO, 0.33%; Na_2O, 0.02%; $H_2O(+)$, 1.56%; $H_2O(-)$, 0.11%; total, 99.91%.

The rare yttrium sorosilicate mineral thalenite, $Y_2Si_2O_7$, was first described by Benedicks2) in 1898 on the basis of a specimen from a granite pegmatite at Österby, Sweden; then it was described on the basis of samples found at Askagen, Sweden,3) and from Hundholmen and other places, Norway.4) The localities of this mineral added thereafter include Kofu, Japan,5) Arizona6) and Colorado7), U. S. A., and Siberia, U. S. S. R.8)

Suishoyama pegmatite, Kawamata-machi, Fukushima Prefecture, is found in a Mesozoic biotite granite body, which also contains several other pegmatites, smaller than the Suishoyama one. This pegmatite has a well-developed zonal arrangement of felsic minerals and has been worked for quartz and feldspar for many years. It is also very famous for the occurrences of many rare element-bearing minerals, such as abukumalite

---

* This paper was read at the 18th Annual Meeting of the Chemical Society of Japan, held at Kansai University, April, 1965.

1) Part LIX: K. Nagashima, A. Kato and M. Chiba, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **86**, 913 (1965).

** Present address: Department of Chemistry, Faculty of Science, Tokyo Kyoiku University, Otsuka, Tokyo.

2) C. Benedicks, *Geol. Fören. Förn.*, **20**, 308 (1898).

3) H. Sjögren, ibid., **28**, 93 (1906).

4) W. C. Brøgger, Th. Vogt and J. Schetelig, *Vid.-Selsk. Skrifter*, Kristiania, 1. Mat-Nat., Kl. No. 1 (1922).

5) K. Nagashima, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **73**, 600 (1952).

6) F. W. Galbraith and D. J. Brennan, *Univ. Arizona Bull.*, **30**, No. 2, 116 (1959); "Minerals of Arizona," 3rd Ed.

7) J. W. Adams, F. A. Hildebrand and R. G. Havens, "U. S. Geol. Survey Professional Paper," No. 450-D, 6 (1962).

8) T. I. Stolyrova, *Doklady Acad. Nauk. U. S. S. R.*, **155**, 100 (1964).

(type locality),[9] yttrialite,[10] fergusonite,[11] tengerite,[12] thorogummite,[13] allanite,[14,15] uraninite,[16] zircon,[17] gadolinite,[18] keilhauite[19] and some secondary uranium minerals, such as autunite, torbernite and zeunerite.[20] Most of these minerals are found in aggregates of large blades of a lepidomelane containing a small amount of lithium.[21] Abukumalite, allanite, a fergusonite-uraninite mixture and zircon also occur as larger crystals in the intermediate zone composed of large crystals of microcline, albite and quartz. It is in this zone that the thalenite here described was found together with a fergusonite-uraninite mixture. The largest thalenite crystals are fist-size and weigh about 1 kg. Some of them display a few crystal faces, though they are not goniometrically measurable due to their ruggedness.

The mineral thalenite also provides an example of the selective assemblage of rare earth elements in which dysprosium is dominant and which is known under the name "thalenite-type", by Goldschmidt and Thomassen.[22] The mode of the distribution of rare earth elements in the thalenite we have studied is not of the "thalenite-type" but rather of the "thortveitite-type," in which the maximum content of rare earth is in ytterbium. It is worthy to note that another Japanese thalenite, from Kofu, Yamanashi Prefecture, shows the same tendency.

Physical Properties

The outer parts of the thalenite grains are white and have a clouded, porcelain-like appearance, while the inner parts range from colorless to a very light gray or are transparent. The X-ray powder studies showed the former to be a mixture of more or less metamictized thalenite and tengerite, and the latter, to be thalenite itself, but more metamictized than the former. The physical properties, including the optical properties, of the core part are given in Table I. Among them, the refractive indices which are lower than those of thalenite from other localities are so significant as to constitute one of the characteristics of the metamictized minerals (e. g., $\alpha=1.725$, $\beta=1.746$, and $\gamma=1.762$ for thanlenite from Kofu, Japan[5]). However, the conoscopic figure is unexpectedly sharp irrespective of the broader and weaker X-ray diffraction peaks, as will be established in the succeeding.

TABLE I. OPTICAL AND OTHER PRORERTIES

Color	colorless
Luster	resinous to glassy
X-Ray powder diffractions	broad and weak
Optical property	α 1.709±0.002
	β 1.716±0.002
	γ 1.723±0.002
	$(-)2V\sim70°$, $\rho<v$
Specific gravity	4.16
Hardness	6 1/2

X-Ray Powder Studies

The X-ray powder studies were made on unheated and heated materials from the inner parts using a Norelco X-ray Diffractometer. The former gives a few, broad diffraction peaks, as is shown in Table II. After the material has been heated for one hour at about 900°C in the air, the diffraction peaks become very sharp and the powder data are very similar to those for thalenite (non-metamict) obtained from Snowflake pegmatite,[7] Colorado, U. S. A., as is shown in Table II. The positions of all the diffraction peaks of the unheated material shift to the high angle side when heated, without any significant changes in their relative intensities. This means a complete recovery from the metamict to the crystalline state after thermal treatment up to about 900°C; the recovered crystalline state is crystallographically identical with that of ordinary nonmetamict thalenite. Also, the metamictization of this mineral yields the expansion of the unit cell, which is substantially responsible for the lowering of the refractive indices.

Chemical Composition

Chemical analyses were carried out on handpicked material from the inner part. The average atomic weight of the rare earth elements was determined by titrating the weighed mixed oxides with EDTA after first dissolving them in hydrochloric acid. The water content was determined by igniting the sample and by then absorbing the liberated water in calcium chloride. Sodium and potassium were determined by flame-photometry.

The results of the chemical analyses are given in Table III, together with the molecular ratios of the components. The higher uranium content and the presence of thorium that characterize

---

[9] S. Hata, *Sci. Pep. Inst. Physic. Chem. Research*, **34**, 1018 (1938).

[10] S. Hata, ibid., **34**, 455 (1938).

[11] S. Iimori and S. Hata, ibid., **34**, 504 (1938).

[12] T. Iimori, ibid., **34**, 832 (1938).

[13] S. Iimori and S. Hata, ibid., **34**, 447 (1938).

[14] S. Hata, ibid., **36**, 112 (1939).

[15] T. Iimori, ibid., **36**, 53 (1939).

[16] T. Iimori, ibid., **39**, 208 (1941).

[17] S. Hata, ibid., **34**, 619 (1938).

[18] S. Hata, *Reports of the Scientific Research Institute*, **29**, 488 (1953) (in Japanese).

[19] K. Kimura, T. Kawai, K. Morinaga, K. Nagashima and H. Shibata, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **74**, 692 (1953).

[20] K. Hemmi, *Min. Jour.*, **2**, 134 (1957).

[21] H. Hamaguchi and N. Shimoda, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **74**, 879 (1953).

[22] V. M. Goldschmidt and L. Thomassen, *Vidensk. Skrift. I. Mat. Naturv. Klasse*, No. 5 (1924).

TABLE II. X-RAY DIFFRACTIONS OF THALENITES*

Teller County[7]		Suishoyama heated		Suishoyama unheated	
d(Å)	Intensity	d(Å)	Intensity	d(Å)	Intensity
6.3	5	6.36	10		
6.07	4	6.11	5		
5.57	2	5.57	30	5.59	mb
5.50	20	5.51	30		
5.16	3	5.16	5		
4.98	1	5.02	5b		
4.67	5				
4.44	5	4.43	10		
4.17	4	4.17	15		
3.95	1	3.95	5		
3.79	25	3.79	40	3.83	w
3.63	5	3.65	5b		
3.49	4	3.50	20		
3.44	11	3.47	20b	3.49	w
3.31	2	3.30	5		
3.27	18	3.27	80	3.31	s
3.16	18	3.17	40	3.16	w
3.13	11	3.14	20		
3.10	100	3.10	100	3.13	s
3.05	4	3.04	5		
2.96	1	2.964	10		
2.86	6	2.864	5		
2.81	40	2.812	30		
2.75	30	2.754	30		
		2.715	5		
		2.670	5		
2.61	2	2.605	5		
2.57	5	2.577	20		
2.51	4	2.520	5		
2.46	3	2.460	5b		
2.42	1	2.428	5		
2.40	3	2.409	15		
2.37	1	2.368	5		
2.34	3	2.332	5		
2.30	2	2.306	5		
		2.254	5		
2.24	30	2.240	50	2.26	w
2.21	1				
2.20	1				
2.18	9	2.176	60		
2.127	6	2.120	15		
2.103	0.7	2.110	15		
2.076	0.7				
2.053	3	2.047	5		
2.027	2	2.032	5		
1.994	3	1.994	5		
1.977	4	1.979	10		
1.953	2	1.947	5		
1.922	0.7	1.922	5		
		1.901	5		
1.895	3	1.893	5		
1.873	7	1.872	15		
1.859	0.7				
1.845	3	1.844	10		
1.817	4	1.816	10		
1.797	3	1.798	5		
1.781	2	1.779	5b		
1.768	1				
1.746	0.7				
1.740	0.7	1.737	5		
1.728	1				
1.716	4	1.715	10		
1.704	2	1.711	5		
1.681	1	1.682	5		
1.670	5	1.670	30		
1.658	2	1.659	30		
1.645	5	1.645	10		
1.631	5	1.631	10		
1.616	4	1.617	5		
1.603	1				
1.583	0.5				
1.570	5	1.567	20		
1.558	2				
1.547	2	1.545	5		
1.523	1	1.531	5b		
1.510	2	1.514	5b		
1.497	0.7				
1.478	2				
1.465	2				
1.455	3	1.455	10		
1.445	1				
1.429	0.7				
1.425	1				
1.415	0.7				
1.408	1	1.409	10		
1.404	1				
1.391	0.7				
1.382	0.7				
1.370	2	1.369	10		

* b ……broad m……medium
s ……strong w……weak

this material are responsible for the metamict state.

As is shown in Table III, the experimental formula of the thalenite from Suishoyama is (Y, Yb, Er, Dy, U, Ca, etc.)$_{2.012}$(Si, Al)$_{2.009}$O$_{7.000}$·0.38H$_2$O, which is very close to the ideal formula, (Y, Yb)$_2$Si$_2$O$_7$, except for an additional 0.38 mol. of H_2O.

The crystallochemical nature of the water in thalenite is still unknown. In Doelter's handbook,[23] the formula is given as $Y_2Si_2O_7\cdot{}^1/_2H_2O$; this has lately been revised to $Y_2Si_2O_7$. However, judging from the results of a survey of the literature concerned, no significant study has hitherto been made of the water in this mineral.

---

23) C. Doelter, "Handbuch der Mineralchemie," Band II, 2 Hälfte, Teodor Steinkopff, Dresden und Leipzig (1917), s. 170.

TABLE III. CHEMICAL ANALYSIS

		%/F.W.	No. of oxygens	No. of metal atoms	No. of metal atoms × 3.919	
SiO_2	30.68	0.5106	1.0212	0.5106	2.0010	2.009
Al_2O_3	0.10	0.0010	0.0030	0.0020	0.0078	
Fe_2O_3	0.17	0.0011	0.0033	0.0022	0.0086	2.012
$^*\sum Y_2O_3$	64.89	0.2430	0.7290	0.4860	1.9046	
UO_2	1.12	0.0041	0.0082	0.0041	0.0160	
ThO_2	0.20	0.0008	0.0016	0.0008	0.0031	
CaO	0.35	0.0062	0.0062	0.0062	0.0243	
MnO	0.38	0.0054	0.0054	0.0054	0.0212	
MgO	0.33	0.0082	0.0082	0.0082	0.0321	
Na_2O	0.02	0.0003	0.0003	0.0006	0.0024	
$H_2O(+)$	1.56	0.0975			0.3819	
$H_2O(-)$	0.11					
	99.91		1.7864			

* Average atomic weight 109.5
Specific gravity 4.16

Proton magnetic resonance studies[24] of water molecules in this material proved that they are not in a merely absorbed state, but that they combine with the mineral rather tightly at room temperature, and that they (more precisely, the protons) do not exist as isolated OH^- ions, either. Nearly 10% water (by weight) has been found in the white outer part of the mineral, which is in a less metamictized state than the inner part, according to the X-ray powder study. Even though the presence of a small amount of tengerite in the outer part is taken into consideration, a considerable amount of water should be in thalenite itself; it is responsible for the less metamictized state.

The Distribution Pattern of Rare Earth Elements

The distribution pattern of rare earth elements was determined by the X-ray fluorescent method; yttrium, neodymium, samarium, gadolinium, terbium, dysprosium, erbium and ytterbium were thus found. Lutetium may be present, but its presence was not confirmed due to the overlapping diffractions of other spectra with stronger intensities. A quantitative estimation is given in Table IV, in which the total of the detected oxides is calculated to be 100% and is compared with those for the Siberia thalenite.[8] The present material has predominances of dysprosium, erbium and ytterbium among the lanthanides, and a very high concentration of yttrium in rare earths. The concentration of cerium-group lanthanides is too low to be detected. The average atomic weight calculated by adopting the values rendered by the X-ray fluorescent analysis was 108, which coincides rather well with that determined by the ordinary chemical method shown in Table III.

TABLE IV. COMPOSITION OF RARE EARTH ELEMENTS

	Siberia[8]	Suishyoyama
$\sum Ce_2O_3$	1.1	
Nd_2O_3		0.3
Sm_2O_3		0.2
Gd_2O_3	1.1	1.2
Tb_2O_3	0.6	0.2
Dy_2O_3	6.4	4.3
Ho_2O_3	2.4	
Er_2O_3	9.1	5.9
Tu_2O_3	2.9	
Yb_2O_3	9.1	11.6
Lu_2O_3	0.9	
Y_2O_3	67.5	76.4
	100.1	100.1

The authors wish to express their thanks to Professor Takeo Watanabe, Geological Institute, Faculty of Science, the University of Tokyo, for making the X-ray diffraction and fluorescent analysis instruments available for their present work, and to Mr. Hideo Katagiri, the Manager of the Suishoyama quarry, for his help in collecting the minerals studied.

---

[24] K. Nagashima and Y. Sugitani, 18th Annual Meeting of the Chemical Society of Japan, Osaka, 1965.