

Willemite from the Ilímaussaq alkaline Intrusion

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SUMMARY. During the summer of 1967 willemite was found for the first time in the Ilímaussaq alkaline intrusion, South Greenland. The willemite occurs in an albitite together with aegirine/acmite, albite, analcime, arfvedsonite, apatite, chkalovite, hemimorphite, microcline, monazite, natrolite, naujakasite, neptunite, sphalerite, and polyolithionite. Analytical, optical, and X-ray data were obtained from the willemite. Willemite from a calcite vein at Franklin Furnace, New Jersey, and from a quartz vein at Mussartût, South Greenland, were also examined.

One of the willemite crystals from Ilímaussaq was a trilling on $\langle 10\bar{1}0 \rangle$. This is the first time willemite has been found as a trilling.

DURING field work in the summer of 1967 in the northern part of the Ilímaussaq alkaline intrusion, South Greenland, the writer collected a few samples of an albitite from the slope between Quanit Qaqa and Steenstrups Fjeld. In 1970 when the material was fortuitously examined in ultraviolet radiation, discrete crystal aggregates gave off a brilliant blue-green fluorescence, identified as emanating from the α -zinc orthosilicate willemite.

This is the second discovery of willemite in Greenland, the first being made by Rink and Steenstrup in quartz veins at Mussartût, Tunugdliarfik Fjord, Julianehaab district, South Greenland (Bøggild, 1953).

Mineralogy of the albitite. The albitite has the form of an elongated subhorizontal lens striking approximately NE-SW and plunging gently northward; its total length is 31 m and maximum width 1 m. The bedrock consists mostly of an aphanitic to porphyritic lava and there is no significant contact zone between the bedrock and the albitite.

The following minerals have been identified in the albitite: aegirine/acmite, albite, analcime, arfvedsonite, apatite, chkalovite, hemimorphite, microcline, monazite, natrolite, naujakasite, neptunite, sphalerite, polyolithionite, and willemite.

In the following the minerals will be described briefly except for the willemite, which will be described in detail.

The matrix of the albitite consists of one generation of microcline and two generations of albite. The microcline form white blocky crystals ($40 \times 10 \times 20$ mm), which exhibit a mosaic-like extinction pattern owing to penetration twinning on the albite law. The crystals are filled with fluid inclusions except for a narrow rim, which may indicate a recrystallized zone (Spry, 1969), and show maximum obliquity in accordance with microcline described by H. Sørensen (1962) elsewhere in the intrusion. The first albite phase crystallized in miarolitic cavities in the microcline as fine grained (0.01 to 0.05 mm) white saccharoidal albite, which in parts has replaced the microcline. The second albite phase grew in cavities in the first albite phase as waterclear albite twins of cleavelandite habit. A small proportion of the crystals show carlsbad-albite and polysynthetic albite twins. The crystals have lobate impingement boundaries and an inclusion-free outer zone owing to recrystallization. The composition of this phase is $Ab_{94}An_{6(3)}$.

Small (0.1 to 0.05 mm) dark-green arfvedsonite inclusions are scattered in the microcline. The arfvedsonite is partly replaced by aegirine/acmite, which also is found as subhedral

crystals in the albite and as sheaves of crystals in cavities. In common with pyroxenes elsewhere in the intrusion the partly recrystallized aegirine/acmite crystals are flattened parallel to $\{010\}$.

Apatite occurs in cavities as abundant blue sheaves or semi-spherulites, composed of con-focal submicroscopic fibrils branching in a non-crystallographic way. The radius of the semi-spherulites is 1 to 2 mm.

Chkalovite and neptunite occur as rare inconspicuous crystals in cavities and the second albite phase; they are common minerals in the intrusion. Albitites elsewhere in the intrusion have an abundance of beryllium minerals like chkalovite, sørensenite, tugtupite, and bert-randite and it is surprising that this albitite only contains a few chkalovite crystals.

Spherulites of natrolite occur in the feldspar phases; some have a rim of analcime suggest-ing that they are replacing the feldspar. Natrolite is also found in cavities as small (2×5 mm) acicular crystals showing the pyramid $u \{111\}$ and the pseudotetragonal prism $m \{110\}$. Analcime is also found in cavities as 10 mm large icositetrahedra, which may be overgrown by polythionite and by earthy monazite. The monazite is radioactive, and together with two unidentifiable phases it occurs in the feldspar as infillings in negative crystals with trigonal habit. The infilled crystals may be pseudomorphs after eudialyte (Sørensen, 1962).

A very unusual occurrence in the albitite besides the willemite is the presence of a naujakasite phase $((\text{Na}, \text{K})_6(\text{Fe}^{2+}, \text{Mn}, \text{Ca})(\text{Al}, \text{Fe}^{3+})_4[\text{Si}_8\text{O}_{26}] \cdot \text{H}_2\text{O})$ in the miarolitic cavities. Previously, this magmatic mineral has been found only in the lujavrites of the intrusion and in contact facies around naujaite xenoliths in lujavrite (S. Andersen, personal communication). The presence of the mineral in a hydrothermal vein is remarkable. The naujakasite occurs as rhomb-shaped monoclinic crystals ($2 \times 3 \times 0.4$ mm), which may be truncated by cleavelandite. The naujakasite is later than the willemite and has not recrystallized. The crystals may have a narrow rim of analcime, which may be a product of alteration (Petersen, 1967).

Numerous heavily corroded sphalerite grains with up to 5 mol % FeS are found in the feldspar; very small quantities of hemimorphite have been identified in the corrosion products.

Willemite. In addition to the occurrence in the albitite willemite is also found as rare inconspicuous crystals in small albite lenses around the albitite, in analcime-pyroxhlore veins on the Quanit Qaqa plateau, and in naujaite pegmatite lenses at the border of the intrusion. Due to lack of material only the albitite has been described in some detail. Willemite is one of the latest minerals in the miarolitic cavities of the albitite; it occurs as granular, anhedral crystals in small cavities and as euhedral tabular crystals in larger cavities. The crystals contain liquid inclusions and have not suffered any recrystallization. The willemite crystallized after the aegirine/acmite sheaves and was followed by naujakasite, earthy monazite, and natrolite.

In the naujaite pegmatites cut by veinlets of analcime the willemite occurs together with polythionite, aegirine, sodalite, and natrolite.

The two generations of willemite in the albitites and analcinites respectively are in contrast to the several generations of willemite encountered at Franklin Furnace, New Jersey, where willemite occurs in contact facies around pegmatitic intrusions, as a pneumatolytic mineral, in hydrothermal veins, and as a product of alteration of skarn minerals (Palache, 1935).

Of the three crystals of willemite found in hand-specimens one was a single tabular crystal (4×2 mm) and the two others were intergrown crystals (6×2.5 mm). The prism zone and basal pinacoid of the euhedral single crystal showed intricate striations impeding crystallo-metric measurements. In order to identify the forms comparisons were made with Franklin willemite (Palache, 1935) and with Balmat willemite (Pough, 1940). The adopted forms were $a \{11\bar{2}0\}$, $c \{0001\}$, and $e \{01\bar{1}2\}$. The crystal is depicted in fig. 1a. The grey white tabular Ilmaussaq willemite contrasts the blue Mussartût willemite, which has a prismatic habit in common with most willemites from other localities around the world (Pough, 1941).

The intergrowths were also impossible to measure owing to vicinal faces and complex striations. However, observations performed with the Waldmann sphere (Waldmann, 1947) and two-circle goniometer showed that one of the intergrowths was a probable trilling on $\langle 10\bar{1}0 \rangle$, with a re-entrant angle of 60° between two prism faces. The composition plane is wavy due to differential growth of adjacent individuals. The forms present are a , c , e , and r $\{10\bar{1}1\}$ a form not found on the single crystal (fig. 1b). Phenakite also forms trillings on $\{10\bar{1}0\}$. Willemite has not before been encountered as trillings, but a twin has been described from Altenberge, Moresnet, Belgium, by Arzruni (1874), with the twin plane $(3.3.\bar{6}.10)$ normal to the composition plane and with a re-entrant angle of 73.32° measured between two prism faces.

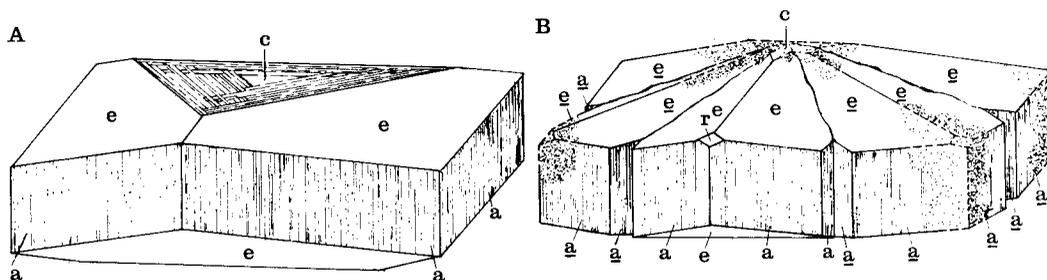


FIG. 1. Ilímaussaq willemite. A. Single crystal showing the forms a $\{11\bar{2}0\}$ striated, c $\{0001\}$ striated, and e $\{10\bar{1}2\}$ brilliant. B. Trilling on $\langle 10\bar{1}0 \rangle$ showing an additional form r $\{10\bar{1}1\}$ brilliant. Assumed faces are dotted.

In thin section the crystals are colourless with a good $\{11\bar{2}0\}$ cleavage. The birefringence measured with a Berek compensator is $0.021(1)$. The principal indices of refraction have been determined using Emmon's λ - T variation method as modified by Micheelsen (1957); the results are ϵ $1.7131(20)$ and ω $1.6920(11)$.

In common with Franklin and Mussartût willemites the Ilímaussaq willemite exhibits a striking blue-green fluorescence making it easy to depict inconspicuous grains in the albite matrix. The phosphorescence of Ilímaussaq and Mussartût willemite is of a less blue-green intensity than the fluorescence and visible only in complete darkness. The phosphorescence may last for 30 seconds.

X-ray data. A preliminary unit cell was derived from single-crystal photographs and refined using powder photographs. The powder data of the three willemites (Table I) are in agreement with the data for synthetic willemite, P.D.F. no. 8-492. The unit cell dimensions and calculated densities are given in Table II, together with the measured densities obtained by the method proposed by Lonsdale (1965). ρ_{calc} and ρ_{obs} agree rather well except for the Franklin willemite.

Electron-probe microanalysis of the Ilímaussaq and Franklin willemites are given in Table II. The runs were executed at acceleration voltages of 10 kV and 15 kV respectively, with a sample current of 0.2 mA, and a dead-time of 2.5×10^{-6} sec. on each spectrometer. The standards used were synthetic zincite, high grade Zn, quartz, wollastonite, and high grade Mn. The Zn-standard was found unsatisfactory as a standard because of its reactivity, consequently the statement by Sweatman and Long (1969), that the elements of the first transition series may be used as standards does not hold for Zn.

In contrast to the almost pure Ilímaussaq willemite the 7.35 % of $\text{MgO} + \text{MnO} + \text{FeO}$ in the Franklin willemite effects a measurable contraction of both cell parameters; in the Mussartût willemite the 0.39 % of $(\text{Fe}, \text{Mn})\text{O}$ has resulted in the smallest cell dimensions of the three minerals.

TABLE I. X-ray powder data for willemite from Ilmaussaq, Franklin Furnace and Mussartût

hkl	I/I_1	Ilmaussaq Willemite GGU 108067			Franklin Willemite MM 15 830			Mussartût Willemite MM 340		
		$\text{Sin}^2\theta_{\text{obs}}$	$\text{Sin}^2\theta_{\text{calc}}$	$d(hkl)_{\text{obs}}$	$\text{Sin}^2\theta_{\text{obs}}$	$\text{Sin}^2\theta_{\text{calc}}$	$d(hkl)_{\text{obs}}$	$\text{Sin}^2\theta_{\text{obs}}$	$\text{Sin}^2\theta_{\text{calc}}$	$d(hkl)_{\text{obs}}$
22	110	0.0122	0.0122	6.9807	0.0122	0.0122	6.9757	0.0122	0.0122	6.9757
4	012	0.0314	0.0314	4.3512	0.0314	0.0313	4.3567	0.0316	0.0315	4.3409
17	211	0.0353	0.0353	4.1027	0.0355	0.0355	4.0939	0.0355	0.0355	4.0939
33	300	0.0365	0.0365	4.0336	0.0368	0.0368	4.0208	0.0368	0.0368	4.0208
81	220	0.0487	0.0488	3.4912	0.0489	0.0488	3.4890	0.0492	0.0491	3.4789
4	122	0.0556	0.0557	3.2679	0.0560	0.0559	3.2603	0.0560	0.0559	3.2603
7	131	0.0597	0.0597	3.1545	0.0600	0.0599	3.1504	0.0601	0.0600	3.1476
97	113	0.0737	0.0738	2.8384	0.0739	0.0738	2.8377	0.0742	0.0741	2.8320
3	312	0.0802	0.0803	2.7201	0.0804	0.0803	2.7202	0.0804	0.0803	2.7202
100	140	0.0855	0.0856	2.6351	0.0856	0.0855	2.6367	0.0860	0.0858	2.6311
2	042	0.0923	0.0924	2.5358	0.0928	0.0927	2.5322	0.0929	0.0928	2.5304
3	330	0.1102	0.1103	2.3208	0.1101	0.1100	2.3245	0.1101	0.1100	2.3244
4	033	0.0980	0.0981	2.4610	0.0987	0.0986	2.4551	0.0987	0.0986	2.4552
1	232	0.1044	0.1045	2.3850	0.1049	0.1048	2.3813	0.1049	0.1048	2.3815
47	223	0.1102	0.1103	2.3211	0.1115	0.1114	2.3100	0.1109	0.1107	2.3167
2	104	0.1134	0.1135	2.2881	0.1138	0.1136	2.2871	0.1137	0.1136	2.2869
1	241	0.1204	0.1205	2.2205	0.1211	0.1209	2.2169	0.1212	0.1211	2.2156
4	502	0.1290	0.1292	2.1448	0.1293	0.1291	2.1452	0.1297	0.1296	2.1416
< 1	511	0.1331	0.1333	2.1113	0.1331	0.1330	2.1141	0.1334	0.1333	2.1118
1	214	0.1373	0.1375	2.0789	0.1380	0.1378	2.0765	0.1385	0.1383	2.0726
5	422	0.1409	0.1411	2.0520	0.1414	0.1412	2.0514	0.1421	0.1419	2.0464
7	600	0.1465	0.1467	2.0130	0.1469	0.1467	2.0125	0.1470	0.1468	2.0124
9	143	0.1480	0.1482	2.0025	0.1400	0.1470	2.0104	0.1476	0.1474	2.0078
2	152	0.1528	0.1531	1.9705	0.1538	0.1536	1.9671	0.1544	0.1542	1.9631
< 1	431							0.1581	0.1579	1.9397
9	250	0.1580	0.1583	1.9377	0.1593	0.1591	1.9329	0.1594	0.1592	1.9319
1	134	0.1625	0.1628	1.9108	0.1629	0.1628	1.9109	0.1630	0.1628	1.9105
36	333	0.1713	0.1716	1.8611	0.1720	0.1718	1.8600	0.1723	0.1721	1.8583
< 1	342	0.1779	0.1782	1.8261	0.1786	0.1784	1.8251	0.1791	0.1789	1.8226
1	161	0.1820	0.1823	1.8058	0.1826	0.1824	1.8049	0.1828	0.1826	1.8043
1	324	0.1862	0.1865	1.7851	0.1870	0.1868	1.7835	0.1875	0.1873	1.7814
< 1	440	0.1967	0.1970	1.7369	0.1956	0.1954	1.7442	0.1957	0.1955	1.7436
< 1	205				0.1878	0.1876	1.7801	0.1882	0.1880	1.7778
< 1	125	0.1993	0.1996	1.7255	0.1998	0.1996	1.7256	0.2005	0.2003	1.7226
< 1	351, 701				0.2065	0.2062	1.6975	0.2067	0.2065	1.6964
7	603	0.2079	0.2082	1.6894	0.2088	0.2085	1.6881	0.2093	0.2091	1.6860
1	054	0.2114	0.2114	1.6765	0.2116	0.2114	1.6767	0.2123	0.2121	1.6739
2	621	0.2157	0.2161	1.6584	0.2190	0.2187	1.6483	0.2191	0.2189	1.6476
7	523	0.2196	0.2199	1.6441	0.2210	0.2207	1.6409	0.2213	0.2211	1.6395
< 1	244				0.2237	0.2234	1.6309	0.2244	0.2241	1.6284
< 1	315	0.2237	0.2240	1.6289	0.2245	0.2243	1.6276	0.2251	0.2248	1.6259
< 1	532, 072	0.2268	0.2272	1.6174	0.2273	0.2271	1.6177	0.2280	0.2277	1.6154
10	170	0.2317	0.2321	1.6000	0.2326	0.2324	1.5991	0.2330	0.2328	1.5978
< 1	514	0.2362	0.2366	1.5849	0.2362	0.2359	1.5871	0.2364	0.2362	1.5863
< 1	045				0.2365	0.2363	1.5858	0.2371	0.2368	1.5840
11	006	0.2462	0.2467	1.5521	0.2466	0.2464	1.5531	0.2476	0.2473	1.5501
< 1	443	0.2562	0.2566	1.5218	0.2576	0.2574	1.5196	0.2582	0.2579	1.5179
9	360	0.2565	0.2569	1.5208	0.2567	0.2565	1.5221	0.2569	0.2566	1.5218
< 1	505	0.2740	0.2724	1.4771	0.2725	0.2723	1.4772	0.2740	0.2737	1.4734
< 1	452				0.2769	0.2767	1.4656	0.2769	0.2767	1.4656
< 1	271	0.2785	0.2788	1.4601	0.2808	0.2806	1.4554	0.2816	0.2814	1.4533
< 1	036				0.2834	0.2831	1.4488	0.2846	0.2843	1.4458
< 1	164				0.2853	0.2851	1.4458	0.2858	0.2855	1.4429
30	713	0.2927	0.2931	1.4239	0.2944	0.2942	1.4213	0.2947	0.2944	1.4209
		+ 12 lines to		1.2112	+ 12 lines to		1.2103	+ 15 lines to		1.2075

Guinier de Wolf exposure at 20 °C using Cu-K α radiation, λ 1.5418 Å. With Ge as internal standard. The specimen numbers are the catalogue numbers in the collections of the Geological Survey of Greenland and The Mineralogical Museum, Copenhagen.

It is not clear how the Al₂O₃ and Cr₂O₃ in the Ilmaussaq analysis fit into the structure because they cannot enter a simple A \rightleftharpoons B substitution; however, no inclusions were detected with the microprobe.

A spectrographical analysis of Ilmaussaq willemite gave the following elements in ppm, Mg < 100(25), Cr trace, Mn 1500(375), Fe 80(20), Cu 8(2), Ag 80(20), Pb 140(35), Bi trace. The standard deviations are large owing to the willemite not burning satisfactorily in the arc.

Conclusions. Willemite from other deposits is usually considered as being secondary after primary sulphides like sphalerite and this seems also to be the case for Ilímaussaq willemite.

The univariant p-T curve for the reaction $Zn_4Si_2O_7 \cdot (OH)_2 \cdot H_2O \rightleftharpoons 2Zn_2SiO_4 + 2H_2O$ varies in temperature from 240 °C at 10 000 lb. in.⁻² to 260° at 40 000 lb. in.⁻² (Roy and Mumpton, 1956).

TABLE II. *Chemical and X-ray data for willemite; the Ilímaussaq and Franklin analyses are by electron-probe, the Mussartût analysis a wet-chemical one*

	Si ₂ O	ZnO	MnO	MgO	FeO	Al ₂ O ₃	CuO	Cr ₂ O ₃	Total	ρ_{calc}	ρ_{obs}
Ilímaussaq	27.7	73.3	0.17	tr.	0.02	0.04	tr.	0.04	101.27	4.227(10)	4.23(5)
Franklin	29	66.0	2	5.2	0.15	0.01	0.05	—	102.41	4.02(8)	4.26(4)
Mussartût	26.9	72.8	0.39*	—	—	—	—	—	100.09	4.06(4)	4.11

Ions to a basis of 72 oxygen					Unit cell dimensions			
	Si	Zn	Mn	Mg	Fe	a	c	V
Ilímaussaq	18.165	35.561	0.095	—	0.012	13.969 Å	9.32 Å	1575.95 Å ³
Franklin	17.948	30.189	1.042	4.792	0.078	13.95	9.317	1570.07
Mussartût	17.958	35.861	0.22	—	—	13.942	9.299	1565.29

* In Bøggild (1953) given as (Fe,Mn)O.

Albite, chkalovite, and sodalite have been synthesized in the temperature range 400 to 600 °C at pressures varying from 6000 to 8000 lb. in.⁻²; at higher pressures and temperatures this assemblage became unstable with sodalite becoming more and more dominant over the two other phases.

Considering that sodalite has not been identified in the albitite it may be concluded with qualifications that the Ilímaussaq willemite and probably the albitite crystallized around 400 to 600 °C at pressures that probably did not exceed 8000 lb. in.⁻² The trace amounts of hemimorphite may indicate local temperature fluctuations.

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REFERENCES

- Arzruni (A.), 1874. *Ann. Phys. Chem. (Poggendorff)*, **152**, 281.
 Bøggild (O. B.), 1953. *Medd. Grønland*, **149**, no. 3, 184-5.
 Lonsdale (K.), 1965. *International Tables for X-ray Crystallography*, Kynoch Press, 3.
 Micheelsen (H.), 1957. *Medd. Dansk Geol. Forn.* **13**, 177-91.
 Palache (C.), 1935. *U.S. Geol. Surv. Prof. Pap.* **180**, 1-135.
 Petersen (O. V.), 1967. *Medd. Grønland*, **181**, no. 6, 1-18.
 Pough (F. H.), 1940. *Amer. Min.* **25**, 488-96.
 ——— 1941. *Ibid.* **27**, 92-102.
 Roy (D. M.), and Mumpton (F. A.), 1956. *Econ. Geol.* **51**, 432-43.
 Sørensen (H.), 1962. *Medd. Grønland*, **167**, no. 1.
 Spry (A.), 1969. *Metamorphic Textures*, Pergamon Press.
 Sweatman (T. R.) and Long (J. V. P.), 1969. *J. Petrol.* **10**, 332-79.
 Waldmann (H.), 1947. *Schweiz. Mineral. Petrogr. Mitt.* **27**, 472-520.

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