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Westerveldite from Igdlúnguaq, Ilímaussaq alkaline massif, South Greenland[1]

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SUMMARY. Microprobe and X-ray investigation of a mineral occurring with breithauptite, nickeline, and other arsenides in the naujaite at Igdlúnguaq, Ilímaussaq alkaline massif, S. Greenland, shows that this mineral, which was formerly misidentified as 'maucherite', is a westerveldite $(Fe_{0\cdot85}Ni_{0\cdot15})As$, of much iron-richer composition than the nickeloan westerveldites from the only two other known occurrences of this mineral. Westerveldite from Igdlúnguaq was presumably formed by reaction of nickeline with iron-rich solutions under conditions of reheating at temperatures of about 450° C and under partial pressures of arsenic below those necessary to stabilize nickeline. Sulphur-bearing löllingite occurs as exsolution blades in the westerveldite. Iron-rich nickeline, up to a composition $(Ni_{0\cdot82}Fe_{0\cdot18})As_{0\cdot95}Sb_{0\cdot05}$, was presumably formed by recrystallization of nickeline in the transition stage just before this mineral became unstable and was replaced by westerveldite.

THE occurrence of Ni-arsenides and breithauptite in a few aggregates of mm-size in a naujaite rock at Igdlúnguaq in the Ilímaussaq alkaline massif, South Greenland, was described by Oen and Sørensen (1964). The naujaite is a rock composed of several-cm large poikilitic crystals of microcline, nepheline, aegirine, and eudialite, containing numerous inclusions of sodalite. However, the naujaite samples with arsenides are from a natrolite- and sodalite-rich reaction zone along the contact with a younger natrolite–sodalite–analcime-bearing acmite–arfvedsonite vein. The arsenides and breithauptite occur as inclusions in natrolite and along cracks and cleavages in aegirine, which shows partial replacement by arfvedsonite. The intricate intergrowths of the arsenides and breithauptite were interpreted as due to the reaction of earlier formed nickeline and breithauptite with later hot fluids from the acmite–arfvedsonite vein. The nickeline shows reaction rims and network intergrowths of a mineral described as 'maucherite'; this mineral also forms myrmekite-like poikiloblasts with breithauptite inclusions. Oen and Sørensen (1964) maintained doubts with regard to their identification of this 'maucherite' and they stated that although paragenesis, etching effects, and optical properties are consistent with those of maucherite, the X-ray powder diffraction lines are not sufficiently so; it was suggested that the mineral might be a new one, with properties resembling those of maucherite (Oen and Sørensen, 1964, p. 21).

Westerveldite was first described by Oen *et al.* (1972) as a mineral in the orthorhombic FeAs–(Fe,Ni)As series, occurring in chromite–nickeline ores at La Gallega, Spain. The strongest powder diffraction lines of westerveldite correspond to those of 'maucherite' from Igdlúnguaq and microprobe analysis has confirmed that the latter mineral is in fact westerveldite. This is the third report of an occurrence of westerveldite; the second occurrence was

[1] Contribution to the mineralogy of Ilímaussaq no. 44.

reported by Sizgoric and Duesing (1973) near Birchtree mine, Manitoba, Canada, in serpentinized peridotite. A paper on recent finds of Ni-free westerveldite in veins in the Ilímaussaq intrusion is now in preparation by Karup-Møller and Mackovicky (1976).

Paragenesis and textural relations

Textural relations and paragenesis were elaborately described and illustrated by Oen and Sørensen (1964). Nickeline and breithauptite contain corroded inclusions of skutterudite and galena; these four minerals crystallized earlier than the westerveldite. The decomposition of nickeline and its replacement by westerveldite is clearly indicated by network or cell textures of recrystallized granular nickeline, veined by a fine intergranular network and surrounded by thin rims of westerveldite (fig. 1D). Skeletal crystals and poikiloblasts of westerveldite have grown across grain boundaries in breithauptite aggregates; the poikiloblasts show myrmekite-like intergrowths with inclusions of breithauptite (figs. 1A–D). Frequently there is some recrystallization and new formation of breithauptite in later rims and crack fillings around nickeline–breithauptite–westerveldite aggregates (fig. 1D; Oen and Sørensen, 1964, Plate I, Fig. 2, Plate II, Figs. 1 and 3). Rarely the breithauptite shows gudmundite rims. The westerveldite often contains fine exsolution blades of löllingite, which are oriented parallel to {111} in the host (Figs. 1C and 1D; Oen and Sørensen 1964, Plate II, Fig. 4, Plate III, Fig. 2, and Plate IV, Fig. 1); small grains of löllingite appear locally along the westerveldite grain boundaries.

Chemistry of westerveldite, löllingite, nickeline, and breithauptite

Microprobe analyses were obtained with a Cambridge Instrument Co. Geoscan operated at acceleration potentials of 20 kV and 25 kV. Pyrite and pure metals were used as standards for the determination of S and the other elements, respectively. Results were corrected according to a computer program adapted from Springer (1967).

The westerveldite shows a homogeneous composition with an average formula $(Fe_{0\cdot85}Ni_{0\cdot15})As_{1\cdot00}$ indicated by nine out of the ten microprobe analyses (Table I). The mineral is very low in Sb, although it occurs associated with breithauptite. The westerveldite from Igdlúnguaq contains only traces of Co and it is much higher in Fe and lower in Ni than the westerveldite from La Gallega, for which Oen *et al.* (1972) give the average formula $(Fe_{0\cdot635}Ni_{0\cdot400}Co_{0\cdot015})As_{1\cdot000}$, and the westerveldite from Birchtree, for which Sizgoric and Duesing (1973) give the average formula $(Fe_{0\cdot73}Ni_{0\cdot32}Co_{0\cdot01})As_{1\cdot00}$.

Accurate analyses of löllingite could not be obtained due to the very fine grain of the mineral. Some variation in As, Sb, and S is suggested by the analyses given in Table I. The löllingite was presumably exsolved from the westerveldite, which originally must have contained excess As and some S in solid solution.

Analyses of the nickeline indicate significant variation in Ni:Fe and As:Sb ratios. Three of the six analyses (Table I) combine unusually high Fe contents for natural nickeline (7·1 wt % Fe or 18 mole % FeAs) with higher As and lower Sb contents (4·6 wt % Sb or 5 mole % NiSb). The other three analyses show lower, but also significant contents of Fe, with the lowest contents of Fe (1·3 wt % Fe or 3 mole % FeAs) in the most Sb-rich nickeline (9·4 wt % Sb or 11 mole % NiSb). Textural evidence indicates that recrystallization of nickeline preceded its decomposition and replacement by westerveldite. The original nickeline was presumably crystallized together with breithauptite as an Fe-poor, NiSb-rich nickeline with more than 11 mole % NiSb. The recrystallization of this nickeline presumably occurred under transitional conditions with Fe-richer, Sb-poorer nickeline forming in the transition stage before the mineral became unstable and replaced by westerveldite. The high NiSb contents in

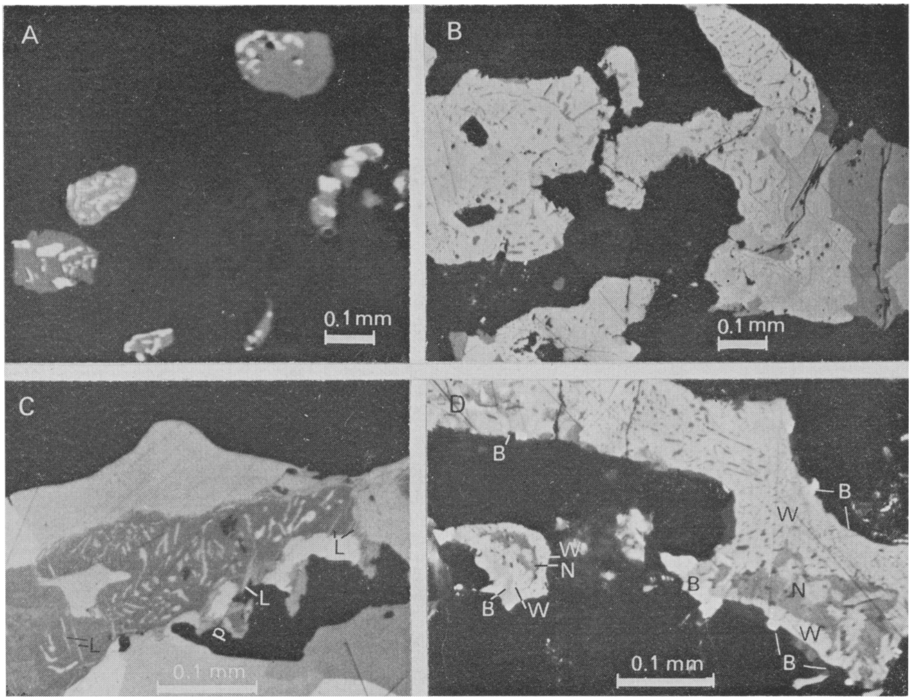

FIG. 1. A. Breithauptite grains (dark grey) showing incipient replacement by skeletal aggregates of westerveldite (white); black are silicates. B. Aggregates of breithauptite grains (different tints of light and dark grey) showing replacement by myrmekitic westerveldite poikiloblasts (white) with breithauptite inclusions; the poikiloblasts have apparently developed across the breithauptite grain boundaries; black are silicates. C. Myrmekitic westerveldite poikiloblasts (dark grey) with breithauptite inclusions and löllingite blades (L) in an aggregate of breithauptite grains (white and light grey); in centre of figure, above black area of silicates, are some recrystallized finer grains of breithauptite. D. Myrmekitic westerveldite poikiloblasts (W) with inclusions of breithauptite, and locally also of nickeline, surrounding relict aggregates of recrystallized nickeline (N); rims of recrystallized fine-grained breithauptite (B) surround the westerveldite–breithauptite–nickeline aggregates; black are silicates.

the original nickeline explains the formation of later breithauptite rims around the nickeline–westerveldite intergrowths.

Analyses of breithauptite indicate a homogeneous composition of the mineral (Table I); two of the ten analyses are somewhat lower in As and higher in Sb, but differences between two generations of breithauptite cannot be indicated.

Some ore-microscopic properties of westerveldite

Westerveldite from Igdlúnguaq is whitish grey with faint brownish and bluish tinges; the brownish tinge is less distinct compared to that of westerveldite from La Gallega (Oen *et al.* 1972). Bireflection is very weak in air and in oil. Anisotropy effects under crossed nicols are distinct in air and strong in oil. The polishing hardness is between those of the softer nickeline and breithauptite and that of the harder löllingite.

Table II lists reflectance values of westerveldite, nickeline, and breithauptite from Igdlúnguaq. The reflectance values and dispersion curve of the Fe-rich westerveldite (average reflectance at 546 nm is 48·3 %) differ from the data given by Sizgoric and Duesing (1973) for the Ni-rich westerveldite from Birchtree (average reflectance at 546 nm is 50·1 %). The differences are within the range of the effects of sample preparation and instrumentation; the somewhat lower reflectance values obtained for the Igdlúnguaq westerveldite may be related in part to the coarser grain of the mineral allowing the use of a lower power objective to reduce the effects of secondary glare and to the use of a reflectance standard with reflectance

TABLE I

	Westerveldite				Nickeline							
	Wt. %		At. ratios		Wt. %				At. ratios			
	1–9	10	1–9	10	1–3	4	5	6	1–3	4	5	6
Fe	35·9 ±0·3	36·5	0·85	0·86	7·1±0·15	1·35	3·25	2·15	0·18	0·03	0·08	0·05
Ni	6·6 ±0·2	5·65	0·15	0·13	35·3±0·2	40·65	39·25	40·9	0·82	0·97	0·92	0·95
As	57·2 ±0·25	57·2	1·00	1·01	52·5±0·2	48·0	51·65	52·6	0·95	0·89	0·94	0·95
Sb	0·15±0·05	0·15	—	—	4·6±0·1	9·4	5·2	4·95	0·05	0·11	0·06	0·05
Σ	99·85*	99·5*	2·00	2·00	99·5†	99·4†	99·35†	100·6†	2·00	2·00	2·00	2·00

	Löllingite								Breithauptite			
	Wt. %				At. ratios				Wt. %		At. ratios	
	1	2	3	4	1	2	3	4	1–8	9–10	1–8	9–10
Fe	26·45	26·9	26·6	27·0	0·96	0·98	0·98	0·99	—	—	—	—
Ni	0·85	0·85	0·65	0·2	0·03	0·03	0·02	0·01	31·95±0·15	31·95±0·15	0·98	0·98
Co	0·1	0·1	0·1	0·1	—	—	—	—	—	—	—	—
As	66·25	67·5	69·65	67·9	1·79	1·84	1·93	1·87	0·75±0·1	0·35±0·1	0·02	0·01
Sb	5·05	2·15	0·65	2·8	0·09	0·04	0·01	0·05	67·45±0·2	68·45±0·3	1·00	1·01
S	1·6	1·7	0·85	1·2	0·13	0·11	0·06	0·08	—	—	—	—
Σ	100·3	99·2	98·5	99·2	3·00	3·00	3·00	3·00	100·15‡	100·75‡	2·00	2·00

* Also Co < 0·1, Cu < 0·05, S < 0·05 %. † Also Co < 0·1, Cu < 0·05 %. ‡ Also Cu < 0·1 %.

For series of approximately similar analyses the average composition and range in analytical values are given.

TABLE II

	Westerveldite*		Nickeline†		Breithauptite†	
λ	R_{max}	R_{min}	R_{ω}	R'_{ϵ}	R_{ω}	R'_{ϵ}
470 nm	48·4	46·9	45·5	40·0	46·3	39·0
546	48·9	47·6	52·0	47·8	48·6	37·9
589	49·3	48·3	56·2	53·4	53·1	43·2
650	50·1	49·5	60·9	58·4	57·9	49·8

* Mean maximum and minimum reflectances of four grains.

† Reflectance values of grain showing highest bireflectance.

Reflectance values (in %) measured with a Leitz MPV microscope photometer equipped with a Knott 9592A photomultiplier tube, a Veril B–200 continuous-band interference filter, and a 16:1 objective of 0·40 NA, on an area of 10 μm square; a tungsten carbide WC–6 reflectance standard provided by Messrs. Carl Zeiss, Oberkochen, was used.

much nearer to that of the measured specimen. The reflectance data of the nickeline and breithauptite in Table II agree with the data for these minerals in the literature (Petruk *et al.* 1969; Uytenbogaardt and Burke, 1971).

The micro-indentation hardness (VHN) of the Fe-rich westerveldite from Igdlúnguaq was measured with a Leitz Durimet–Pol hardness tester; applying a load of 100 g and an indentation time of 15 sec the mean minimum and maximum VHN obtained from 10 indentations on randomly oriented westerveldite grains is 916 to 973 kg/mm². Sizgoric and Duesing (1973) give a much lower VHN of 707 to 798 kg/mm² for the Ni-rich westerveldite from Birchtree.

The difference in measured hardness may possibly be related in part to factors of cohesion in the specimens; the Birchtree westerveldite forms small grains along cracks in maucherite.

X-ray powder diffraction data of westerveldite

The measured X-ray powder diffraction lines of westerveldite listed in Table III were obtained by elimination of the breithauptite lines in Debye–Scherrer diagrams of several powder samples, carefully drilled out of grains of westerveldite–breithauptite intergrowths. Unit cell dimensions were obtained by a least-squares refinement procedure that includes correction for the systematic error in θ proportional to $\sin^2 2\theta/\theta + \sin^2 2\theta/\sin\theta$, using θ values of 21 selected diffraction lines and *hkl*-indices in the crystal setting adopted by Strunz (1970) for synthetic orthorhombic FeAs. The orthorhombic unit cell of Fe-rich westerveldite from Igdlúnguaq has: $a = 3{\cdot}423(4)$ Å, $b = 5{\cdot}985(6)$ Å, $c = 5{\cdot}356(4)$ Å; $a{:}b{:}c = 0{\cdot}572{:}1{:}0{\cdot}895$.

Comparison of the X-ray powder data of synthetic westerveldite (FeAs) (ASTM—X-ray Powder Data File, card 12–799), Fe-rich westerveldite from Igdlúnguaq, and Ni-rich westerveldite from La Gallega (Oen *et al.* 1972) shows a regular shifting of the diffraction lines of westerveldite with the Fe/Ni ratio of the mineral.

TABLE III

I	d_{meas}	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl
1	2·964	2·971	110	5	1·726	1·724	130	1	1·402	1·399	123	3	1·170	1·169	232
3	2·617	2·612	021	2	1·711	1·711	200	1	1·340	1·339	004			1·168	051
10	2·603	2·598	111			1·711	013	—	—	1·307	014	4	1·150	1·151	124
1	2·453	2·444	012	—	—	1·600	032	3	1·301	1·299	222	—	—	1·142	223
2	2·114	2·110	102	4	1·533	1·533	023	1	1·262	1·262	231	1	1·114	1·112	034
3	2·080	2·077	121			1·530	113	2	1·246	1·247	104	2	1·105	1·106	151
8	1·996	1·996	022	2	1·447	1·449	132	—	—	1·221	114	4	1·089	1·097	311
		1·989	112			1·441	041	3	1·211	1·210	213			1·087	143
2	1·875	1·869	031	1	1·433	1·432	221					3	1·059	1·054	015
														1·054	204

Debye–Scherrer diagrams were made with 57·54 and 114·83 mm diameter Straumanis-type cameras, a Philips PW 1008 X-ray generator, Mn-filtered Fe-$K\alpha$ radiation (λ 1·93735 Å), 30 kV and 13 mA, and exposure times about 24 hrs; powders were taken in balls of rubber; intensities were visually estimated; indexed on an orthorhombic cell with a 3·423(4) Å, b 5·985(6) Å, c 5·356(4) Å, in the crystal setting adopted by Strunz (1970) for orthorhombic FeAs (PDF card 12–799 gives indices for a setting with a and c reversed).

Phase relations of westerveldite in the Fe–Ni–As system

The network or cell textures of granular nickeline, veined and rimmed by westerveldite, resemble the textures resulting from the decomposition of nickeline into maucherite and arsenic vapour, when NiAs is heated in sealed tubes to temperatures of about 450 °C (Hawley and Hewitt, 1948). There is thus textural evidence indicating that, presumably under conditions of reaction with Fe-rich solutions, nickeline was replaced by westerveldite under release of arsenic vapour (Oen and Sørensen, 1964). This suggests that the equilibrium partial pressure of arsenic (P_{As}) necessary for the stabilization of westerveldite is lower than that necessary for the stabilization of nickeline.

The condensed phase relations at about 450 °C in the As-richer portion of the Fe–Ni–As system, as derived from available experimental data (Yund, 1961; Roseboom, 1962; Buseck, 1963; Maes and De Strycker, 1967) and paragenetical observations (Oen *et al.*, 1971), are schematically shown in fig. 2A; under appropriately high P_{As} nickeline and the higher

N-arsenides are stable minerals. The phase relations at the same temperatures but under deficient P_{As} are depicted in fig. 2B, which applies when P_{As} is below the value necessary to stabilize nickeline, but above that necessary to stabilize westerveldite and löllingite.

In the naujaite at Igdlúnguaq breithauptite and Sb-rich nickeline were presumably crystallized at higher temperature under higher P_{As} (fig. 2A); with cooling P_{As} decreased, and when in connection with adjoining veins reheating took place, recrystallization occurred under deficient P_{As} (fig. 2B). Under the latter conditions and in the presence of Fe-rich solutions Sb-rich nickeline was decomposed and replaced by Fe-rich westerveldite and breithauptite. The

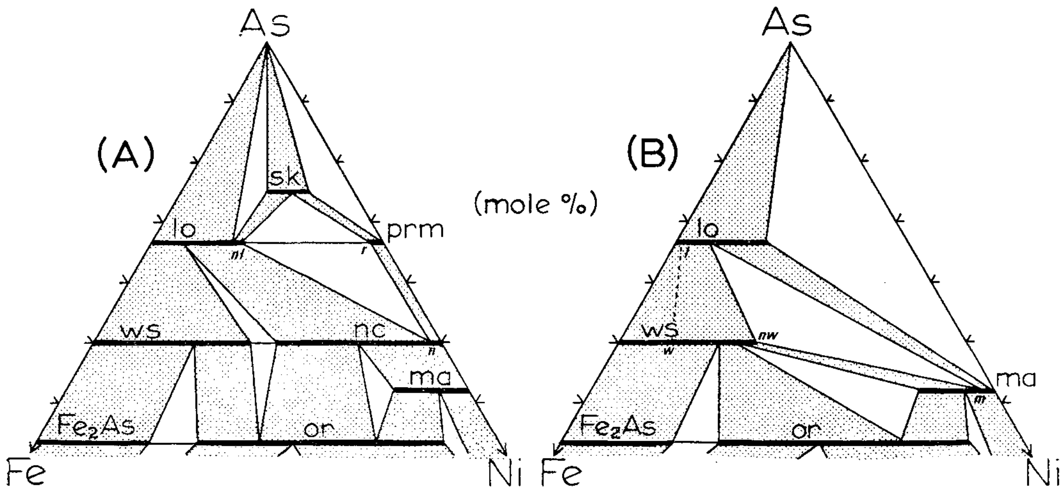

FIG. 2. Schematic phase relations in the system Fe–Ni–As at temperatures around 450 °C. A. The condensed phase relations; partial pressures of arsenic are above that necessary to stabilize the arsenides shown in the diagram; *nl*, *r*, *n* compositions of coexisting Ni-rich löllingite, (para)rammelsbergite, and nickeline in ores from La Gallega, Spain (Oen *et al.*, 1971). B. The phase relations under arsenic partial pressures below that necessary to stabilize nickeline and the higher Ni-arsenides; *m*, *nw* compositions of coexisting maucherite and Ni-rich westerveldite from La Gallega (Oen *et al.*, 1972); *w*, *l* compositions of coexisting westerveldite and löllingite from Igdlúnguaq, S. Greenland. sk—Skutterudite, lo—löllingite, prm—(para)rammelsbergite, ws—westerveldite, nc—nickeline, ma—maucherite, or—oregonite.

decomposition of the nickeline involved transition stages of recrystallization into metastable Fe-richer, Sb-poor nickeline. Fig. 2B also shows that in a less Fe-rich environment nickeline may be replaced by Ni-rich westerveldite and maucherite; the latter mineral pair occurs in the ores of La Gallega (Oen *et al.*, 1972) and is indicative for conditions of deficient P_{As}, for under higher P_{As} the stability of nickeline precludes the stable coexistence of maucherite and westerveldite.

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