

SAMARSKITES. CHEMICAL COMPOSITION, FORMULA AND CRYSTALLINE PHASES PRODUCED BY HEATING

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Four new chemical analyses from Norwegian samarskites are presented. Plotting of these analyses together with other published data indicates the existence of two types of samarskites. This theory is confirmed by heating experiments and X-ray data.

The X-ray pattern of samarskites heated to 1000° consists of three phases – monoclinic, orthorhombic, and cubic – present in different proportions according to variations in the chemistry. All three phases have been indexed. Axial ratios of the rhombic phases are in good agreement with goniometer measurements of natural crystals, thus indicating that the rhombic phase represents the original non-metamict structure of the mineral.

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Samarskite, a complex oxide of Nb, Ta, RE, Fe and Ca, usually with some Ti, was first mentioned from Norwegian localities by Brøgger (1882) and two analyses from pegmatites in south-eastern Norway were published by him in 1906. Since then, no new complete analyses from well-defined Norwegian localities have been published, although samarskite has now been identified from quite a number of pegmatites, both in southern and in northern Norway.

Lima de Faria (1964) made a semiquantitative analysis of a samarskite from 'Sætedalen' South Norway, but the identity of this mineral is apparently not well established since it is referred to as samarskite (euxenite), and Butler (1958) and Vlasov (1956) give data for rare earth distribution of Norwegian specimens, but no complete analyses.

In the present paper samarskites from four localities were investigated. Chemical analyses are given, together with results of X-ray diffraction work and heating experiments.

Localities and mineral association

1. Rømteland, Vest-Agder, South Norway. Pegmatite quarry described by T. Sverdrup (1960). The pegmatite is surrounded by farsundite. Minerals of the 'mineralized zone' are microcline, plagioclase, quartz, biotite, muscovite,

magnetite, hematite, ilmenite, anatase, sphene, spessartine, orthite, euxenite, columbite, samarskite, alvite, zircon, thorite, uraninite and secondary uranium minerals.

2. Ljoslandsåsen, Iveland, Vest-Agder. Investigated by H. Bjørlykke (1935). Minerals: microcline, plagioclase and quartz with biotite, muscovite, samarskite, columbite, beryl and monazite.

3. Bjellåsen, Fromland, Aust-Agder. Investigated by the author during the last few years (unpublished). The pegmatite is situated ca. 1 km NNE of the large quarries at Lauvrak, Froland, described by O. Andersen (1926, 1931), and is, generally speaking, of the same type. It consists of a pegmatite lens, one of a whole series of lens-shaped or irregular pegmatite bodies of various sizes which follow a north easterly trend for some 15 km, beginning at the Herefoss granite in the south and ending and disappearing in the great South-Norwegian friction breccia near Nelaug to the north. The surrounding rocks consist of banded gneiss, and mica- and hornblende schists. Minerals: microcline, plagioclase, quartz, muscovite, biotite, garnet, magnetite, beryl, orthite, samarskite, fergusonite, uraninite and secondary uranium minerals.

4. Pegmatite quarry N of Aspedammen, about 10 km south-east of Halden

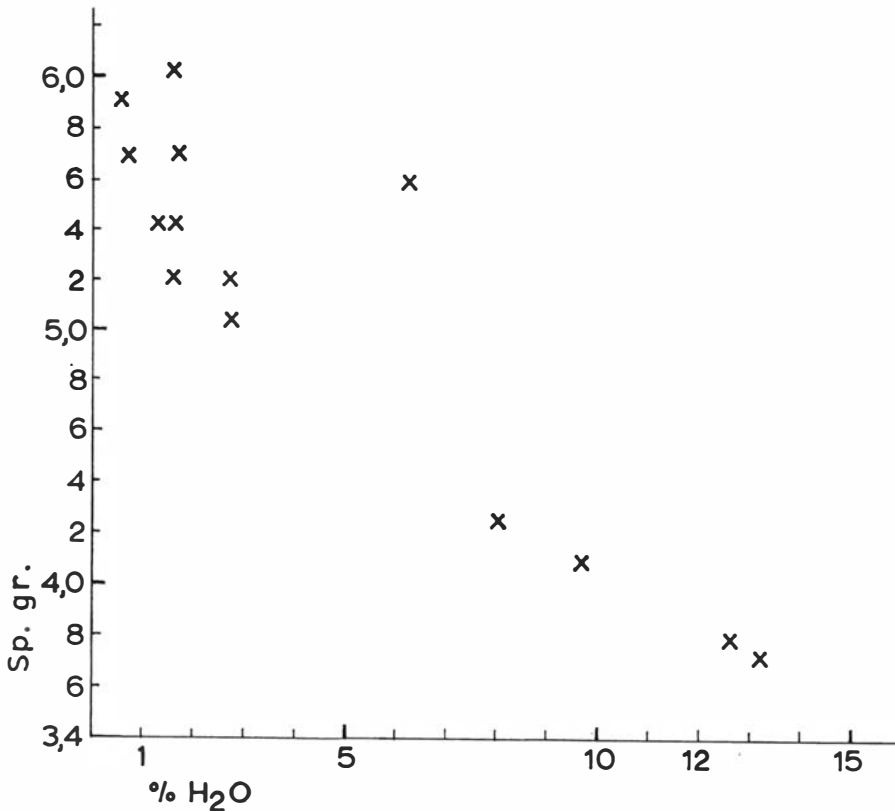


Fig. 1. Specific gravity of samarskites as function of water content.

Table 1. Samarskites, weight per cent

	1	2	3	4	5
SiO ₂	1.05	0.77	1.05	4.09	7.10
TiO ₂	2.19	4.56	1.27	4.04	3.98
ZrO ₂	0.38	0.26	0.30	0.33	
Al ₂ O ₃	0.16	0.55	0.97	0.70	4.34
Fe ₂ O ₃	5.05	2.53	4.32	2.63	2.86
FeO	4.06	5.89	2.75	0.56	0.03
MnO	1.19	2.94	0.48	0.32	0.15
MgO	0.10	0.03	0.07		0.35
CaO	2.90	1.04	5.16	4.05	1.55
PbO	1.61	0.47	1.30	1.20	1.55
K ₂ O	0.03	0.03	0.03		0.18
Na ₂ O	0.06	0.06	0.17		0.18
Nb ₂ O ₅	40.94	52.20	44.77	38.51	39.80
Ta ₂ O ₅	7.28	3.86	4.24	3.06	3.38
UO ₃	16.26	0.39	1.27		
UO ₂	0.56	6.37	11.83	19.81	10.21
Y ₂ O ₃	7.86	8.43	8.32	4.7	4.3
La ₂ O ₃	tr.	tr.	tr.		
CeO ₂	0.16	0.18	0.21	0.3	0.5
Nd ₂ O ₃	0.19	0.28	0.40	0.3	0.2
Pr ₂ O ₃	0.03	0.03	0.06	0.05	0.1
Sm ₂ O ₃	0.49	0.31	1.03	0.3	0.2
Eu ₂ O ₃	tr.	0.01	tr.		
Gd ₂ O ₃	0.64	0.50	2.51	0.5	0.2
Tb ₂ O ₃	0.16	0.11	0.46	0.2	0.1
Dy ₂ O ₃	0.80	0.64	1.85	1.2	0.6
Ho ₂ O ₃	0.19	0.22	0.18	tr.	tr.
Er ₂ O ₃	0.48	0.56	0.26	0.5	0.2
Tm ₂ O ₃	0.10	0.07	0.06		
Yb ₂ O ₃	1.54	0.99	0.08	0.5	0.2
Lu ₂ O ₃	0.14	0.10	tr.		
ThO ₂	2.08	2.89	2.01	2.5	4.4
H ₂ O ⁻	1.53	1.43	2.60	6.23	6.16
CO ²	0.04	0.37	0.17	3.59	6.40

1. Ljoslandsåsen, Iveland

2. Rømteland

3. Bjellåsen, Froland

4. Aspedammen, Østfold

5. Aspedammen, Østfold, yellow alteration product

in Østfold. The quarry is most probably identical with the one called Bø by O. A. Broch (1934), but it has been extensively quarried since then. The uncovered part of the pegmatite is 15 m wide and ca. 100 m long, stretching west-southwest and dipping south. Surrounding rocks are granite to the north and gneiss or migmatite to the south. Main minerals are microcline, muscovite, and quartz, partly smoky. Plagioclase is fairly scarce. There is some cleavelandite. Other minerals are fluorite, dark green and colourless clear, monazite, rutile, columbite, beryl, spessartine, topaz, uraninite and secondary uranium minerals, and samarskite surrounded by a yellow mineral, which was also found in cracks in the samarskite.

Table 2. Cation percentage of waterfree composition of samarskites.

	1	2	3	4	5	6	7	8	9	10	11
Si	2.10	1.60	2.23	9.60							
Ti	3.65	7.15	2.51	7.14				1.12	1.09	2.37	
Zr	0.41	0.26	0.31	0.39	0.74	0.91		1.10	2.55		2.75
Al	0.42	1.35	2.43	1.94	1.04	1.25		0.49	2.27		
Fe ³⁺	8.41	3.97	6.92	4.65				3.52		16.66	16.24
Fe ²⁺	7.52	10.27	4.89	1.10	9.03	8.07	20.63	20.47	14.83	3.98	0.66
Mn	2.23	4.61	0.86	0.64	1.79	1.58	1.51	1.28	3.34		1.62
Mg	0.33	0.09	0.22		0.48	0.67		1.34		0.07	
Ca	6.88	2.32	11.76	10.18	11.31	9.61	1.35	1.20	2.43	0.80	0.71
Pb	0.96	0.26	0.74	0.76	0.51	0.62		0.09		0.20	0.48
K	0.09	0.08	0.01		0.25	0.24					
Na	0.26	0.24	0.07		3.62	2.84					
Nb	40.99	49.17	43.07	40.82	42.54	49.67	38.91	31.77	36.81	42.80	30.89
Ta	4.39	2.09	2.46	1.95	7.15	1.16	11.36	6.68	17.62	9.03	18.09
U ⁶⁺	7.56	0.17	0.57				6.05	5.18			
U ⁴⁺	0.28	2.95	5.60	10.37	5.28	5.69			2.33	3.94	2.20
Sn					0.56	0.14	0.07	0.69			0.93
W								0.80	1.19		1.43
RE	12.55	12.44	14.37	8.81	12.65	12.13	20.11	23.53	16.57	15.04	21.96
Th	1.05	1.40	0.97	1.34	1.40	1.40		0.86	2.32	1.78	2.04
Be					1.77	3.64					
Ba					0.37	0.35					

1. Ljoslandsåsen, Iveland

2. Rømteland

3. Bjellåsen, Froland

4. Aspedammen, Østfold

5. Ødegården, Våler, Østfold

6. Aslaktaket, Våler, Østfold

7. Mitchell County, N.C.

8. Miask, Urals

9. Tschoroch River, Caucasus

10. Glastonbury, Conn.

11. Devil's Head Mt., Colorado

Chemical analyses

Samarskites from all four localities, as well as the yellow mineral surrounding the samarskite from Aspedammen, were prepared for analysis by crushing and separation, using heavy liquids and magnetic separation. The purity of the samples was controlled by X-ray powder diagrams. Densities were determined by pycnometer filled with toluene:

Ljoslandsåsen 5.42

Rømteland 5.20

Bjellåsen 5.06

Aspedammen 4.10

The density is almost directly proportional to the water (+CO₂) content, but there are of course other factors which play a role here, such as the Nb/Ta ratio.

Chemical analyses were carried out by a combination of conventional wet methods and X-ray fluorescence spectrometry. Results are given in Table 1. The analytical data were first calculated in the usual way by converting weight percents to atomic proportions.

Since some of the published chemical analyses give very low H₂O contents (as low as 0.22 % in one case), it seems unlikely that water enters into the structure of unaltered samarskite. The cation proportions were therefore recalculated to cation percent of the waterfree composition to facilitate comparison between published data and the present new determinations (Table II).

Several chemical formulae have been proposed for the samarskite group minerals. They are all of the type A_mB_nO_x, with RE, U, Ca and Fe²⁺ in group A, and Nb, Ta, Ti and mostly Fe³⁺ in group B, but the number of cations in each group varies. None of the proposed formulae fit all the published data. This in itself is not very surprising, since the chemistry shows considerable variations. Also all the chemical analyses are quite old, and may not be as reliable as modern analyses, since analytical techniques (particularly for the rare earth elements) and separation methods have improved considerably in recent years.

Proposed chemical formulae for samarskite:

AB ₂ O ₆	(Dana 1944)
AB ₂ (O,OH) ₆	(Strunz 1966)
(RE,U,Fe ²⁺ ,Ca) (Nb,Ta,Fe ³⁺)O ₆	(Gorshevskaya 1964)
(Fe,RE,U) ₂ (Nb,Ta,Ti) ₂ O ₇ where Nb(group)/O=2/7	const.
	(Vlasov 1966)
AB _{2+x} (O,OH ₂) _{6+2.5x} nH ₂ O (altered samarskite)	(Van Wambeke 1960)

The available chemical data from the literature as well as the present four new analyses were critically studied, and different ways of grouping the atoms were considered in an attempt to find a formula which satisfied as much of the data as possible. Some minor adjustments to the analyses were made prior to recalculation. Al is usually determined by difference, but as it seemed very unlikely that Al entered into the samarskite structure, all Al was discarded. This is not a very big alteration since Al is never higher than about 1 %, and is usually much lower. Si was also left out. Since samarskites are always found in granite pegmatites Si may very well be accounted for by very small inclusions of quartz, or of feldspars in the cases where alkalis and Al are also present.

Be, which was determined in some samples, was also assumed to be due to impurities and consequently left out. These corrections mean, of course, that the analysis will not give a total of 100 %, but only in one case is the deficiency as high as 6 % (Kalita No. 2).

As to the grouping of cations, Ca, Mg, Mn (and alkalis) must certainly be placed in group A with the RE elements, as well as U, Th and Zr. Lead is considered to be of radiogenic origin and calculated as U in the calculation of the oxygen content (1U giving 1Pb). All U was calculated as U⁴⁺.

There is also no doubt that Ti follows Nb and Ta in group B. Fe, however, represents a greater problem. Many authors prefer to place Fe²⁺ in

group A, and Fe^{3+} in group B, but some analysts give all Fe as FeO, while others give practically all iron as Fe_2O_3 . Since there is no way of determining whether Fe has been affected by weathering or other subsequent oxidizing processes, the analytical result is no proof of the original oxidation state of the iron. Reduction of Fe^{3+} to Fe^{2+} seems unlikely and would be rather difficult to explain. I have, therefore, preferred to assume that all Fe originally occurred in the lowest oxidation state to place it in group B with Nb and Ta. This is in accordance with the findings of Roth & Waring (1964). They explain the ixiolite structure by supposing that Fe^{2+} substitutes for Nb^{5+} in an order-disorder distribution. Plotting of the atoms with this distribution in a triangular diagram (Fig. 2) shows that of the 18 samples (14 from the literature + the present four) 13 cluster closely about one point whilst the remaining 5 form a subsidiary cluster somewhat removed from the first, having a lower A/B ratio. The samarskites from Aspedammen, Bjellåsen, and Ljoslandsåsen fall in the main group as does the original samarskite from Miask, Urals, while some of the other Russian specimens

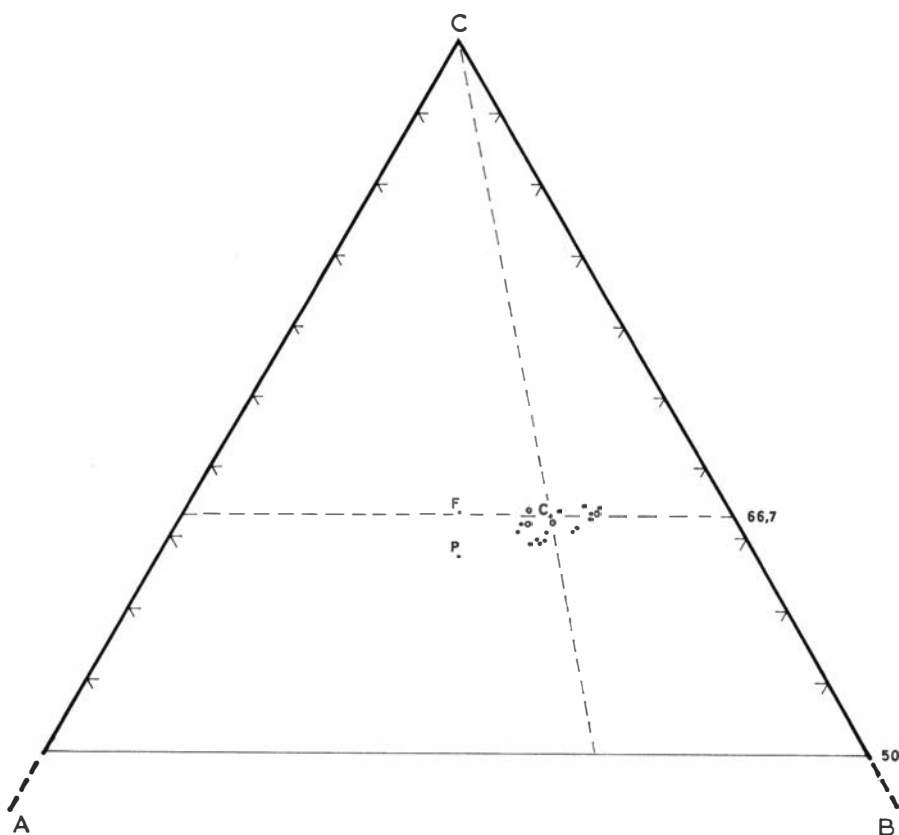


Fig. 2. Chemical composition of samarskites.
 A - RE, U, Th, Zr, Ca, Mn, Mg, Pb, K, Na
 B - Nb, Ta, Ti, Fe, W
 C - O

Table 3. Cation percentage of mineral composition used for plotting in triangular diagram.

Locality or author	'RE' = A	'Nb' = B	O = C	A/B
Ljoslandsåsen, Iveland	11.34	22.60	66.01	0.50
Rømteland, Vest-Agder	8.31	25.04	66.65	0.33
Bjellåsen, Froland	12.71	21.34	65.94	0.60
Aspedammen, Østfold	12.07	20.90	67.03	0.58
Ødegårdsletten, Våler	13.60	21.00	65.40	0.65
Aslaktaket, Våler	13.38	21.91	64.71	0.61
Berg, Råde	12.00	22.66	65.33	0.53
Hattevik, Dillingøy	12.66	22.69	64.65	0.55
Mitchell County	9.95	24.34	65.70	0.41
Miask, Urals	12.36	22.84	64.80	0.54
Glastonbury	8.34	24.81	66.85	0.34
Devil's Head Mt., Colorado	10.47	22.50	67.03	0.47
Tschoroch River, Caucasus	8.89	23.87	67.29	0.37
Kalita No. 1	10.26	24.24	65.50	0.42
Kalita No. 2	12.85	22.45	64.70	0.57
Kalita No. 3	12.79	21.18	66.02	0.60
Nudelmann and Sidorenko	8.57	24.84	66.58	0.35
Adun Cholon	8.03	25.21	66.75	0.32

'RE' = A = RE, U, Th, Zr, Ca, Mn, Mg, Pb, K, Na

'Nb' = B = Nb, Ta, Ti, Fe, W

(Nudelmann & Sidorenko (1963), Konkretova et al. (1968)) plot in the smaller group together with the Rømteland mineral. This latter mineral also distinguishes itself from the other Norwegian samples in its reaction to heating as revealed by X-ray data, (see later).

Distribution of rare earths

Rare earths, as oxides, may form up to 22 weight percent of the samarskite according to published data. The present minerals have RE contents from 8.5 to 15.4 %. The composition is plotted in the usual way by joining the even and odd-numbered elements separately. Yttrium forms from $\frac{1}{2}$ to $\frac{2}{3}$ of the total rare earth content. The distribution is very similar in the minerals from Aspedammen, Ljoslandsåsen, and Rømteland, showing a Dy high. The high Yb in the two latter places seems odd, and is a bit difficult to explain unless it is due to an analytical error, but the same tendency has also been reported by other authors (Konkretova et al. 1968, Semenov & Barinskii 1958).

Bjellåsen is different. It has a pronounced Gd top. This seems, however, to be a distribution which is known from samarskites from different localities all over the world, and is in fact even more common than the Dy top. In particular I should mention an analysis published by Butler (1958) from a specimen labelled (erroneously) Bjortjern, Iveland. (The locality should be Bjortjern, Mykland.) This specimen has a RE distribution almost identical to the one from Bjellåsen. Furthermore its X-ray pattern, on heated

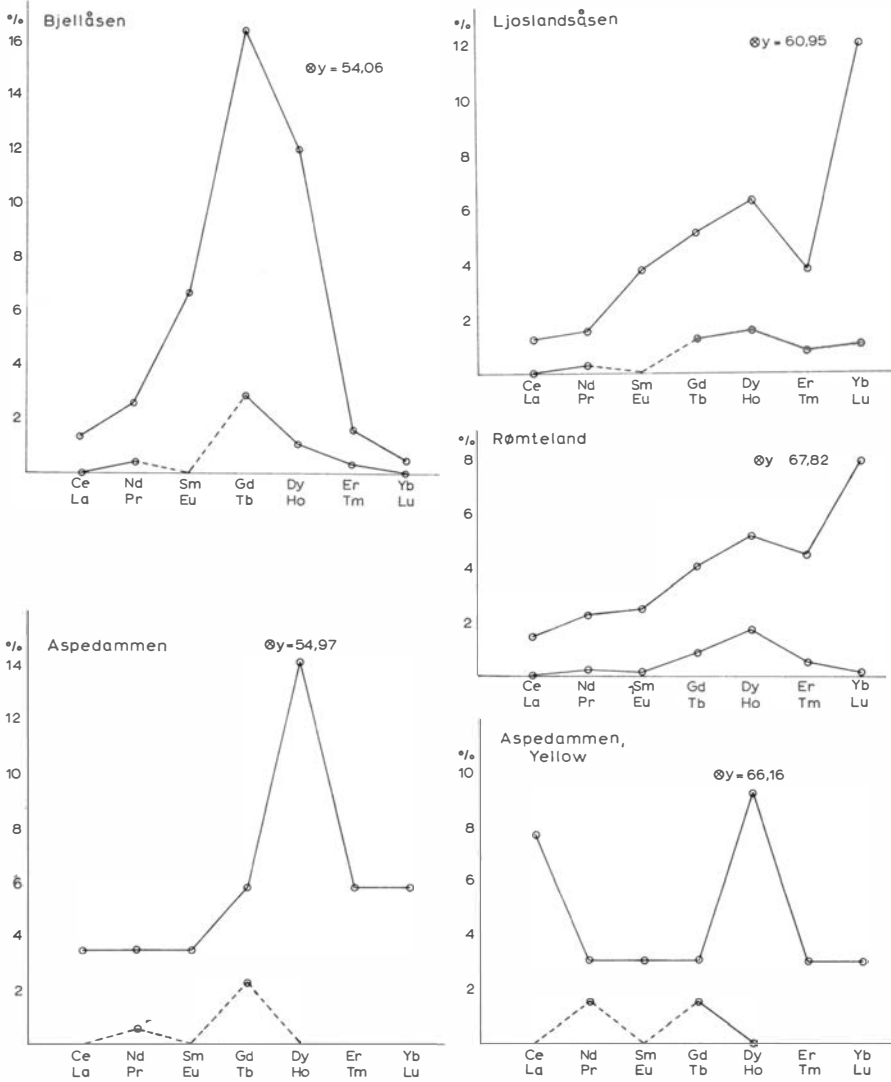


Fig. 3. Distribution of yttrium and rare earth oxides as weight percent of total yttrium and rare earth oxide content.

material (see later) is also identical to the Bjellåsen samarskite, even to the detail of lacking the innermost line with the highest d-value. Bjortjern, Mykland is located some 2 km NE of Bjellåsen and in the same pegmatite trend. Rosenqvist (1949) described a samarskite-yttrotantalite from this locality. Unfortunately no complete analysis exists of the mineral from Bjortjern, Mykland.

D.T.A.

D.T.A. diagrams were prepared at the Geotechnical Institute from the four analysed samarskites (Fig. 4). They all indicate an endothermic reaction

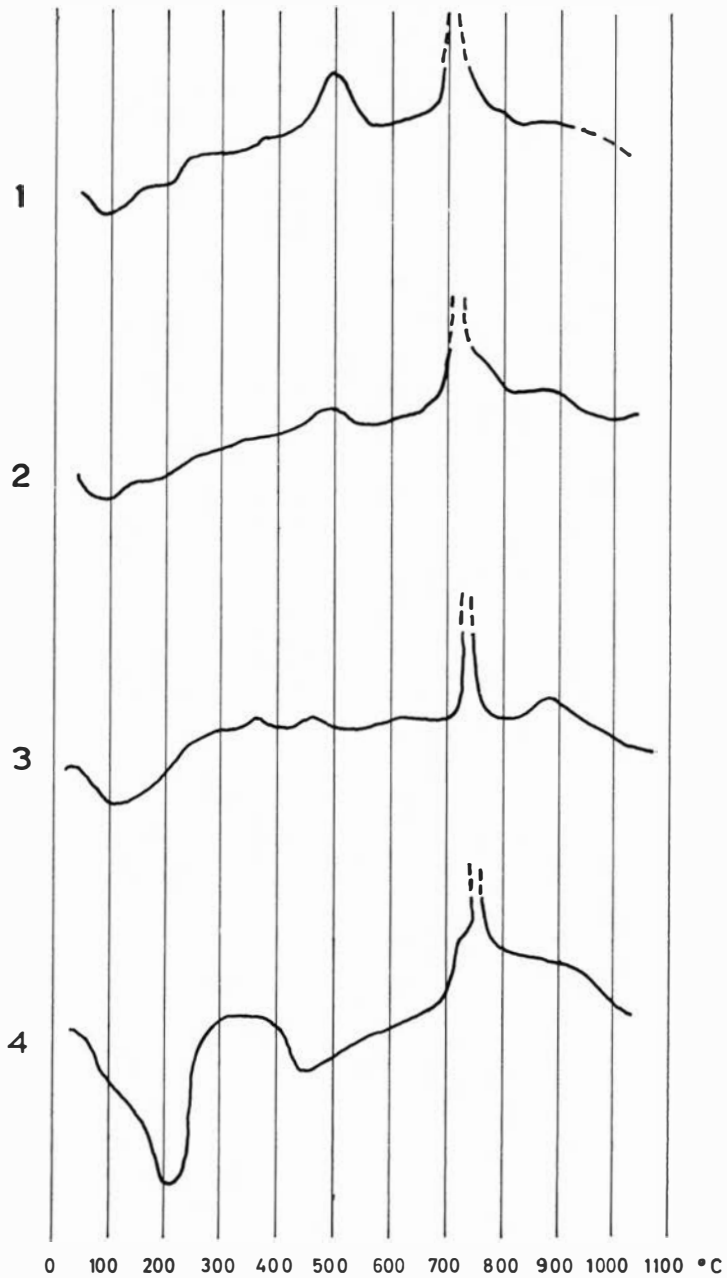


Fig. 4. D. T. A. diagram of samarskites.
 1 Ljoslandsåsen, 2 Rømteland, 3 Bjellåsen, 4 Aspedammen.

between 100 and 200°C. This peak (inverted) represents loss of water, and is directly proportional to the water content. The different position of this peak in different samples is probably due to delayed reaction, since the peak occurs at highest temperatures in the sample from Aspedammen, which

Table 4. Samarskites heated in air

Locality	gl. point	700°	780°	1000°	1400°
Rømteland	C	C(+R?)	C	F+C	F+C
Bjellåsen	R	R	R+	S-	F+
Aspedammen	R+	R	R+	S+R	F+R+
Ljoslandsåsen	R	C+R	R+S	S	F+
Dillingø	R+		(S)	S	F+
Jennyhaugen	R			S-	F †

Samarskites heated with 15000 psi H ₂ O pressure					
	500°	600°	700°	850°	
Rømteland	C	C+	C+F	C+(F)	
Bjellåsen	L	R+S	S-	S-	
Aspedammen	R	R+S	S-	S+R	
Ljoslandsåsen	L	R+S(F?)	S-	S-	
Dillingø	L	R+C	S-	S-	

S samarskite heated to 1000° in air, checks various published data

S- lacking one or more reflections

R regular, pyrochlore structure

C 'columbite' structure

F 'fergusonite' structure

L 'lyndochite' structure

X-ray pattern directly compared with standard films

gl. point is reached when the temperature of the recrystallized mineral produces a sudden glowing caused by the exothermal effect of the crystallization.

has an unusually high content of water. The very pronounced exothermal peak at 700–740°C obviously marks the recrystallizing temperature of the minerals. This temperature is in agreement with the temperature given by Nudelmann & Sidorenko (1967) for the recrystallization of the low-temperature rhombic phase, while a gradual transition to a monoclinic phase as reported by Nudelmann & Sidorenko is not registered by the D.T.A. diagram.

X-ray investigations

Samarskites from Ljoslandsåsen, Rømteland, Bjellåsen, and Aspedammen, as well as one from Dillingø, described by Brøgger (1906), and one unanalyzed from Jennyhaugen, Drag, Tysfjord, North Norway, were heated to different temperatures with and without water pressure. They were all completely metamict to X-rays in the unheated condition. As will be seen from Table 4, there are only small differences in the X-ray diffraction diagrams of the different samples. Under given conditions of temperature and pressure, the same phases are commonly present, but the relative proportions vary. In some cases certain reflections are missing, such as the innermost lines in the patterns of the Bjellåsen and Jennyhaugen samples, the $d = 4.04$ and $d = 3.24$ lines, representing the 111 and 131 reflections respectively of the monoclinic phase (see later).

The mineral from Rømteland again behaves differently from the other samples. Whereas most of the samples develop a pyrochlore type structure up to about 800°C, the Rømteland mineral shows a columbite-like structure and scarcely develops a cubic phase at all (or at least so very, very weak as to be nearly non-existent). With increasing temperature a monoclinic, fergusonite type pattern develops in addition to the 'columbite', and this gradually gets stronger with increasing temperature.

X-ray films of the minerals heated in air to 1000°C correspond very well with films of samarskite from the Urals (type locality) and from Mitchell County taken under the same conditions. The diagrams were taken with 9 cm cameras and Mn-filtered Fe radiation. D-values calculated from films of heated material taken with the Guinier Quadruple Focusing camera (effective diameter 22.9 cm, Fe radiation, quartz monochromator) are also in good agreement with various published data. The intensities of some of the reflections vary from one sample to another. At the highest temperature used, 1400°C, all samples develop a fergusonite-like structure with some additional unidentified lines. The earlier structure disappears almost completely. Aspedammen, which in all stages has a very strong pyrochlore phase, retains this even after being heated to 1400°C, the point when it disappeared from all the others.

Many authors have tried to identify the different phases in the X-ray diagrams of samarskites. Lima de Faria (1964) gives a table of such results, mainly founded on different heating and recrystallizing conditions. Nudelmann & Sidorenko (1967) maintain that samarskite crystallizes in the rhombic system when heated to 700–800°C, and converts to the monoclinic system at 900–1000°C. They were able to index the X-ray reflections and give cell parameters as well as space groups.

Since it took a long time to obtain a copy of the original paper, it was necessary at first to work only from the data of the English abstract, which gave the cell parameters, but not the actual indexing of the X-ray diagrams. The d-values of possible reflections from such a monoclinic phase were calculated from the cell parameters and compared directly with the measured values from samarskites heated to 1000°, taken with the Guinier camera (using lead nitrate as an internal standard). It was possible to index most of the reflections in this way, but a number were still left. Therefore the d-values for the rhombic phase were calculated in the same way. Most of the remaining lines could then be indexed, some even getting a double indexing. A few reflections were still outstanding, however. These can be assigned indices on the assumption that they represent a cubic (pyrochlore type) phase. Examination of the film reveals that these last reflections show particularly noticeable variations in intensity. The minerals from Aspedammen and Bjellåsen have very strong cubic phases, while these reflections are very weak or nearly non-existent in the film of the Rømteland sample. Nudelmann & Sidorenko report no reflection which could represent a cubic phase.

From the measured and indexed d-values of the Aspedammen samarskite, the axial ratios were calculated for the rhombic phase.

The calculated axial ratios were:

	a	:	b	:	c
Aspedammen	0.550	:	1	:	0.508
Brøgger	0.555	:	1	:	0.517
Nudelmann, Sidorenko	0.545	:	1	:	0.520
Mitchell County	0.546	:	1	:	0.518

A study of the complete paper of Nudelmann & Sidorenko revealed the fact that the indexing of the samarskite was carried out by calculating the possible d-values from goniometer-measured axial ratios and fitting these to the X-ray data. The very good agreement in itself is therefore not surprising, but the fact that it is possible to fit these data to the X-ray data is a strong indication that the recrystallized low-temperature phase may be identical with the original non-metamict phase of samarskite. So far samarskites have never been observed in a non-metamict condition.

It is evident from the data given above that the usual X-ray diffraction pattern of samarskites heated to 900–1000°C in air consists of at least three different phases: one monoclinic, one orthorhombic, and one cubic. The three phases occur in varying amounts, depending on the chemical composition of the different samples and perhaps also to some extent on the degree of alteration of the mineral. Thus, a relatively high Ca and U content seems to favour the development of a strong regular phase, although there is no conclusive evidence to prove this.

The average cation distribution of samarskites – using the same grouping as in the discussion and plotting of the chemical data – is very close to the ratio $A : B = \frac{1}{2}$ or 0.5, but varying from the extremes of 0.33 or $\frac{1}{3}$ (Rømteland) to close to $\frac{2}{3}$ or 0.65 (Ødegårdssletten, Våler).

Theoretical atomic proportions:

	A	B	C	A%	B%	C%
Columbite FeNb_2O_6	1	2	6	11.1	22.2	66.7
Fergusonite YNbO_4	2	2	8	16.7	16.7	66.7
Pyrochlore $(\text{Ca}, \text{Na})_2\text{Nb}_2(\text{O}, \text{OH}, \text{F})$	2	2	7	18.2	18.2	63.6

Bjellåsen and Aspedammen, which both give very well developed reflections from a cubic phase, plot near the pyrochlore end of the samarskite cluster in the triangular diagram. The $A : B$ ratio is higher than 0.5 (close to 0.6) and in addition they both have high Ca and U contents, which seem to stabilize the pyrochlore structure.

The absence of the cubic phase in the 'Rømteland group' which includes the Rømteland samarskite and the two Russian samarskites for which both chemical and X-ray data are published, may also be explained by their composition. They plot well away from the pyrochlore position in the triangular diagram. Also their Ca and U contents are comparatively low.

Table 6.

Locality or author	A:B Cations	A:B Charges
Ljoslandsåsen, Iveland	0.50	0.36
Rømteland, Vest-Agder	0.33	0.20
Bjellåsen, Froland	0.60	0.34
Aspedammen, Østfold	0.58	0.38
Ødegårdsletten, Våler	0.65	0.38
Aslaktaket, Våler	0.61	0.36
Berg, Råde	0.53	0.33
Hattevik, Dillingøy	0.55	0.44
Mitchell County, N. C.	0.41	0.31
Miask, Urals	0.54	0.44
Glastonbury, Conn.	0.34	0.25
Devil's Head Mt., Colorado	0.47	0.36
Tschoroch River, Caucasus	0.37	0.27
Kalita No. 1	0.42	0.32
Kalita No. 2	0.57	0.36
Kalita No. 3	0.60	0.40
Nudelmann and Sidorenko	0.35	0.27
Adun Cholon	0.32	0.23
Average	0.49	0.33

The samarskite from Ljoslandsåsen represents in many ways the average samarskite. Its X-ray diffraction pattern, from material heated to 1000° in air, has a moderately well developed cubic phase. Its atomic proportions are very close to A : B : C = 1 : 2 : 6 or, to be exact, 1.03 : 2.05 : 6.00 as compared to columbite which is 1 : 2 : 6, and consequently they plot in the same place in the triangular diagram. The X-ray patterns, however, are different. This may be explained by the fact that the charge distribution between groups A and B are different. Ljoslandsåsen has a charge distribution of 3.2 : 8.8 : 12.0 against 2.0 : 10.0 : 12.0 for columbite, the A group of columbite consisting (theoretically) of Fe²⁺, while samarskite has mainly RE³⁺ in this position.

The cation : oxygen ratio or (A+B) : C is very close to 3 : 6 for all the studied samarskites, with an average of 3.1 : 6.0. This is also the cation : oxygen ratio of the samarskite from Ljoslandsåsen. The ratio of charge distribution between the two cation groups varies from 0.20 (Rømteland) to 0.44 (Miask, Ural, and Hattevik), with an average of 0.33. The distribution ratio in the mineral from Ljoslandsåsen is 0.36.

Plotting of the A : B cation ratio against the A : B charge distribution gives a grouping which is very similar to that in the triangular diagram, with the 'Rømteland group' distinctly separated from the others.

Since the cation to oxygen ratio of samarskites according to chemical data is close to 3 : 6, and in most cases somewhat higher, it is difficult to construct a theoretical formula consisting of RE, Nb, and O only. This would give a composition RENb₂O_{6.5}, with too many atoms in the O position. Substitution of Ca in group A or Ti or Fe in group B will prevent this to

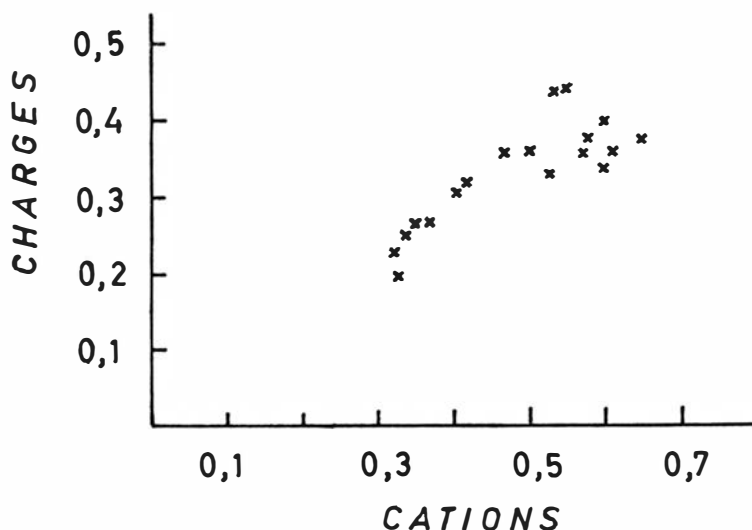


Fig. 5. A:B cation ratio plotted against A:B charge distribution.

some extent. As for group A, however, none of the samarskites have enough Ca to more than just compensate for the U, Th and Zr of this group. In most cases there is in fact far less.

The low A : B cation ratio in the minerals from the 'Rømteland group' may be adjusted to an A : B ratio closer to 1 : 2 by placing some of the Fe atoms in group A instead of in group B. Indeed, it seems reasonable to assume that some of the Fe is substituting in group A in these minerals. For the main group of minerals, where the A : B cation ratio is higher than 1 : 2, there is nothing which can be placed in group B rather than in group A. All Fe is already placed in that group. Mn and perhaps Zr, which are the only other possible candidates, are present in such small amounts that moving them will make no appreciable difference.

The samarskite formula may be given as $A_{1\pm x}B_{2\mp x}O_6$ where A consists mainly of RE, with U, Th and Ca, but where U, Th (and Zr) may be balanced not only by Ca, Mg or Mn in group A, but also by Fe or Ti in group B. Group B contains mainly Nb, Ta, Ti and Fe. Fe can also to some extent substitute in group A in the low A : B cation ratio group of minerals.

Balancing of the charges could also have been effected by 'empty' holes in particular positions in the structure. This mechanism does not seem to have been used to any great extent in the case of samarskites, since the ratio $A+B : C$ is so nearly constant at 3 : 6.

Alteration product from Aspedammen

The yellow mass which surrounds the samarskite from Aspedammen, and also fills cracks in it, consists almost certainly of a single mineral. It is completely metamict to X-rays, but gives, after being heated to 1000° in

Table 7. X-ray diffraction data for alteration products

I	d	d	I
80	4.06	4.03	45
20b	3.74	3.70 diff.	7
20	3.59	3.56	8
20	3.34		
30	3.29		
100	3.18	3.16	100
60	3.04		
20	3.00		
40	2.91	2.88	20
10	2.67	2.76	12
10b	2.61		
10	2.54		
80	2.51	2.49	70
20	2.04	2.03 diff	15
		1.96	13
50	1.84	1.83	36
50	1.72	1.70	35
50	1.63	1.59	18

Aspedammen, yellow alteration product
I Visually estimated

Ca- samarskite très altéré couleur jaune-miel, alluvions d'Elota, van Wambeke (1960)

air, a very distinct pattern. Both randomly handpicked specimens and grains from different portions of the purified material give exactly the same pattern, indicating either that it truly represents a single mineral or else that the phases are so intimately mixed that it is virtually impossible to separate them by ordinary methods.

The mineral was isolated and analyzed in the same way as the samarskites, and the chemical data are given in the last column of Table 1. The specific gravity is 3.82, that is, even lighter than the samarskite from Aspedammen, but this is easily explained by the high water content.

The d-values were measured and the data are given in Table 7. They show great similarities with data given by van Wambeke (1960) for a yellow altered Ca-samarskite from Elota, Congo Belge. The rare earth distribution in the samarskite from Aspedammen and its alteration product are very similar (Fig. 3). The altered Ca-samarskite from Elota is very poor in Y due to leaching, while the Y content in the yellow alteration product from Aspedammen is very similar or, if anything, slightly higher than in the samarskite itself.

It is clear both from the mode of occurrence and from the chemical data that the mineral is an alteration product of the samarskite. The samarskite from Aspedammen has an unusually high content of water, indicating that it has undergone a high degree of alteration and metamictisation, and this may have led to the formation of the yellow mineral, which seems to have formed by leaching (especially of Ca and U) some oxidation and a further

uptake of water. The apparent enrichment of Th is more difficult to explain.

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