

# CONTRIBUTIONS TO THE MINERALOGY OF NORWAY

## No. 34. Stillwellite in the Langesundfiord nepheline syenite pegmatite dykes

BY

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**Abstract.** Stillwellite,  $(\text{Ce,L a})\text{BSiO}_5$ , from Langesundfiord is described. Composition of the rare earths is determined by X-ray fluorescence. X-ray powder data and other physical data are compared with natural stillwellites and with synthetic  $\text{CeBSiO}_5$ ,  $\text{LaBSiO}_5$ ,  $\text{PrBSiO}_5$ , and  $\text{NdBSiO}_5$ .

Stillwellite,  $(\text{Ce,L a})\text{BSiO}_5$ , was identified a few years ago in two specimens from the Langesundfiord nepheline syenite pegmatite dykes. The dykes are exceptionally rich in minerals, among them uncommon silicates of rare earths, and with this last addition to the list 79 species have been recorded from these deposits altogether.

Because of the rarity of stillwellite, it seemed desirable to examine it further to provide new information about it, and the data obtained are given below.

### Previous work on stillwellite

Stillwellite was first described by McANDREW and SCOTT (1955) from the uranium deposit Mary Kathleen in Queensland, Australia, where it occurs in quantity along with allanite, garnet, uraninite, and other minerals as 'a metasomatic replacement of metamorphosed calcareous sediments'. They made a preliminary analysis, and on the basis of this analysis, and the unit cell size, and density measurements, they suggested the chemical formula  $(\text{Ln,C a})\text{BSiO}_5$  with  $Z = 3$ . GAY (1957) confirmed and refined those data and presented a more accurate

Table 1. Powder data for natural and synthetic stillwellite

	hkil	Stillwellite Norway unheated	La- synthetic d obs A	Stillwellite Norway 1000°C d obs A	Stillwellite Australia 900°C (P. Gay) d obs A	Stillwellite Australia (P. Gay) d calc A	Ce- synthetic d obs A	Pr- synthetic d obs A	ND- synthetic d obs A	Stillwellite Tadzhikistan d obs A	Stillwellite Jakutja USSR d obs A
2	10 $\bar{1}$ 0	5.990	5.955	5.944	5.96	5.97	5.931	5.920	5.902	4.40	4.43
9	10 $\bar{1}$ 1	4.478	4.468	4.447	4.44	4.46	4.442	4.424	4.411	3.44	3.41
9	11 $\bar{2}$ 0	3.452	3.438	3.431	3.43	3.44	3.423	3.413	3.405		
4	11 $\bar{1}$ x			3.124	3.13		3.126				
3	11 $\bar{2}$ 1	3.078	3.067	3.055	3.05	3.06	3.047	3.039	3.027		
8	20 $\bar{2}$ 0	2.988	2.977	2.970	2.96	2.98	2.964	2.953	2.946		
10	10 $\bar{1}$ 2	2.943	2.935	2.921	2.91	2.92	2.916	2.908	2.895	2.926	2.917
3	20 $\bar{2}$ 1		2.722	2.715	2.79*	2.73		2.701	2.693		
1	200x			2.709	2.71		2.708				
4	11 $\bar{2}$ 2		2.406	2.399	2.40	2.40	2.392	2.389	2.370		
3	21 $\bar{3}$ 0		2.250	2.244	2.24	2.25	2.240	2.229	2.226		
4	0003	2.249	2.247	2.236	2.23	{2.23	2.234	2.227	2.213	2.234	2.218
4	20 $\bar{2}$ 2		2.230	2.223	2.23	{2.23	2.217	2.210	2.202		
7	21 $\bar{3}$ 1	2.136	2.133	2.129	2.13	2.14	2.123	2.115	2.110	2.141	2.109
2	10 $\bar{1}$ 3		2.097	2.093	2.09	2.09	2.087				
1	3030		1.981	1.979	1.979	1.989					
3	222x			1.912	1.935*						
3	30 $\bar{3}$ 1		1.901	1.899	1.896	1.906					
3	11 $\bar{2}$ 3		1.879	1.874	{1.864	1.874	1.860	1.853	1.848	1.880	1.851
8	21 $\bar{3}$ 2	{1.88	1.870	1.867	1.864	1.871					
2	20 $\bar{2}$ 3			1.787	1.785	1.788					
1	22 $\bar{4}$ 0			1.714	{1.704	1.723					
3	3032			1.705	{1.704	1.710				1.718	1.697

2	2241	1.661	1.646	1.668
3	3140	1.648		1.655
1	311*	1.632		
3	1014	1.614	1.612	1.612
1	3141	1.601		1.606
1		1.584		
3		1.525	1.526	
2		1.506		
2		1.478	1.476	
3		1.462	1.458	
1		1.448	1.448	
2		1.358	1.357	
1		1.343	1.341	
			1.335	
2		1.326	1.324	
2		1.262	1.259	
1		1.209	1.205	
1		1.199		
1		1.187	1.185	
1		1.175		
1		1.151		
1		1.142		
2		1.122	1.118	
1		1.113		
2		1.065		
1		1.057		
2		1.026		
2		1.017		
2		1.004		

\* Cerianite lines.  
 \* Extraneous lines.  
 Intensities given are for Norwegian stillwellite heated to 1000°C.

Table 2. *Physical data for natural and synthetic stillwellite*

	Stillwellite Norway unheated	La- stillwellite synthetic	Stillwellite Norway 1000°C	Australia 900°C	Tadzjikistan USSR	Jakutija USSR	Ce- stillwellite synthetic	Pr- stillwellite synthetic	Nd- stillwellite synthetic
$a_0$ ...	6.907	6.876	6.858	(6.89)6.85	$6.85 \pm 0.01$		6.845	6.823	6.807
$c_0$ ...	6.768	6.744	6.709	(6.70)6.64	$6.70 \pm 0.01$		6.694	6.681	6.638
$c/a$ ...	0.980	0.981	0.978	(0.972)0.969	0.978		0.978	0.979	0.975
Ne ..	1.782			1.78	1.787	1.787			
No...	1.765			1.76	1.778	1.778			
Sp.gr.	4.612		$\pm 0.005 \text{ \AA}$ for $a_0$ and $c_0$	4.58	4.60	4.70			

analysis of more carefully prepared material. (For data see Tables 1 and 2.) On a basis of single crystal oscillation and Weissenberg photographs, he also suggests the space group  $P3_12$  or one of the related groups giving 0002 reflections for  $2 = 3n$  only.

A few years later DUSMATOV, EFIMOV, and SEMENOV (1963) described stillwellite from two Russian localities, the Imaglinsk alkaline massif in South Jakutija and the Alkali Mountains in Tadzikistan. The Jakutian stillwellite is found in a 3–5 cm wide hydrothermal quartz vein cutting a syenite porphyry, together with minor amounts of chessboard microcline, reddish-brown alkali amphibole, eudyalite, sphene, elpidite, and wolframite. The Tadzikistanian stillwellite occurs in alkali pegmatites cutting genetically related syenites. The pegmatites contain essentially microcline microperthite and arfvedsonite, with subordinate amounts of astrophyllite, zircon, pyrochlore, and quartz.

Analyses of the Russian stillwellite confirm the chemical formula given by Andrew and Scott, and the physical data given are in good agreement with corresponding values for the type material (see Tables 1 and 2).

A preliminary report on the crystal structure of stillwellite has been published by VORONDOV, BAKALIEVA, and PJAKENKO (1964). The building units are  $\text{SiO}_4$ - and  $\text{BO}_4$ -tetrahedra as well as irregular Ce-polyhedra. Columns of alternate  $\text{SiO}_4$ -tetrahedra and Ce-polyhedra are arranged parallel to the C-axis with chains of  $\text{BO}_4$ -tetrahedra running along the open channels between these columns. The structure is compared to that of rhabdophanite ( $\text{CePO}_4 \cdot n\text{H}_2\text{O}$ ) described by MOONEY (1950).

### Stillwellite from Langesundfiord

In the collections of the Geologisk Museum in Oslo, there are two specimens of stillwellite from Langesundfiord with elongate brownish yellow prisms with a trigonal appearance originally identified (by W. C. Brögger) as tourmaline. One of these, labelled Langesundfiord, was bought from G. Flink in 1898, and the other, labelled Barkevikkjærne, Langesundfiord, was bought from Ad. Johannesen in 1906. Since that time no stillwellite has to our knowledge been found in the Langesundfiord dykes.

V. M. Goldschmidt examined this material around 1940 and noted that it gives 'a beautiful absorption spectrum of Nd and Pr', and stated that it is 'a boron-silicate of the cerium lanthanides, probably a La, Ce, Pr, Nd-tourmaline'. (Black tourmaline had been found earlier as a great rarity in the Langesundfiord dykes by BRÖGGER (1890).)

The authors re-examined the two specimens and X-ray powder diagrams proved the mineral to be stillwellite.

Together with feldspar, nepheline, leather-coloured zircon, fluorite, aegirine, pyrophanite, and non-metamict pyrochlore, the stillwellite is found embedded in feldspar as brownish yellow prisms with a maximum size of 20 mm by 3 mm. The prismatic faces are strongly striated and have the same curved appearance that is so characteristic for tourmaline crystals.

An X-ray fluorescence analysis of the rare earths gave the following results:

$\text{La}_2\text{O}_3$  25%,  $\text{Ce}_2\text{O}_3$  30%,  $\text{Pr}_2\text{O}_3$  1%,  $\text{Nd}_2\text{O}_3$  2%, and  $\text{Sm}_2\text{O}_3$  0.25%.  
Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y are all below 0.1% and  $\text{ThO}_2$  about 0.5%.

Optical data:

Uniaxial positive with  $N_o = 1.765$ ,  $N_e = 1.783 \pm 0.003$ . Specific gravity = 4.612.

X-ray powder data are given in Table 1; they were obtained with a Guinier-de Wolff quadruple focussing camera using Fe-radiation and  $\text{Pb}(\text{NO}_3)_2$  as an internal standard. Cell dimensions derived from these data are given in Table 2, together with cell dimensions published for other stillwellites for comparison.

A slight diffusiveness of the lines of the powder diagrams of the unheated stillwellite from Langesundfiord is probably caused by an incipient metamictization. When heated to 1000°C the mineral gives a powder diagram with very sharp and well-defined lines. Cell dimensions were calculated for unheated as well as for heated material (see Table 2), and on heating a certain unexpected shrinkage of the cell has clearly taken place. As an additional difference the diagram of the heated material has four more lines than that of the unheated mineral, and these comparatively strong lines cannot be indexed as stillwellite reflections from the crystallographic data given above.

They do coincide, however, with the strongest lines of cerianite corresponding to the reflections 111, 200, 222, and 311. A calculation of the cell size of this cerianite from the  $\text{\AA}$ -values of the observed four reflections gives a cell edge of  $5.413 \pm 0.005 \text{ \AA}$ , while the reported value for pure synthetic  $\text{CeO}_2$  is  $5.411 \text{ \AA}$  (FRONDEL 1958). When stillwellite is heated in air, part of its  $\text{Ce}^{3+}$  content is clearly oxidized to  $\text{Ce}^{4+}$ , which forms a pretty pure  $\text{CeO}_2$  phase, while the stillwellite cell is correspondingly reduced in size by removal of parts of its largest ions.

In all probability, this phenomenon explains the extraneous line at  $3.13 \text{ \AA}$  reported by GAY (1957) for heated stillwellite from Australia.

In GAY'S (1957) Table V the strongest stillwellite reflection ( $2.91 \text{ \AA}$ ) has been accidentally omitted (but it is mentioned in the text). His data are quoted by DUSMATOV *et al.* (1963) and their correlation Table is therefore also incorrect. For that reason, we present here as Table 1 the complete list of observed d-spacings of stillwellite.

Synthetic stillwellite has been prepared according to the formulae:  $\text{CeBSiO}_5$ ,  $\text{LaBSiO}_5$ ,  $\text{PrBSiO}_5$ , and  $\text{NdBSiO}_5$ . Attempts to synthesize stillwellite with the heavier rare earths were not successful.

The La and Nd compounds were synthesized by grinding together stoichiometric proportions of the oxides and heating them in air to  $1000^\circ\text{C}$ . The samples were then reground and heated again 3–4 times, each time for one day.

The Ce-stillwellite was treated differently, since  $\text{Ce}_2\text{O}_3$  was not available, and is also very easily oxidized to  $\text{CeO}_2$ .  $\text{CeF}_3$  was used, thereby introducing a new complication since both  $\text{SiF}_4$  and  $\text{BF}_3$  evaporate far below  $1000^\circ\text{C}$ . This difficulty was overcome by adding enough  $\text{B}_2\text{O}_3$  and  $\text{SiO}_2$  to allow the fluorine to evaporate with either  $\text{SiO}_2$  or  $\text{B}_2\text{O}_3$ . The mixture was placed in a small graphite 'bomb' and heated under evacuation for 3–4 hours. The product gave an excellent stillwellite film with some extra reflections of  $\text{CeO}_2$ , the surplus amount of  $\text{SiO}_2$  or  $\text{B}_2\text{O}_3$  being too small to give visible reflections.

The Pr-stillwellite was prepared from  $\text{PrO}_2$  and heated in the same way as the Ce-compound as Pr had to be reduced from  $\text{Pr}^{4+}$  to  $\text{Pr}^{3+}$ .

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