

YTTRIALITE FROM IVEDAL, IVELAND, SOUTH NORWAY

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Yttrialite from Ivedal, Iveland has a chemical composition very close to the theoretical formula $RE_2Si_2O_7$. Some Th and U substitutes for RE, their higher valencies being balanced by Ca, Fe^{2+} and Mn. X-ray data indicate the existence of three different minerals with the chemical composition $RE_2Si_2O_7$: thalenite, yttrialite and a third mineral with a thortveitite structure which should have a new name. The structural type formed in a given situation is chiefly determined by small differences in chemical composition, but may also be influenced by pT conditions.

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Introduction

The rare earth silicate yttrialite was identified in samples from Ivedal, Iveland in 1955 on the basis of an X-ray powder diffraction diagram obtained from heated material. The mineral has been reported in small quantities from a few other places in South Norway, but has never been described from Norwegian localities.

The present mineral was found in a small pegmatite quarry near Ivedal farm in Iveland; the first published description of the locality is that of Schetelig (1931). The main minerals are microcline, plagioclase, quartz and micas. Apart from these the paragenesis studied by Schetelig consists of fergusonite, xenotime, alvite, thalenite, gadolinite, thortveitite, orthite, pyrite, magnetite and spessartine. The new hydrous rare earth silicate tombarthite has also recently been identified in material from this quarry.

The mineral assemblage closely resembles that of Högetveit, Evje (type locality of tombarthite), where yttrialite has also been found recently. Both pegmatites appear to have some genetical relationship to the Iveland-Evje amphibolite described by Barth (1947).

The yttrialite from Ivedal occurs in dark reddish brown masses, usually surrounded by biotite and partly covered by a thick crust of tenerite. It is very difficult to distinguish from thalenite in hand specimen, since this mineral occurs in an analogous manner in the pegmatite. The yttrialite is

Table 1. Yttrialite, Ivedal, Iveland.

	Wt %	Cat. prop.	
SiO ₂	28.70	47.82	
Fe ₂ O ₃	1.18	1.48	} 48.55
MnO	0.48	0.68	
MgO	0.15	0.37	
CaO	0.93	1.66	
UO ₂	2.59	0.96	
ThO ₂	6.97	2.64	
Y ₂ O ₃	31.37	27.78	
La ₂ O ₃	0.14	0.09	
Ce ₂ O ₃	0.66	0.40	
Pr ₂ O ₃	0.15	0.09	
Nd ₂ O ₃	1.09	0.65	
Sm ₂ O ₃	1.17	0.67	
Eu ₂ O ₃	0.05	0.03	
Gd ₂ O ₃	2.44	1.35	
Tb ₂ O ₃	0.61	0.33	
Dy ₂ O ₃	5.35	2.87	
Ho ₂ O ₃	1.00	0.61	
Er ₂ O ₃	3.69	1.93	
Tm ₂ O ₃	0.75	0.40	
Yb ₂ O ₃	5.58	2.83	
Lu ₂ O ₃	1.45	0.73	
H ₂ O	3.68	(40.84)	
	100.18	168.91	

metamict-amorphous and isotropic with mean refractive index 1.723. Specific gravity is 4.31 determined with a pycnometre filled with toluene.

The mineral was purified for analysis by crushing and separating with heavy liquids and magnetic separation (with a Frantz Isodynamic Separator). The purity of the material to be analyzed was controlled by X-ray diffraction analyses of heated material. Chemical analysis was carried out by a combination of conventional 'wet' methods and X-ray fluorescence spectrometry. Results are given in Table 1. The calculated cation proportions give the formula RE₂Si₂O₇. The rare earths are partly replaced by U and Th, the higher valencies of the latter being balanced by corresponding substitution of lower valence elements Fe²⁺, Ca and Mn. RE₂Si₂O₇ is also the theoretical formula of yttrialite and thalenite (and thortveitite although the RE group in the latter is to a great extent replaced by Sc).

X-ray studies

RE₂Si₂O₇ compounds were synthesized by Warshaw & Roy (1964) and by Ito & Johnson (1968). Warshaw & Roy synthesized Y₂Si₂O₇ in two different modifications, giving two distinct X-ray diffraction patterns which they called α and β type. Ito & Johnson found an additional γ structure.

Lima de Faria (1964) published X-ray data for natural yttrialites from Llano County, Texas (type locality), and from Iisaki Fukushima, Japan. By heating to 1000 °C a pattern is obtained which corresponds to the γ type, while heating to 1300 °C produces the α type pattern of the synthetic compounds.

As mentioned before the yttrialites are completely metamict amorphous giving no reflections on X-ray film in unheated condition. After heating to 850 °C in air the Ivedal mineral gave patterns (registered with a 9 cm. camera, Mn filtered Fe-radiation) which are in very good agreement with those obtained from yttrialites from Llano County and from Iisaka, Fukushima, treated in the same manner.

D-values of yttrialite from Ivedal heated to 850 °C and to 1000 °C in air are given in Table 2. The d-values from the low temperature (850°)

Table 2. X-ray data from powder diagrams.

1000°		850°		1000°		850°	
I	d	I	d	I	d	I	d
50	6.65					90	2.39
10	6.01			10	2.19		
50	5.77			30	2.18		
50	5.36			10	2.16		
50	4.60	80	4.68	10	2.15		
40	4.45			20b	2.14	10	2.14
50	4.39	20	4.38	20b	2.10	10	2.10
70	4.33	diff.	4.36	10	2.06	90	2.05
50	4.19	10	4.19			50	2.02
		80	4.04			50	2.01
10	3.79			diff.	1.90		
10	3.63				1.89		
		90	3.46			60	1.86
10	3.44			20	1.85	40	1.85
10	3.34			20	1.83		
90	3.30	20	3.31	40	1.80		
50	3.24			50b	1.77	60	1.74
90	3.20						
40	3.12	50	3.19				
50b	3.09						
30	3.02	100	3.05				
100	2.99	50	2.99				
90	2.90	30	2.90				
80	2.85	10	2.82				
30	2.80						
40	2.78						
20	2.72	10	2.71				
40	2.70						
40b	2.68						
20	2.64	90	2.63				
20	2.58						
30	2.54						
20	2.47						
20	2.43						

phase corresponds very well with the values from Lima de Faria's low temperature (1000°) phase and even better with the synthetic γ phase. In the same way the values from the high temperature product (1000°) corresponds to Lima de Faria's 1300° values and to the synthetic α type pattern. Heating of the Ivedal mineral to higher temperatures produces no further change in the diffraction pattern.

Some extra lines in the low temperature (850°) pattern correspond to strong reflections in the high temperature pattern. Similarly the high temperature α phase pattern contains extra lines both from the low temperature phase and also from the β phase of the synthetic compounds.

Discussion

Four different X-ray diffraction patterns are known for material with the general formula $\text{RE}_2\text{Si}_2\text{O}_7$.

Type 1. The thalenite pattern produced by non-metamict minerals from, among others, Österby, Dalane, Sweden (type locality of thalenite, described by Benedicks in 1889); Åskagen, Värmland, Sweden (Sjögren 1906); Hundholmen, North Norway (Vogt 1922); and Teller County, Colorado (Adams et al. 1962). So far no one has succeeded in synthesizing a compound with this X-ray pattern.

Type 2. Pattern produced by a non-metamict mineral from Åskagen, Värmland, and from Högetveit, Evje and by the heating products of several metamict so-called thalenites. It corresponds to the synthetic β phase. This is a thortveitite structure, but with a larger cell size.

Type 3. Pattern produced by heated yttrialites from Llano County, Texas (type locality described by Hidden & Mackintosh 1889); Iisaki, Fukushima, Japan; and also by the present mineral from Ivedal, heated to 1000°C or more. This is a high temperature form and corresponds to the synthetic α phase.

Type 4. This pattern corresponds to the synthetic γ phase of Ito & Johnson. The yttrialites mentioned above, producing the α phase or type 3 pattern after heating to 1000°C or more, produce the type 4 pattern by heating to $750\text{--}1000^{\circ}\text{C}$ in air. This pattern is also identical to Lima de Faria's low temperature phase. The transition temperature from γ to α phase seems to vary somewhat from one mineral to another, most probably due to small variations in chemical composition.

These four pattern types are, in my opinion, characteristic of three different minerals, very closely related chemically.

Thalenite – pattern type 1 – is always found in a non-metamict-amorphous condition. Only in one case has it been reported partly metamict. Nagashima & Kato (1966) describe a thalenite from Suishoyama, Fukushima, Japan, which unheated gives only a few X-ray reflections belonging to the thalenite, type 1 pattern. By heating to 900°C in air, however, it gives a clear and sharp thalenite pattern.

Opinions differ as to the role of water in the thalenite structure. Benedicks gives the thalenite formula as $Y_2Si_2O_7 \cdot \frac{1}{2}H_2O$. Sjögren (1906) and Vogt (1922) are of the opinion that water does not enter the crystal lattice. Sjögren reports that the freshest parts of the mineral from Åskagen contains the smallest amounts of water. The Hundholmen thalenite which is completely fresh and non-metamict, contains only 0.75 % water (determined as loss on ignition).

Nagashima & Kato again maintain that water is a part of the thalenite molecule. They also report that the fresh portion of the mineral contains more water than the metamict-amorphous, and that this water content is responsible for the *less* metamict state. This is not in accordance with the common experience with metamict minerals, which is that metamictization is usually accompanied by an *increase* in water content. These authors also find that the partly metamict-amorphous parts of the mineral recrystallize on heating to 900 °C in air, and that the recrystallization product gives a thalenite (i.e., type 1) pattern. This is hardly consistent with the theory that the high content of water is responsible for the less metamict state.

The X-ray patterns of thalenites are not changed by heating to 1000 °C in air. This has been tested in the case of the Österby and the Hundholmen thalenites. Heating to higher temperatures 1300 °C or heating to 500 °C under water pressure – 20000 psi, changes the structure to a thortveitite structure, i.e., $\beta RE_2Si_2O_7$, pattern type 2.

The minerals which give the type 2 pattern are mainly the metamict so-called thalenites from S. Norway, but a non-metamict mineral with this structure has also been found in Åskagen, Värmland, together with the genuine thalenite. Yttrialite is most probably also present (i.e. a mineral which by heating gives the high temperature, type 3, X-ray pattern, although so far it has not been possible to reproduce the low temperature, type 4, pattern). A second non-metamict mineral with type 2 structure has been found at Högetveit, Evje, S. Norway (J. Hysingjord, personal communication).

This mineral, which will shortly be described in detail, should have a new name and be recognized as a specific mineral. Already Schetelig (1931) was of this opinion. On page 512 he writes: 'It is for different reasons probable that the mineral from the mentioned localities in Southern Norway (in this paper described as "thalenite") is an independent species related to thalenite on the one side and to hellandite on the other.' Ito & Johnson (1968) write: 'A mineral described as thalenite from Ånneröd, Vaaler, Norway by Sabina and Traill (1960), subsequently identified by Warshaw and Roy (1964) as $\beta Y_2Si_2O_7$ (isomorphous with thortveitite; Strunz, 1957) should be given a new name. If an yttrialite described by Nishimura and Ueda (1954) also is truly isostructural with thortveitite, it must be the same mineral.'

Yttrialite is always metamict amorphous. Its heating products give the α phase structure (pattern type 3) by heating to relatively high temperatures

in air and the γ phase (pattern type 4) by heating to lower temperatures in air.

The formation of these three different minerals with nearly identical composition is difficult to explain since they are known to occur at least in pairs and in some cases probably even all three together. In Ivedal, 'thalenite' – the metamict variety, isostructural with thortveitite – is found in close contact with yttrialite. It is difficult here to explain the different structures as due to varying temperature pressure conditions of formation. On the contrary they seem to have formed simultaneously.

Another and more probable explanation is a chemical control of the structure. Unfortunately there are few analytical data available. The real thalenites, the minerals which give a distinct thalenite pattern (type 1) and which have been identified as thalenites by their outer crystallography, such as Benedick's original thalenite, Sjögren's from Åskagen and Vogt's from Hundholmen, are all extremely pure RE silicates with only traces of other elements present.

Metamict 'thalenites', giving a type 2 pattern on heating, seem to be fairly high in CaO (2–3%) as well as Fe and Mn and also contain some Th and U.

Yttrialite usually has a high content of Th and sometimes U. These two elements are electrostatically balanced by a corresponding content of Ca,

Table 3. Chemical composition recalculated to 100 % waterfree.

	1	2	3	4	5	6	7	8	9	10	11
SiO ₂	29.74	29.48	29.81	29.09	33.00	29.21	30.16	31.64	29.93	31.63	31.23
FeO	–	2.92	1.22	2.34	0.22	0.05	0.07	–	–	–	–
Fe ₂ O ₃	1.22	–	1.89	0.76	4.49	1.44*	2.44*	0.32	0.47	tr.	0.17
MnO	0.55	0.78	2.11	1.59	0.34	0.28	0.61	–	–	–	0.39
MgO	0.15	–	0.77	0.09	0.34	1.03	1.02	0.22	0.05	–	0.34
CaO	0.96	0.61	3.68	0.54	2.02	3.33	2.35	0.52	0.11	–	0.36
UO ₂	2.68	0.84	0.75	4.60	1.12	–	–	–	–	–	1.14
ThO ₂	7.22	12.13	6.22	10.24	1.80	–	–	–	0.19	–	0.20
RE ₂ O ₃	57.51	51.84	50.89	50.32	53.31	64.66**	63.32**	67.09	69.25	68.39	66.06
PbO	tr.	0.86	0.05	–	–	–	–	–	–	–	–
Al ₂ O ₃	–	0.56	2.54	0.41	3.37	–	–	0.46	–	–	0.10

- 1 Yttrialite Ivedal, Iveland. Analyst B. Bruun, S. Bergstöl
- 2 Yttrialite Llano County, Texas. Hidden & Mackintosh (1889)
- 3 Yttrialite Komenono, Japan. Ueda & Nishimura (1954)
- 4 Yttrialite Suishoyama, Japan. Ueda & Nishimura (1954)
- 5 'Thalenite' Högetveit, Evje, S. Norway. Schetelig (1931)
- 6 'Thalenite' Ivedal, Iveland, S. Norway. Schetelig (1931)
- 7 'Thalenite' Ånneröd, Vaaler, S. Norway. Schetelig (1931)
- 8 Thalenite Österby, Dalane, Sweden. Benedicks (1898)
- 9 Thalenite Åskagen, Värmland, Sweden. Sjögren (1906)
- 10 Thalenite Hundholmen, Tysfjord, N. Norway. Vogt (1922)
- 11 Thalenite Suishoyama, Japan. Nagashimo & Kato (1966)

* U₃O₈ included in Fe₂O₃

** ThO₂ included in RE₂O₃

Fe²⁺ and Mn. A high Th content seems to favour the formation of the γ and α structure characteristic of natural yttrialites.

Studying available data for RE elements distribution for the three minerals in question does not seem to reveal any significant differences, either by plotting in the conventional way by joining even and odd numbered elements separately or by using the method of Coryell, Chase & Winchester (1963). There is a general depletion in the La end and an enrichment of the elements with a smaller ionic radius in the Yb–Lu end.

Even if there is no significant difference in the content of RE it is likely that the content of cations with relatively small cation radii such as Fe and Mn as well as a high content of Yb is responsible for the β structure (pattern type 2) of the metamict 'thalenites'. The best example of this effect is of course thortveitite itself, where most of the RE is substituted by Sc which has a much smaller ionic radius than Y and the RE elements.

This explanation does not cover all cases. If the yttrialites described by Ueda & Nishimura (1954) really have a thortveitite structure these minerals belong to the 'thalenite' (type 2) minerals and are not yttrialites, even if they have high contents of Th. On the other hand a thalenite from SW Finland described by Vormaa et al. (1966), which is metamict and by heating gives the γ phase characteristic of yttrialite, should be named yttrialite even if the content of Th is low. Unfortunately only a semiquantitative analysis exists of this mineral.

There are reasons to believe that the chemical composition is commonly the decisive factor determining the structure of these minerals, but that other factors such as temperature and pressure of formation play an important role under special conditions.

Heating experiments carried out on natural minerals, prove that it is possible to convert genuine thalenite as well as yttrialite to the β structure (giving pattern type 2) by heating to 500 °C and 18,000 psi hydrostatic pressure. The minerals which already have this structure, mainly the metamict 'thalenites', the mineral from Åskagen and thortveitite itself, preserve their structure under these conditions.

Heating to 1350 °C in air also converts thalenites from Österby as well as from Hundholmen to minerals giving pattern type 2, the β phase. It is evident therefore that the β phase (i.e., the thortveitite structure) may exist over a wide range of pT conditions.

To prove these theories more analytical data are necessary, and also X-ray data from more heating experiments on natural minerals as well as synthetic work under varying conditions.

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