Discreditation of tombarthite-(Y)

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ABSTRACT

Tombarthite-(Y) is discredited as a mineral species. No type material was available, but material used for the original description has been located and neotype material defined. The main reason for the erroneous description of tombarthite-(Y) is the result of chemical analyses being carried out on heated material, which removed elements such as C and F. New semi-quantitative chemical analyses show that at least F is present in the fresh material, but absent after a heating scheme identical to that of the original description. Modern powder X-ray diffraction methods (XRD) confirm that the material identified as tombarthite-(Y) is a mixture of metamict and crystalline phases. Consequently, what was known as tombarthite-(Y) is not a mixture of the same minerals in equal amounts in different samples, but mixtures of various minerals depending on the sample. The main minerals identified are thalénite-(Y), xenotime-(Y) and kainosite-(Y). The discreditation of tombarthite-(Y) relies on new analyses of a large number of samples from the collection of the Natural History Museum (NHM) in Oslo and has been approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (proposal 16-K).

Keywords: tombarthite-(Y), discreditation, Høgetveit farm, Evje and Hornnes, Aust-Agder, Norway, powder X-ray diffraction.

Introduction

TOMBARTHITE-(Y), $Y_4(Si,H_4)_4O_{12-x}(OH)_{4+2x}$ with $x \le 4$, was first described as a new species (IMA) 1967-031) from a pegmatite at the Høgetveit farm, Evje and Hornnes, Aust-Agder, Norway by Neumann and Nilssen (1968). Tombarthite-(Y) was named after Tom F. W. Barth (1870-1953) former Professor in Geology at the Natural History Museum (NHM) in Oslo. Since the original description, tombarthite-(Y) has only been observed at the following three localities: Ivedal, Iveland, Aust-Agder, Norway (Nilssen, 1971); the Reiarsdal pegmatite (also known as Tjomsås), Vest-Agder, Norway (Griffin et al., 1979); and the Mont Blanc Massif (Rolland et al., 2003). In connection with the move of the mineral collection at the NHM in Oslo, the type material of tombarthite-(Y) was sought as no material in the collection was labelled

E-mail: geofriis@yahoo.com https://doi.org/10.1180/mgm.2018.111 as being the type material. As a result, a detailed review of the original description raised several concerns about the scientific approach and consequently the validity of tombarthite-(Y) as a mineral species.

Type material

In the original description of tombarthite-(Y) no collection number was given for the type material, but it states: "*Type material is preserved at the Mineralogical-Geological Museum, Oslo University, Norway*" (Neumann and Nilssen, 1968). Raade (1996) attempted to identify potential type material in the collection of the museum in Oslo and wrote: "*The Oslo Museum possess a large number of tombarthite specimens from Høgetveit, stored in seven drawers. Numerous specimens have been X-rayed, most of them with pointers showing from where the samples have been taken. Unfortunately, the labels do not indicate on which specimen or specimens the description was actually*

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	Sample I	Sample II
a (Å)	7.12	7.12
$b(\mathbf{A})$	7.29	7.24
$c(\dot{A})$	6.71	6.69
β (°)	102.41	102.29
<i>d</i> -values (Å) and intensities	6.95(20);	6.95(100);
for unit-cell determination	6.55(100);	6.53(100);
	3.23(70);	5.38(20);
	2.97(60)	3.21(50)
Density (g/cm ³)	3.51	3.65

TABLE 1. Summary of data from the original description of tombarthite-(Y)

based, and it is therefore not possible to designate any of them in particular as holotype or cotype specimens". Consequently, no samples in the collection of the museum in Oslo could be identified as material used for the description of tombarthite-(Y).

Identifying potential type material

In order to discredit a mineral species the type material should be analysed, but if it cannot be located efforts should be undertaken to find it or related material, which can then be defined as the neotype (Dunn, 1990; Nickel and Grice, 1998). Therefore, substantial work was carried out to locate material at the NHM (Oslo), which could be the type material or material that was part of the original description.

Neumann and Nilssen (1968) used two samples for their description and labelled them Sample I and Sample II. They mentioned that analyses were performed on material free of inclusions and

FIG. 1. Pages from the mineral separation lab book. (*a*) Entry from May 26th 1964 stating that separate 16/64 is a 90 mesh created from a "*thalénite*" sample. (*b*,*c*) mineral separate 3/65 was made on February 18th 1965 from the same sample as 15009 (which is a Debye-Scherrer film number) and subsequently material was further separated into fractions (sample 4/65). Of these fractions T4 and T5 were combined for XRD. Further it can be seen that T3 was sent for DTA on March 4th 1965 and has Debye-Scherrer number 16756. Note the density determination of 3.66 g/cm³ does not match those given in the original publication, but see below for further details.



FIG. 2. Pages from B. Nilssen's lab book, showing density determination of the two samples 16/64 and 4/65, respectively.

impurities, which indicates that the material used was from mineral separates. The results for the two samples used in the original description of tombarthite-(Y) are summarized in Table 1.

The mineral collection of the NHM in Oslo has 24 samples registered as tombarthite-(Y), of these only 18 state when they entered the collection and these were all acquired in 1971 or more recently, i.e. minimum of three years after the description was published and therefore cannot be type material. Sample KNR 39591 has a note[†] stating "*Remains of material given to Professor Barth*", but this collection number consists of three pieces of feldspar and nothing resembling tombarthite-(Y).

As mentioned by Raade (1996), the NHM in Oslo has a large volume of unregistered pegmatite material in its storage. However, most of the material was acquired post the description of tombarthite-(Y), hence could readily be excluded as potential type material. Both registered and unregistered samples often have a pointer identifying where material has been removed for XRD analyses, mostly Debye-Scherrer, and the corresponding film number. A systematic review of all Debye-Scherrer films (~150) identified as tombarthite-(Y) revealed that a lot of analyses and heating experiments were performed on only a few samples. Of particular interest were some labelled 16/64 and 4/65, as some had "*analytical material*" written on the film sleeves. Labels in that format is not used for specimens in the collection, however among the storage material some boxes and vials containing separates were found with such labels.

Old laboratory books from Borghild Nilssen (second author of the original description) were retrieved from the archive, which confirmed that the material was mineral separates labelled in the format of Batch/Year (Fig. 1). It is written that 16/64 was made from a "thalénite" specimen, but no further information. For 4/65 it states that material was from the same sample as Debye-Scherrer film no. 15009 (Fig. 1b). A search did not provide a sample with such a pointer, but a vial containing a few fragments has a XRD pointer with the number 15009 written on it. Subsequently, a sample with 15009 written on the specimen label was located. The sample was registered as thalénite-(Y) from Høgetveit (KNR 39585) and is likely to be the sample from which separate 4/65 was generated. Neither in the lab books nor on the X-ray film sleeves was it written how the samples 16/64 and 4/65 corresponded to Sample I and Sample II of the original description. However, based on Fig. 1c and Table 1, it is inferred that 4/65 corresponds to Sample II, as it states that material was sent for DTA (differential thermogravimetric analyses) and Neumann and Nilssen (1968) wrote that only Sample II was sent for DTA.

Borghild Nilssen's lab books contained a series of density calculations revealing that the measured densities for 16/64 and 4/65 were $3.506 \approx 3.51$ and $3.651 \approx 3.65$ g/cm³, respectively (see Fig. 2 and Table 1). Consequently, Sample I corresponds to the material labelled 16/ 64 and 4/65 is Sample II of the original description of tombarthite-(Y). The material in the vial labelled with XRD number 15009 is from the same specimen as Sample II. Therefore, the material in the vial has been registered in the collection as the neotype for this work as KNR 43777. It is highly likely, but not conclusive, that the neotype originates from sample KNR 39585; a sample that was collected in 1931. The remaining mineral separates of 16/64 and 4/65

[†]Original notes in Norwegian are translated in the text for clarity.

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FIG. 3. Scan of Guinier film (no. 1533) of tombarthite-(Y) used for unit-cell determination of Sample I. (a) 4/65; (b) 16/64; (c) 16/64 + Pb(NO₃)₂; (d) Pb(NO₃)₂. Note 16/64 and 4/65 refers to Samples I and II, respectively.

TABLE 2.	Observed	and c	calculated	d-values	(Å)) of	tombarthite-(Y) from the	e original	publication
							· · · · · · · · · · · · · · · · · · ·		/		

h k l 0 1 0 1 0 0 0 0 1	d _{obs.} 7.32 6.95* 6.55*	<i>I/I₀</i> 30 20 100	d _{calc.} 7.29	d _{obs.}	I/I ₀	d _{calc.}
0 1 0 1 0 0 0 0 1	7.32 6.95* 6.55*	30 20 100	7.29			
1 0 0 0 0 1	6.95* 6.55*	20 100				7.24
0 0 1	6.55*	100		6.95*	100	
		100		6.53*	100	
$\bar{1} 0 1$			5.39	5.38*	20	
101			5.03			5.01
0 1 1			4.87	4.83	20	4.84
	4.66#	20		4.63#	30	
	4.55#	20				
111			4.34			4.32
101			4.30	4.28	50	4.31
	4.24#	30		4.23#	20	
111			3.71			3.71
020			3.64	3.60	100	3.62
200	3.54	30	3.47	3.52	50	3.48
$\frac{1}{2}$ 0 1	3.42	80	3.39	3 42	40	3.39
0 0 2	3.28	10	3.27	3.29	60	3.26
120	3.23*	70		3.21*	50	
210	3.11	20	3.14	3.13	10	3.13
$\overline{\overline{2}}$ 1 1	3.02	20	3.08	3.04	50	3.07
ī 2 1	3.00	30	3.02	2.99	50	3.00
012			2.99			2.97
$\overline{1}$ 1 2	2.97*	60	2.97			2.95
2.0.1	2.89	50	2.82	2.87	50	2.83
121	2.77	30	2.78	2.74	50	2.77
102			2.74			2.73
2 0 2			2.70	2.68	20	2.69
2 1 1			2.63	2100	20	2.63
112	2.57	20	2.56			2.56
$\frac{1}{2}$ 1 2	,		2.53			2.52
2 2 0			2.52			2.51
2.2.1			2.48			2.47
022	2 44	30	2 44	2 44	10	2 42
$\frac{1}{1}$ 2 2	2.40	40	2.43	2	10	2.41
301			2.36			2.35
130	2.30	30	2.29	2.30	50	2.28
$\frac{1}{1}$ 0 3	2.22	30	2.23	2.24	20	2.20

* Reflections used for unit-cell refinement; # reflections considered contaminations in the original description.

Reference Method Sample	l Wet chem I	1 Wet chem II	2 EPMA [#] Light	2 EPMA [#] Dark	3 EPMA
SiO	12.60	15.90	14.8	20.5	27.81
P_2O_5	-	-	2.1	4.1	0.84
FeO	0.78	5.52	2.2	2.3	_
MnO	3.68	1.02	4.9	10.0	_
MgO	0.33	0.26	0.2	0.2	_
CaO	3.56	4.88	4.7	4.4	_
SrO	0.05	*	_	_	_
ThO ₂	3.08	0.85	6.1	1.3	0.71
UO ₂	1.31	0.57	1.0	1.83	0.18
$Y_2 \tilde{O_3}$	29.96	28.00	33.0	34.7	22.08
Total REE ₂ O ₃	20.88	19.54	18.75	8.73	26.39
Na ₂ O	0.08	-	_	_	_
K ₂ Ô	0.08	-	_	_	_
F	_	_	_	_	_
H_2O $-O = F^{\ddagger}$	21.19	22.71	19.2 7.6	14.9 7.9	_
Total in paper	97.58	99.20	99.35	95.06	77.98
Total without H ₂ O	76.39	76.54	87.75	88.06	78.01

TABLE 3. Published composition of tombarthite-(Y)

References: (1) Neumann and Nilssen (1968); (2) Griffin et al. (1979); and (3) Rolland et al. (2003).

* The CaO contained 5% SrO; # Scanned over an area of $300-500 \ \mu m^2$; – below limit of detection or not analysed for; [‡]note that no F was found in the analyses.

have been assigned collection numbers KNR 43778 and KNR 43779, respectively.

Original data

Diffraction data

Neumann and Nilssen (1968) carried out a series of Debye-Scherrer analyses on tombarthite-(Y) and noticed that the material had some degree of metamictization. The unit-cell determinations were carried out using a Guinier camera with Mn-filtered FeK α -radiation and Pb(NO₃)₂ as the internal standard. The only Guinier films for 16/64 and 4/65 with internal standards are the films 1533 and 1113, respectively. Film 1533 is shown in Fig. 3 and it is apparent that there are significant differences in the diffraction pattern of the two samples (Fig. 3*a*,*b*).

The observed and refined d values for the published tombarthite-(Y) are given in Table 2. The variations between the two samples is particularly emphasized by the strong reflection (020) with 100% intensity in Sample II being absent in Sample I, indicating that the two samples

are not the same material or at least not a pure phase. In addition, while Neumann and Nilssen (1968) ascribed the (020) reflection observed in only one sample to originate from tombarthite-(Y) they assumed the relative strong reflections with d values of 4.66 and 4.24 Å (Sample I) and 4.63 and 4.23 Å (Sample II) to be caused by contamination despite being present in both samples.

The unit-cell refinements of tombarthite-(Y) were reported in the monoclinic space group $P2_1/$ *n* because of the similarity in the diffraction pattern to that of monazite. The refined unit cells were based on only four reflections for each sample of which two to three were among the highest d values observed and all reflections used had d > 2.97 Å (see Tables 1+2). That is, the reflections used for the cell refinements are those that have the lowest accuracy in a measured position. Another peculiarity in the reflections chosen for the cell refinements, is that the strong reflection $(\bar{1}12)$ is used for the refinement in Sample I, but it is absent in Sample II. Correspondingly, the $(\bar{1}01)$ reflection used for the refinement of Sample II is not present in Sample I. Furthermore, Neumann and Nilssen (1968) mention that several of the observed



FIG. 4. Powder XRD of a fragment of tombarthite-(Y) from the vial labelled 15009 compared with Sample II (4/65) from Table 2. The lower part of the figure shows the minerals identified with their PDF record number and tombarthite-(Y) (Tomb) for comparison. Kainosite-(Y) (Kain), xenotime-(Y) (Xtm), clinochlore (Chl) and cerianite-(Ce) (Ceri).

reflections should have been absent in the chosen space group, e.g. (100), (001), (010) and $(\overline{2}01)$.

Chemical data

An overview of all published compositions of tombarthite-(Y) is provided in Table 3. It is important to note that the water content from Neumann and Nilssen (1968) was not determined directly, but: "...water was determined as loss on ignition, and the ignited sample was afterwards used for the main analysis". In other words, the entire loss of mass during the heating experiment was ascribed to water (H₂O and OH). Furthermore, the chemical composition was not determined on fresh material, but only on heated material. The heating experiment revealed that all water had been removed when the temperature reached 1000°C. Under such conditions other elements such as C (in the form of CO_3^{2-}) or F are likely to be lost. From the pegmatites of the region Y-minerals such as kainosite-(Y) and thalénite-(Y) have been described, hence it is very likely that the original material contained CO_3^{2-} or F⁻.

The large variation of published tombarthite-(Y) compositions is shown in Table 3. For example, the SiO₂ varies from 12.6 to 27.8 wt.%, MnO from 1.0 to 10.0 wt.% and total REE₂O₂ between 8.7 and 26.4 wt.%. In this paper REE solely refers to the lanthanides. The compositional data for tombarthite-(Y) by Griffin et al. (1979) subtracts 7.6 and 7.9 F for O equivalents despite not having any F in the analyses. If the cited F for O equivalents are true they correspond to F content in the two samples of 18.04 and 18.76 wt.%, respectively. Either way the published totals are wrong. The conclusion from the published compositions of tombarthite-(Y) is that they show a greater variation than what is possible for a single mineral species. In addition, the fact that the original composition was based solely on heated material makes the compositional data doubtful.

New data

Diffraction data

Powder X-Ray diffraction (PXRD) data were collected on a Simens D5005 diffractometer using

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FIG. 5. Semi-quantitative EDS analyses of sample KNR 39583, where Debye-Scherrer identified it as tombarthite-(Y).

Cu*K* α radiation housed at the NHM in Oslo. Material was taken from several samples from Høgetveit and Reiarsdal, where old XRD pointers indicated previous analyses had identified the mineral as tombarthite-(Y). In addition, various separates labelled 16/64 and 4/65 were also analysed. The material was ground and placed on zero-background plates. Data were collected typically between 2 and 70°20, with 0.02° stepsize and counting for 3 s. For identification purposes the PDF2 (powder diffraction files from the International Centre for Diffraction Data, http:// www.icdd.com/) and other databases were used, both with and without chemical constrains, e.g. must contain Y.

Three findings were characteristic for the new PXRD analyses: (1) all diagrams showed high

backgrounds indicative of metamictization; (2) none of the analysed samples were automatically identified as tombarthite-(Y) when applying the search-match function in EVA (Bruker software); (3) all samples were mixtures of several mineral species. The PXRD of sample XRD 15009 is shown in Fig. 4, which could be explained by a mixture of xenotime-(Y), kainosite-(Y), cerianite-(Ce) and clinochlore. The PXRD analyses of other samples gave similar results; the actual phases present varied but minerals such as keiviite-(Y), iimoriite-(Y) and caysichite-(Y) were typically identified. As seen from Fig. 4 the diffractograms are complex and several of the minerals mentioned above have significant overlaps making it impossible to confidently identify the minerals present in the diagrams. In addition, the XRD pattern reveals a

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FIG. 6. Semi-quantitative EDS analyses of XRD 18055 before and after heating for 1 day at 1000°C. The sample contained small inclusions of galena (Gn), chlorite-group mineral (Chl) and thalénite-(Y) (Tha).

large portion of metamict material in the sample. A recalculation of the original data for sample 4/65 is also given in Fig 4 and it is clear it can be explained by a mixture of the minerals identified from the same material with modern XRD.

Neumann and Nilssen (1968) ascribed the reflections with *d* values of 4.66, 4.55 and 4.24 Å (Sample I) and 4.63 and 4.23 Å (Sample II) to impurities in the samples, but from Fig. 4 it is evident that some of these can be attributed to the minerals listed above e.g. clinochlore, xenotime-(Y) and kainosite-(Y). The PXRD data of one of the 16/64 fractions revealed it to be almost pure xenotime-(Y) showing that this mineral was present in significant quantities in the original sample.

Chemical data

Semi-quantitative energy-dispersive analyses were carried out on a Hitachi S-3600 equipped with a Bruker XFlash 5030 EDS detector housed at the NHM, Oslo. Analyses were carried out in low vacuum to avoid coating the specimens and the

analytical points were the same as for XRD, i.e. where pointers indicated the mineral to be tombarthite-(Y). In addition, heating experiments of material were carried out with the conditions stated in Neumann and Nilssen (1968), i.e. heating for one day at 1000°C. For the heating experiments a sample was broken off a specimen and XRD collected on part of the fragment prior to heating. The other part of the fragment was analysed with energy-dispersive spectroscopy (EDS) before being wrapped in Pt-foil (this was the routine at NHM, Oslo to minimize loss of water) and placed in a muffle furnace. The sample was weighed (with and without the Pt-foil) before and after heating and the loss of mass calculated. The sample was then placed in the scanning electron microscope in the same orientation as before heating and where possible analyses were carried out on the same spots. After EDS analyses the sample was ground and another XRD diagram collected.

Semi-quantitative analyses of sample KNR 39583 is shown in Fig. 5 and it is clear from the EDS spectra that the sample is heterogeneous. Although EDS from just one sample is presented here, all samples investigated with EDS were heterogeneous. In EDS there are some overlaps of importance, which must be considered e.g. FeK α and DyL $\alpha \sim 6.4$; YbM α and AlK $\alpha \sim 1.6$ as well as FK α and FeL $\alpha \sim 0.7$ keV. For these reasons the F content in spectra 1 and 2 may be high due to contribution from FeL α . However, spectrum 4 only has minor, if any, Fe and the peak ~ 0.7 keV must originate from F. It is also clear that the relative contents of Y and Si varies throughout the phases in the sample. The EDS shows that F is present in the material identified as tombarthite-(Y) despite not being present in the original description.

The results of the heating experiment carried out on XRD 18055 are shown in Fig. 6. The heating resulted in a 25.6% loss of mass, which is similar to the 22.7% loss for Sample II reported by Neumann and Nilssen (1968). Another heating experiment carried out on KNR 37812 resulted in 15.4% loss of mass further illustrating the varied composition of what was identified as tombarthite-(Y). In addition, Fig. 6 shows that F was lost during the heating experiment. To ensure that this was not the result of a new surface being formed during the heating, the sample was broken in half. However, no F was observed in the analyses of the freshly broken surface. The heating experiments clearly illustrates that not only H₂O, but also F will be lost under the heating conditions employed by Neumann and Nilssen (1968). The XRD analyses of material before and after heating show that the original phases re-crystallize into a silicate with an apatite structure as described by Neumann and Nilssen (1968).

Conclusions

On the basis of unregistered material from the NHM in Oslo, old XRD-films and laboratory books it was possible to locate the material used for the original description of tombarthite-(Y). Sample I and Sample II from the original description comes from the mineral separates 16/64 and 4/65, respectively. The unit-cell refinements of the original material only relied on four reflections, some of which are only present in one of the samples. In addition, Guinier films of the original material show significant differences indicative of the material being mixtures of different minerals. New XRD and semi-quantitative EDS analyses of material labelled as tombarthite-(Y) from both the type locality and Reiarsdal has unambiguously shown that all analysed samples are heterogeneous, and hence not a single mineral species. Analyses of material identified as tombarthite-(Y) before and after heating shows that F is present in some of the phases and is lost during the heating scheme applied following the original description. As the original description relies solely on chemical data of heated material, not fresh material, F was not detected as a consituent of the mineral. Consequently, the published formula for tombarthite-(Y) is erroneous. Based on the above analyses and detailed investigation of the original description it must be concluded that tombarthite-(Y) is not a valid mineral species, but an intimate mixture of several minerals. It has also been shown that the minerals present vary from sample to sample, hence each sample of tombarthite-(Y) must be analysed to know what minerals it contain. The discreditation of tombarthite-(Y) has been approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (proposal 16-K).

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