

# LOMBAARDITE, A RARE EARTH SILICATE, IDENTICAL WITH, OR VERY CLOSELY RELATED TO ALLANITE

By

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Lombaardite was first described from the Zaaiplaats Tin Mine, Central Transvaal by H. J. Nel, C. A. Strauss and Frans E. Wickman in 1949 (NEL, STRAUSS and WICKMAN 1949). These authors describe lombaardite as a hydrous calcium-aluminium-silicate with the following formula:  $\text{Ca}_{10}\text{Fe}_5\text{Al}_{27}\text{Si}_{18}\text{O}_{89}(\text{OH})_5$ .

They also point out the similarities between the unit cell dimensions of lombaardite and those of epidote. The values are as follows:

Lombaardite	Epidote
$a/2 = 8.05 \text{ kX}$	$a = 8.96 \text{ \AA}$
$b = 5.60 \text{ kX}$	$b = 5.63 \text{ \AA}$
$c/2 = 9.10 \text{ kX}$	$c = 10.20 \text{ \AA}$
$\beta = 115.5^\circ$	$\beta = 115.24^\circ$

While the present authors were trying to produce for chemical analysis a pure sample of thalenite from Åskagen, Värmland, Sweden, we found that this mineral was thoroughly intergrown with a dark mineral, the x-ray pattern of which corresponds closely with a film of lombaardite from Zaaiplaats Tin Mine. Further investigations proved that most of the dark minerals in several hand specimens from the Åskagen pegmatite were of the same material.

Thalenite from Åskagen was described by Hj. Sjögren in 1906 (SJÖGREN 1906). The mineral occurs in a quartz quarry with very pure quartz and some plagioclase as main minerals. Native bismuth, bismuthite and bismuthinite were found in the quartz, while gado-

linite, allanite and thalenite were found in feldspar mainly. The thalenite is usually surrounded and partly penetrated by a dark mineral which Sjögren described as "gadolinite-like". The material with which we worked was kindly provided by professor F.E. Wickman, Swedish Museum of Natural History, Stockholm.

The dark mineral which partly occurs in greenish-black needles around thalenite, was isolated and purified as far as possible by a combination of separation by heavy liquids (acetylene tetra bromide

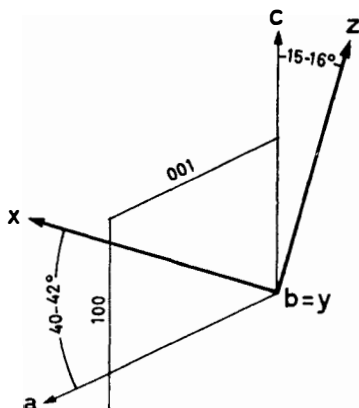


Fig. 1. Optical orientation of "lombaardite", Åskagen. From universal stage measurements by J. Naterstad.

and Clerici solution) and magnetic separation. The sample still contained traces of calcite and feldspar. On this material specific gravity was determined with a pycnometer to 3.86 (Zaaipplaats 3.85). Corrections for feldspar and calcite content (calculated from chemical analysis) increase this to 3.93.

The refractive indices are

$$\alpha = 1.755 \pm 0.03$$

$$\beta = 1.777 \pm 0.03$$

$2V + = 70 - 80^\circ$  which is higher than for the Zaaipplaats lombaardite ( $60 \pm 4^\circ$ ).

Universal stage measurements of the axial angle gave very varying results. A number of cleavages were also measured. They are not identified with certainty, but may be 101 or  $\bar{1}01$ .

TABLE I.

	1.	2.	3.	4.
SiO <sub>2</sub>	31.88	32.35	538.63	498.07
TiO <sub>2</sub>	tr.	0.02		
Al <sub>2</sub> O <sub>3</sub>	35.85	19.69	193.15	186.39
Fe <sub>2</sub> O <sub>3</sub>	4.80	2.60	16.28	16.28
FeO	7.47	8.60	119.71	119.71
MnO	0.18	0.72	10.15	10.15
MgO	1.54	0.47	11.66	11.66
CaO	15.36	9.44	168.33	154.02
Na <sub>2</sub> O	0.50	0.11	1.77	
K <sub>2</sub> O	nil	0.47	4.99	
H <sub>2</sub> O+	1.43	2.37	131.52	131.52
H <sub>2</sub> O—	0.04	0.31		
F	tr.	0.22	11.58	11.58
CO <sub>2</sub>		0.63	14.31	
(RE <sub>2</sub> O <sub>3</sub> )		22.16	71.92	71.92
B <sub>2</sub> O <sub>3</sub>	0.14			
		100.14		
÷ O <sub>2</sub> (F)		0.09		
Sum	99.19	100.05		

1. Lombaardite, Zaaiplaats. (NEL, STRAUSS, WICKMAN 1949)
2. Åskagen mineral. Analyst B. Bruun.
3. Molecular proportions calculated from 2.
4. Molecular proportions corrected for calcite and feldspar. (K<sub>2</sub>O and Na<sub>2</sub>O with Al and Si as feldspar, CO<sub>2</sub> with Ca as calcite).

A chemical analysis of the purified sample is given in table I. The rare earth oxide content of more than 22 percent was rather surprising as no rare earths were reported for the Zaaiplaats mineral.

The composition of the rare earths was determined by X-ray spectrography of the ignited hydroxide precipitate, and the results are given in table II and fig. 2. There is a pronounced maximum for Nd and a regular decrease Nd — Sm — Gd — Dy — Er. Some Th is present, probably also La. —

Ho, Tm, Lu are not present in determinable quantities. The graph indicates a content of Eu of the order of magnitude of 1—1.5 percent. This element has not been found, however.

As the X-ray powder diagrams of the minerals from Zaaiplaats

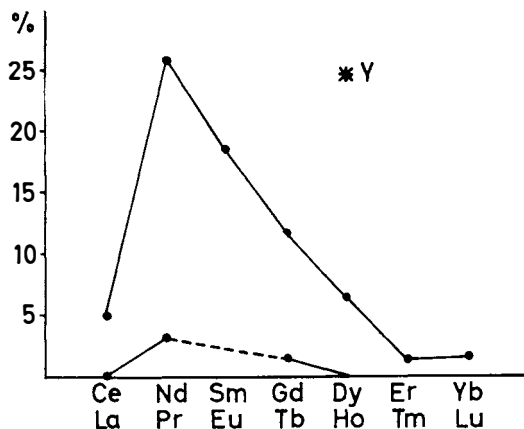


Fig. 2. "Lombaardite", Åskagen, Distribution of the lanthanons in weight percent of total rare earth oxide contents.

and that from Åskagen are practically identical with regard to spacing, a redetermination of the cell size would seem unnecessary, and unit cell dimensions of the Zaaiplaats mineral were used for calculation of the molecular content of the Åskagen mineral. Results are given in Table III.

The second column of this table is calculated on the assumption

TABLE II.  
Composition of rare earths.

	percent	percent of total analysis	molecular proportions
Y <sub>2</sub> O <sub>3</sub>	24.5	5.39	23.87
Ce <sub>2</sub> O <sub>3</sub>	4.8	1.05	3.20
Pr <sub>2</sub> O <sub>3</sub>	3.1	0.68	2.06
Nd <sub>2</sub> O <sub>3</sub>	25.9	5.70	16.94
Sm <sub>2</sub> O <sub>3</sub>	18.6	4.09	11.72
Gd <sub>2</sub> O <sub>3</sub>	12.7	2.79	7.71
Tb <sub>2</sub> O <sub>3</sub>	1.5	0.33	0.90
Dy <sub>2</sub> O <sub>3</sub>	6.5	1.43	3.83
Er <sub>2</sub> O <sub>3</sub>	1.3	0.29	0.76
Yb <sub>2</sub> O <sub>3</sub>	1.8	0.40	1.02
Sum	100.7	22.15	71.92

that the water content is identical in the Zaaipiaats and the Åskagen minerals, and that the excess water in the Åskagen mineral is actually some kind of absorbed or adsorbed water.

A dehydration curve was determined by heating 4.99 g of the min-

TABLE III.  
Unit cell content.

	Sp. gr. 3.93	Sp. gr. 3.96
Si	18.40	18.73
Al	13.78	14.02
Fe <sup>3+</sup>	1.20	1.22
Fe <sup>2+</sup>	4.42	4.50
Mn	0.34	0.38
Mg	0.43	0.44
Ca	5.69	5.79
RE	5.32	5.40
O	73.05	76.33
OH	9.72	5.96
F	0.43	0.44

eral at 50 degree intervals. Heating time at each temperature was 30 minutes with 20 minutes cooling before weighing. The result is illustrated by Fig. 3. A change in the slope of the curve is seen at about 460°. This corresponds to a loss in weight of 1.2 percent. The amount of water left at this temperature 2.69 percent — 1.2 percent = 1.48 percent corresponds closely with the water content of the Zaaipiaats lombaardite, and is also in agreement with the water content demanded by the epidote formula.

If the theory that lombaardite is an epidote with an unusual content of yttrium and rare earths is correct, the Åskagen mineral contains some firmly bound excess water. An incipient metamictization in the Åskagen mineral is revealed by the X-ray powder diagrams (Fig. 3) and is in all probability the cause of the high water content. It is recalled that metamictization is normally accompanied by an increase in water content, a phenomenon which is poorly understood. A discussion of the problems connected with this "water of metamictization" would be outside the scope of this paper.

A portion of the sample was heated to 460° C for 90 minutes. Loss

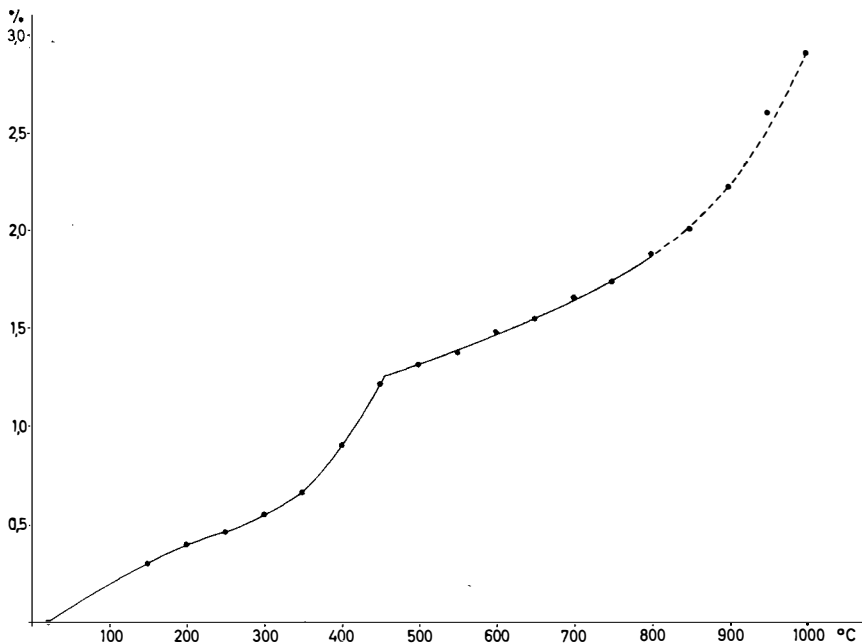


Fig. 3. Dehydration curve for "lombaardite", Åskagen.

in weight after the heating was 1.23 percent. Specific gravity of the heated sample was determined to 3.805 which after correcting for feldspar and calcite as before gives a specific gravity of 3.87. The chemical analysis was now recalculated on this basis and the results are given in Tables IV and V.

The available amount of the Zaaiplaats mineral was very small and it was not possible to make a new analysis of it. The difference in Al content, however, seemed suspicious and a spectrogram of 13 mg. confirmed that there is from 10—15 percent of rare earth oxides present also in this mineral.

We have assumed that the unit cell dimensions of the mineral from Åskagen and that from Zaaiplaats are identical. This may not be absolutely correct, and a small difference may explain the too high cell content. The unit cell is therefore recalculated to  $O = 72$ .

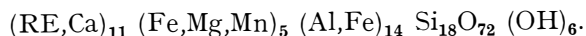
Grouping the  $Fe^{3+}$  with Al, Mg and Mn with  $Fe^{2+}$ , and RE with Ca this gives a formula:

TABLE IV.

Chemical composition of Åskagen mineral heated to 460° C.

	1	2	3	4
SiO <sub>2</sub>	32.64	30.75	32.26	537.13
TiO <sub>2</sub>	0.02			
Al <sub>2</sub> O <sub>3</sub>	19.93	19.17	20.12	197.37
Fe <sub>2</sub> O <sub>3</sub>	2.63	2.63	2.76	17.28
FeO	8.70	8.70	9.13	127.09
MnO	0.73	0.73	0.77	10.86
MgO	0.48	0.48	0.50	12.40
CaO	9.55	8.73	9.16	163.34
Na <sub>2</sub> O	0.11			
K <sub>2</sub> O	0.48			
H <sub>2</sub> O	1.47	1.47	1.54	85.46
CO <sub>2</sub>	0.64			
F	0.22	0.22	0.23	12.10
(RE <sub>2</sub> O <sub>3</sub> )	22.42	22.42	23.45	76.51
Sum	100.00	95.30	100.00	

1. Chemical analysis ÷ water lost by heating to 460° C, recalculated to 100 percent.
2. Corrected for calcite and feldspar.
3. 2 recalculated to 100 percent.
4. Molecular proportions calculated from 3.



The epidote formula according to Ito (Ito 1947) (multiplied by six) is: Ca<sub>12</sub>Fe<sup>3+</sup><sub>6</sub>Al<sub>12</sub>Si<sub>18</sub>O<sub>72</sub> (OH)<sub>6</sub>.

The amount of Fe<sup>2+</sup> in our lombardite (?) formula corresponds almost exactly to the amount necessary to compensate for the higher valency of the rare earths as compared to calcium, but the number of atoms in the Al, Fe group is too high. Either some of the Fe proxies for Ca and the rare earths, which are too low, and in this case some of the Fe must be secondarily oxidized, or, there is also the possibility that there is actually some rare earths which were weighed with Al<sub>2</sub>O<sub>3</sub> as was the case with the Zaaipplaats lombardite. The former alternative is the more probable. It should be noted that the sum of the cations in the formula above is 30, as is demanded by the epidote formula.

TABLE V.  
Calculation of unit cell content.

	1	2
Si	18.50	17.84
Al	13.58	13.09
Fe <sup>3+</sup>	1.18	1.15
Fe <sup>2+</sup>	4.37	4.21
Mn	0.37	0.36
Mg	0.43	0.41
Ca	5.63	5.43
RE	5.26	5.07
OH	5.90	5.68
F	0.42	0.40
O	74.67	72.00

1. Unit cell content calculated for water content 1.54 percent and specific gravity 3.87.
2. Unit cell content recalculated to 72 atoms O.

### X-ray investigations

Powder diagrams have been taken with 9 cm. cameras, Fe radiation, Mn filter. The diagram of the Zaaiplaats and the Åskagen minerals are almost identical and show great similarities with common epidote. The pattern of the Åskagen mineral have some lines which are somewhat broader and more "fuzzy" than the corresponding lines of the Zaaiplaats lombardite. This is clearly seen by direct comparison of the two minerals photographed as two strips of the same film of a Nonius Guinier focusing camera, (fig. 4.) This comparison also shows that the Åskagen mineral is not well crystallized but exhibits a beginning metamictisation, probably due to its larger content of rare earths (and some Th).

By heating the sample to 600° C under water pressure sharper lines were obtained without changing the pattern. Heating to 1 000° C in air gave an entirely different pattern.

Powder diagrams were also taken of the material used for the dehydration curve, and for the material that was heated to 460° C



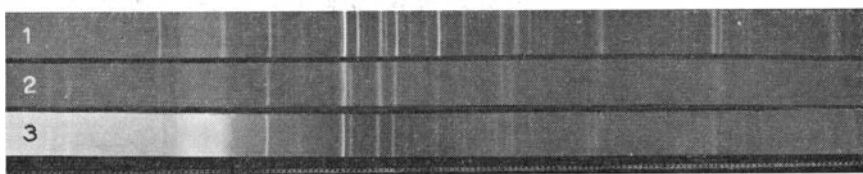


Fig. 4. X-ray powder patterns of:

1. Clinozoisite, Kragerø.
2. Lombaardite, Åskagen.
3. Lombaardite, Zaaipplaats.

Guinier focusing camera, Fe radiation.

for 90 minutes. The last sample was not changed, but the film of the dehydrated material which had been heated to 1 000° C gave a pattern intermediate between the "original" lombaardite pattern and the film of the mineral heated to 1 000° C for one or for three days. This sample was completely changed in colour due to oxidation.

Comparative X-ray spectrograms have been taken from the lombaardite and the thalenite from Åskagen. There is a marked difference in the distribution of the rare earths. Both minerals have much Y, but Ce, Nd, Sm, and Gd are enriched in lombaardite, while Tb, Dy, Er, and Yb seem to be present in greater amounts in thalenite. The smaller ions like Tb, Dy, Er and Yb are concentrated in the rare earth silicate, while the larger ions preferably enter the hydrous Ca — Al compound.

The above data clearly prove that lombaardite is a member of the epidote group with a high content of rare earths. In contrast to the overwhelming majority of allanites it is not or only slightly metamict, perhaps because it does not contain U and very little Th. On the other hand the Y content is much higher than usual for allanites and the Y-Ce proportion is completely reversed. This is at least the case for the Åskagen mineral.

Nevertheless, it is indeed very closely related to allanite chemically and physically, and it is, therefore, very doubtful if lombaardite is a valid species. The question if the name lombaardite should be retained in the mineralogical nomenclature can be definitely settled only after a reinvestigation of lombaardite from the type locality.

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