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SEDERHOLMITE, WILKMANITE, KULLERUDITE, MÄKINENITE and TRÜSTEDTITE, FIVE NEW NICKEL SELENIDE MINERALS [1])

BY

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ABSTRACT

Five new nickel selenide minerals from Kuusamo, NE-Finland are described. The minerals occur in veinlets in albitites associated with uranium mineralisation.

Sederholmite, which is identical with the synthetic hexagonal β-NiSe phase, has $a_0 = 3.62 - 3.65$ Å and $c_0 = 5.29 - 5.34$ Å depending upon composition.

Wilkmanite corresponds to the artificial monoclinic Ni_3Se_4 phase. Its $a_0 = 6.22$ Å, $b_0 = 3.63$ Å, $c_0 = 10.52$ Å and $\beta = 90.55°$.

Kullerudite $NiSe_2$ is an ortho-rhombic nickelian analogue of ferroselite with $a_0 = 4.89$ Å, $b_0 = 5.96$ Å and $c_0 = 3.76$ Å.

Mäkinenite, which is the same as the artificial γ-NiSe phase, has a trigonal symmetry with $a_0 = 10.01$ Å and $c_0 = 3.28$ Å.

Trüstedtite is a cubic spinel type Ni_3Se_4 having $a_0 = 9.94$ Å. It forms a solid solution series with polydymite. Members of this series with 40—70 mole per cent polydymite component have also been found.

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INTRODUCTION

The system nickel-selenium has been studied by various authors. According to the literature the following selenides of nickel are known.

α-NiSe was obtained by Levi and Baroni (1935) by conducting ammonium selenide into a neutral nickel salt solution. The product was amorphous.

β-NiSe, which has a hexagonal structure of the NiAs type (Grønvold and Jacobsen, 1956, Hiller and Wegerner, 1960) has been prepared either by heating appropriate amounts of the elements in evacuated and sealed silica tubes (Grønvold and Jacobsen, 1956) or by precipitating it with hydrogen selenide in a nickel acetate solution containing acetic acid (Levi and Baroni, 1935).

γ-NiSe has been obtained by Levi and Baroni (1935) by conducting hydrogen selenide into a nickel sulphide solution containing sulphuric acid. Hiller and Wegener (1960) have also prepared γ-NiSe by heating powdered nickel and selenium at 225—250 C°. The compound is trigonal with a millerite type structure.

$NiSe_2$ has been prepared by de Jong and Willems (1928) by heating a mixture of NiSe and selenium at 230 C° for 48 hours. It has also been synthetised by e.g. Grønvold and Jacobsen (1956), Hiller and Wegerner (1960) and Klemm (1962). The $NiSe_2$ phase has a pyrite structure.

Ni_3Se_2 has been reported by Hiller and Wegener (1960). The phase is hexagonal with $a_0 = 6.029$ Å and $c_0 = 7.249$ Å.

The Ni_3Se_4 phase has also been prepared by Hiller and Wegenar (1960). According to them it is monoclinic with $a_0 = 12.15$ Å, $b_0 = 3.633$ Å, $c_0 = 10.45$ Å and $\beta = 149°22'$. Grønvold and Jacobsen (1956) have derived the structure of Ni_3Se_4 from that of the deformed hexagonal β-NiSe cell and obtained different unit cell dimensions: $a_0 = 6.196$ Å, $b_0 = 3.634$ Å, $c_0 = 10.464$ Å and $\beta = 90.78°$.

Only two nickel selenide minerals have been reported so far. Blockite $(Ni,Cu)Se_2$ was described by Herzenberg and Ahlfelt (1935) from Bolivia. In fact the mineral is the same as penroseite which was discovered in the same locality and studied by Gordon (1925). Blockite is structurally similar to the artificial $NiSe_2$.

Robinson and Brooker (1952) reported a new nickel-bearing selenide, tyrrelite $(Cu, Co, Ni)_3Se_4$ from Beaverlodge Lake, Saskatchewan. They suggested that the mineral is structurally similar to pentlandite but Machatschki (1952) has pointed out that the powder pattern of tyrrelite resembles those of the spinel and linnaeite groups of minerals.

In connections with the prospecting work carried out by the Outokumpu Co in Kuusamo, in NE Finland during 1961—1963 quite a few new nickel

selenide minerals were encountered. In this paper five of them i.e. β-NiSe, monoclinic Ni_3Se_4, γ-NiSe, ortho-rhombic $NiSe_2$ and cubic Ni_3Se_4 are described.

GEOLOGY OF THE SELENIUM MINERALISATION AREA.

In Kuusamo in NE Finland the Se-mineralisation occurs in albite diabases which form sills in a schist formation. The schist formation is composed of quartzites, dolomites, marls, mica schists and black schists. Also green-schists are encountered. Quartzites are either clastic ortho-quartzites or albite-bearing arkose quarzites grading into dolomites. The marls are fine-grained, predominantly grey, dolomite-bearing sediments which contain, apart from dolomite, quartz, micas and albite as major minerals.

Ripple marks, fossil mud cracks and clastic dikes are found in sediments. Graded bedding which permits the determination of the sedimentation bottom is observed in mica schists and phyllites. In some localities phyllites contain carbon-bearing »bags» with calcite-rich cores. The size of the »bags» is variable but the biggest attain a diametre of about 30 cm. They are believed to be of fossil origin.

The green-schists, which may be, at least partly, of volcanic origin are chlorite-albite-epidote rocks often showing a distinct bedding. The bedding of the schist formation dips subvertically. Folds as well as faults are common. The formation has locally tectonised intensively giving rise to transverse schistosity.

Albite diabase is a hornblende-albite rock of variable grain size. Especially in strongly tectonised places it changes into more fine-grained biotite-bearing rock which contains only a small amount of hornblende or is completely free from it. Pink albitite is associated with these biotite-albite diabases forming dikes or irregular bodies in the latter. Albitites occur preferably at the ends or at the flexure points of the albite diabase sills, or near by the country rock contacts i.e. generally in places where tectonisation has been strongest.

Small amounts of sulphide, selenide and telluride minerals have been found in albitites, among them some hitherto unknown in geological literature. These minerals are intimately associated with low-grade uranium mineralisation and especially nickel selenides seem closely to follow uranium. Outside the uranium mineralisation the nickel content diminishes rapidly, whereas the amount of cobalt relative to that of nickel increases considerably. A similar correlation has been reported from Shinkolobwe by Derriks and Vaes (1955). In the wall rock cobalt is incorporated in the lattice of pyrite which can contain up to 3 per cent cobalt.

The uranium mineralisation, which is confined to albitites, is not homogeneous but the uranium minerals occur as isolated spots and veinlets. The most important mineral is uranite, but brannerite, davidite, kasolite and uranoanatase have also been identified as well as some alteration products of primary uranium minerals.

OCCURRENCE

Among the new nickel selenides β-NiSe and monoclinic Ni_3Se_4 form a natural and interesting pair. The artificial counterparts of these minerals have been prepared and reported by e.g. Levi and Baroni (1935), Grønvold and Jacobsen (1956) and Hiller and Wegener (1960). Since β-NiSe changes into monoclinic Ni_3Se_4 by decreasing nickel content, both minerals occur associated most intimately with each other. They are found almost exclusively in blockite clusters of a few millimetres in diametre, which seem to favour calcite veinlets in the uranium-bearing parts of albitite dikes. β-NiSe and monoclinic Ni_3Se_4 brecciate blockite forming micro-veinlets and flame-like segregations in it as is seen in Fig. 1, Plate I. β-NiSe has also been detected as independent grains in clausthalite. Monoclinic Ni_3Se_4 seems to occur either as a primary or secondary mineral. The latter is an alteration product of β-NiSe. The secondary monoclinic Ni_3Se_4 often gives a diffuse powder pattern with the consequence that only the strongest reflections are visible. Monoclinic Ni_3Se_4 is frequently followed by native secondary selenium and sometimes also by ferroselite. Selenian vaesite and selenian cattierite also belong to the mineral paragenesis but they are younger than blockite, β-NiSe and monoclinic Ni_3Se_4, for they form veinlets cutting the latter. (See Fig. 1, Plate I).

The ortho-rhombic $NiSe_2$ seems to occur almost exclusively as an alteration product of monoclinic Ni_3Se_4. The mineral grains often contain relics of the latter as indicated by Fig. 2, Plate I, but in some cases the primary mineral has completely disappeared. The formation of the ortho-rhombic $NiSe_2$ has taken place soon after the crystallisation of β-NiSe and monoclinic Ni_3Se_4 but before the appearance of selenian sulphides, for they are seen to cut ortho-rhombic $NiSe_2$. In spite of the fact that ortho-rhombic $NiSe_2$ is a nickelian analogue of ferroselite it has never been observed in association with the latter. Ferroselite seems to be primary. It is distinctly yellow in colour and contains about 5 per cent nickel.

γ-NiSe was first found combined with clausthalite (see Fig. 3, Plate I) in stringers at the ends of the veins filled with carbonate, clausthalite, NiTeSe (a new mineral to be described in a forthcoming paper), selenian melonite, hematite and spinel type selenian sulphides. It greatly resembles millerite but

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is considerably softer. Later γ-NiSe was also found as submicroscopic grains in the cracks of selenian melonite associated with clausthalite.

The spinel type Ni_3Se_4 also belongs to the mineral paragenesis of the aforementioned calcite- and uranium-bearing veinlets. It occurs as euhedral crystals in clausthalite in association with blockite and β-NiSe (Fig. 4, Plate II), Cubic Ni_3Se_4 seems to form a solid solution with polydymite with the consequence that $Ni_3(Se,S)_4$ minerals have also been detected. They occupy, together with clausthalite, the very ends of the stringers filled by carbonate, NiTeSe, hematite and Ni-, Co- and Se-bearing pyrite (Fig. 5, Plate II). They have also been found in NiTeSe where they are commonly enveloped by idiomorphic apatite crystals.

PHYSICAL AND OPTICAL PROPERTIES

The optical properties of β-NiSe vary somewhat depending upon composition. In oil the stoichiometric variant is orange yellow in colour. Pleochroism is distinct with different hues of yellow. Anisotropism is strong: pinkish — greenish. The nickel-deficient type is yellow in colour. Its pleochroism is weak: yellow — greyish yellow and anisotropism distinct: pink — greenish. Monoclinic Ni_3Se_4 is pale greyish yellow in colour. Pleochroism is distinct: pale yellow — greyish yellow and anisotropism strong: pink — yellowish green. Both minerals take an easy polish and have a high reflectivity.

The colour of the ortho-rhombic $NiSe_2$ is very similar to that of blockite except that it is slightly paler. Pleochroism in oil is distinct: grey — pale grey and anisotropism very strong: yellowish grey — grey to almost black. The mineral seldom polishes well and is rather soft.

In oil γ-NiSe is pure yellow in colour but in air orange yellow. Pleochroism is strong: pure yellow — greenish yellow and anisotropism extremely strong: pale green — pale orange yellow. In air anisotropism is different: glowing cinder red — blue green or green. The mineral is almost as soft as clausthalite.

Cubic Ni_3Se_4 is yellow in colour and completely isotropic. Its reflectivity is higher than that of β-NiSe and blockite and it is only slightly softer than blockite. The $Ni_3(Se,S)_4$ variant is different in colour. It is olive grey and takes an easy polish. Reflectivity is slightly less than that of sulphur-free Ni_3Se_4. The mineral is considerably softer than selenian linnaeite.

CHEMICAL COMPOSITION

Due to their rarity it was impossible to separate the selenide minerals in quantities sufficient for ordinary wet chemical analyses and their composition had to be determined by X-ray fluorescence methods using chemically ana-

lysed nickel selenides as standards. The analyses were carried out by a Philips's universal vacuum spectrograph provided with a tungsten tube. The composition of β-NiSe was found to vary from $Ni_{1.05}Se$ to $Ni_{0.85}Se$ i.e. from the stoichiometric NiSe to the point at which the β-NiSe phase changes into monoclinic Ni_3Se_4. A typical analysis for a nickel deficient β-NiSe is as follows: 36.8 % Ni, 1.9 % Co and 61.3 % Se. As a rule the mineral contains about 1—2 per cent cobalt, whereas iron and copper are completely lacking or exist only as impurities.

According to an X-ray fluorescence analysis, the most nickel-rich monoclinic Ni_3Se_4 contained 37.6 % Ni and 61.1 % Se, which gives $Ni_{0.83}Se$ as the composition for that particular mineral sample. Cobalt is, of course, added to nickel in the above formula. The transition point between hexagonal β-NiSe and monoclinic Ni_3Se_4 phases represented by the above specimen agrees excellently with the composition of the transition point reported by Grønvold and Jacobsen (1956) i.e. $Ni_{0.82}Se$.

The most nickel deficient monoclinic Ni_3Se_4 contained 33.7 % Ni, 1.0 % Co and 65.3 % Se which corresponds closely to the formula Ni_3Se_4. Again, only traces of copper and iron were detected in this mineral.

An X-ray fluorescence analysis showed ortho-rhombic $NiSe_2$ to contain 23.1 % Ni, 1.4 % Co, 1.91 % Fe, 0.5 % Cu and 73.1 % Se. The chemical formula for the mineral is thus $NiSe_2$ within limits of analytical errors.

The composition of γ-NiSe was also determined by the same method and the mineral was found to contain 41.1 % Ni, 1.0 % Co and 57.9 % Se. Only traces of copper were detected.

An analysed sample of cubic Ni_3Se_4 mineral contained 29.5 % Ni, 6.4 % Co and 64.1 % Se. Traces of copper were also found. Due to the extremely small amount of the material available it was impossible to determine sulphur accurately. Its concentration was in any case very low, if not altogether nil.

According to the length of the a-axes the sulphur-bearing $Ni_3(Se,S)_4$ minerals contain about 40—70 mole percent of polydymite component. As a rule cobalt percentage seems to be lower than that of the sulphur-free Ni_3Se_4.

CRYSTALLOGRAPHY

The unit cell dimensions and powder patterns for the minerals were obtained with a 114.6 mm diametre camera using silicon as an internal standard. The lattice parametres of β-NiSe and monoclinic Ni_3Se_4 vary somewhat depending on the composition. The values for a nickel-rich β-NiSe are: $a_0 = 3.65$ Å and $c_0 = 5.34$ Å and for a nickel-deficient one: $a_0 = 3.624$ Å and $c_0 = 5.288$ Å, respectively. These values are plotted in Fig. 1. as a function of the composition together with the values for the artificial compounds

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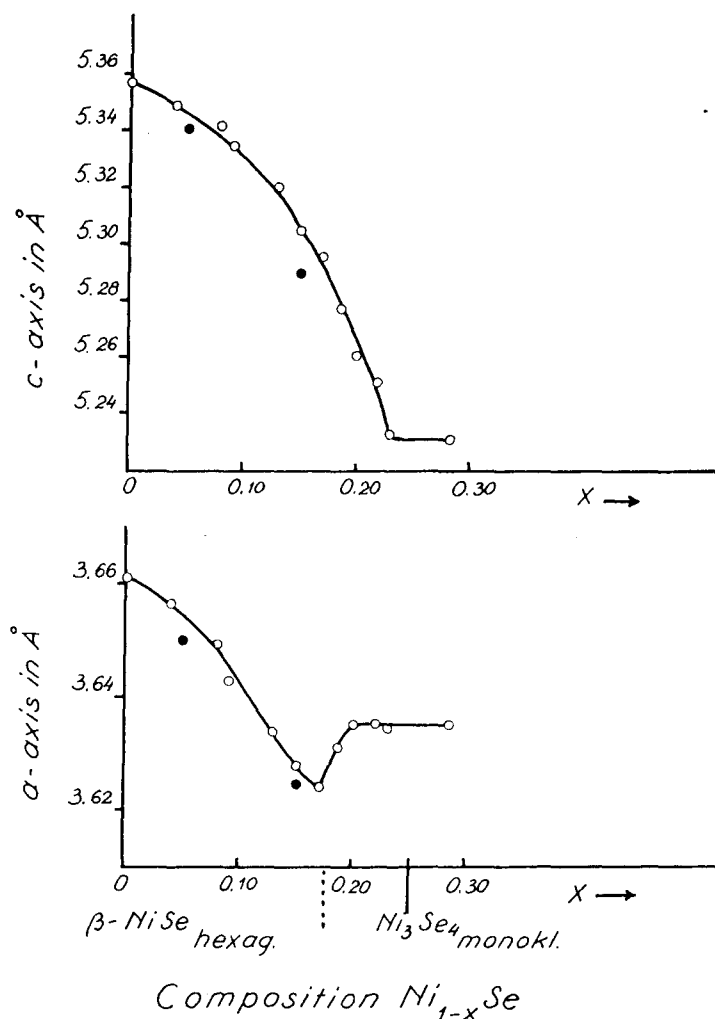
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Fig. 1. The unit cell dimension of hexagonal β-NiSe plotted against the composition. The white circles: values reported by Grønvold and Jacobsen (1956). The black circles: values obtained from the β-NiSe minerals from Kuusamo.

reported by Grønvold and Jacobsen (1956). The lattice parametres of the β-NiSe minerals are slightly smaller than those for the synthetic compounds but the difference is obviously insignificant and may be entirely due to the analytical errors. On the other hand it may also be caused by a small amount of cobalt incorporated in the lattice of the mineral. The space group for β-NiSe is $P6_3/mmc$. In Table 1 the X-ray powder data for the β-NiSe mineral of the composition $Ni_{0.85}Se$ is given.

The indexing of monoclinic Ni_3Se_4 has been based on the information reported by Grønvold and Jacobsen (1956). The powder data for the mineral is shown in Table 2. The data represent the composition of $Ni_{0.78}Se$ which approaches Ni_3Se_4 very closely. The unit cell dimensions for that particular

Table 1. X-ray powder data and lattice dimensions for β-NiSe mineral from Kuusamo, NE-Finland. The composition of the mineral is $Ni_{0.85}Se$. Camera diametre 114.59 mm, Cu/Ni radiation.

hkl	I	$d_{obs.}$	$d_{calc.}$		
001	w	5.27	5.29	a_0	$= 3.624$ Å
101	vvs	2.70	2.699	c_0	$= 5.288$ Å
102	vs	2.015	2.022	Z	$= 2$
110	s	1.806	1.812	V	$= 60.14$ Å³
103	ms	1.535	1.537	$D_{calc.}$	$= 7.06$ g/cm³
112	ms	1.50	1.495		
202	m	1.348	1.350		
004	w	1.32	1.322		
203	mw	1.172	1.173		
211	m	1.155	1.158		
212	m	1.082	1.082		
114	m	1.067	1.068		

Table 2. X-ray powder data and lattice dimensions for monoclinic Ni_3Se_4 mineral from Kuusamo, NE-Finland. Camera diametre 114.59 mm, Cu/Ni radiation.

hkl	int.	$d_{obs.}$	$d_{calc.}$		
002	m	5.25	5.26	a_0	$= 6.22$ Å
011	w	3.42	3.422	b_0	$= 3.63$ Å
$\overline{1}03$	w	3.06	3.078	c_0	$= 10.52$ Å
$\overline{1}12$	vsI	2.70	2.700	β	$= 90.53°$
$\overline{2}02$			2.700	Z	$= 2$
112	m	2.66	2.677	V	$= 237.5$ Å³
013	w	2.52	2.518	$D_{calc.}$	$= 6.96$ g/cm³
211	vw	2.29	2.295		
$\overline{1}14$	vsII	2.02	2.024		
$\overline{2}04$			2.025		
114	s	2.00	2.004		
020	s	1.815	1.815		
310	vsIII	1.800	1.799		
$\overline{1}16$	ms	1.532	1.535		
222	ms	1.497	1.495		
$\overline{4}04$	m	1.343	1.348		
008	w	1.31	1.315		
$\overline{2}26$	wB	1.170	1.172		
$\overline{4}06$			1.173		
$\overline{1}32$	wB	1.158	1.156		
132			1.154		
406			1.154		
512	wB	1.147	1.144		
$\overline{1}34$	wB	1.081	1.081		
$\overline{3}18$	wB	1.066	1.069		
028			1.064		
600	vwB	1.037	1.037		

Table 3. X-ray powder data and lattice dimensions for ortho-rhombic $NiSe_2$ mineral and ferroselite from Kuusamo, NE-Finland. Camera diametre 114.59 mm, Cu/Ni radiation.

Ferroselite $FeSe_2$				Ortho-rhombic $NiSe_2$ mineral				
hkl	I	d		hkl	I	$d_{obs.}$	$d_{calc.}$	
110	vw	3.69	$a_0 = 4.79$ Å	110	f	3.79	3.799	$a_0 = 4.89$ Å
				011	w	3.12	3.125	
101, 020	s	2.86	$b_0 = 5.72$ Å	020	w	2.98	2.980	$b_0 = 5.96$ Å
				101	s	2.935	2.937	
111	vs	2.565	$c_0 = 3.58$ Å	111	vs	2.64	2.634	$c_0 = 3.67$ Å
120	vs	2.47		120	vs	2.545	2.546	
200	w	2.395	Z = 2	200	w	2.44	2.449	Z = 2
210	vw	2.21		210	w	2.26	2.265	
121	w	2.02	V = 98.2 Å³	121	mw	2.095	2.092	V = 107.0 Å³
211	vs	1.88		211	s	1.925	1.928	
130	s	1.79	$D_{calc.} =$ 7.22 g/cm³	130	s	1.84	1.841	$D_{calc.} =$ 6.72 g/cm³
				002			1.835	
031	ms	1.69		031	w	1.75	1.747	
221	w	1.63		221	mw	1.685	1.682	
112	w	1.595		112	m	1.648	1.651	
				131			1.646	
310, 022	w	1.54		310, 022	wB	1.57	1.575	
				320	w	1.435	1.434	
240	w	1.238		240	w	1.275	1.273	
312	w	1.162		312	w	1.195	1.195	

sample are: $a_0 = 6.22$ Å, $b_0 = 3.63$ Å, $c_0 = 10.52$ Å and $\beta = 90.53°$. These values are again in good accordance with the values given by Grønvold and Jacobsen.

As pointed out by Hiller and Wegener (1960) the β-NiSe and monoclinic Ni_3Se_4 phases form a continuous solid solution series with variable concentration of the empty Ni-spaces. These empty spaces are statistically distributed in the hexagonal solid solution range, for there are no reflections in the powder pattern indicating a change of the lattice symmetry. With the increasing concentration of the empty spaces the hexagonal β-NiSe phase changes into the monoclinic Ni_3Se_4 phase, in which the defiency of nickel obviously reaches its maximum. The densities for the β-NiSe and monoclinic Ni_3Se_4 phases have been calculated under the assumption that the changes in composition are caused by subtraction of nickel atoms from the β-NiSe structure. The validity of this assumption has been verified e.g. by Grønvold and Jacobsen (1956) and Hiller and Wegener (1960). Due to the increase of the empty Ni-spaces in the β-NiSe — monoclinic Ni_3Se_4 solid solution the density tends to decrease from β-NiSe towards Ni_3Se_4.

The indexing of the ortho-rhombic $NiSe_2$ has been based on the structure of marcasite. The powder data for the mineral is given in Table 3 together with those for ferroselite. The mineral is ortho-rhombic with $a_0 = 4.89$ Å,

Table 4. X-ray powder data and lattice dimensions for γ-NiSe mineral from Kuusamo, NE-Finland compared with those for millerite. Camera diametre 114.59 mm, Cu/Ni radiation.

Millerite NiS
ASTM 12—41 γ-NiSe mineral

hkl	I	$d_{calc.}$		hkl	I	$d_{obs.}$	$d_{calc.}$	
110	60	4.81	$a_0 = 9.620$ Å	110	m	4.99	5.00	$a_0 = 10.01$ Å
101	40	2.946		101	vw	3.07	3.070	
300	100	2.777	$c_0 = 3.149$ Å	300	vs	2.88	2.890	$c_0 = 3.28$ Å
021	65	2.513		021	vs	2.63	2.617	
220	12	2.406		220	vw	2.49	2.502	Z $= 9$
211	55	2.228		211	vs	2.325	2.319	
131	95	1.8631		131	vs	1.95	1.940	V $= 284.6$ Å
410	45	1.8178		410	w	1.892	1.892	
401	40	1.7372		401	mw	1.81	1.809	$D_{calc.} = 7.22$ g/cm³
321	18	1.6340		321	mw	1.71	1.701	
330	35	1.6037		330	mw	1.665	1.669	
				002	mw	1.64	1.642	
012	25	1.5470		012			1.612	
				331	vw	1.48	1.487	
600	8	1.3884		600	vw	1.445	1.445	
520	4	1.3343		520			1.388	
312	10	1.3008		312			1.355	
042	8	1.2560		042			1.308	
440	6	1.2023		440			1.251	
161	4	1.1783		161			1.226	
502	6	1.1447		502			1.191	
422	16	1.1133		422			1.159	
701				701			1.158	
710	8	1.1033		710			1.148	
152	8	1.0846		152			1.129	
621				621			1.129	
342	12	1.0333		342			1.076	
541	6	1.0104		541			1.051	
612	6	0.9888		612	mw	1.035	1.030	

$b_0 = 5.96$ Å and $c_0 = 3.67$ Å. The space group is probably Pnnm. The X-ray powder pattern of ortho-rhombic $NiSe_2$ has great similarity with that of ferroselite (Kullerud and Donnay, 1958) and marcasite, even though the unit cell parametres for the former are somewhat bigger. The density of the ortho-rhombic $NiSe_2$ has been calculated based on the assumption that its structure is similar to that of ferroselite.

The unit cell dimensions for γ-NiSe have been reported by Levi and Baroni (1935) and Hiller and Wegener (1960). According to the latter $a_0 = 10.007$ Å and $c_0 = 3.333$ Å for the compound. The values obtained from the γ-NiSe mineral are: $a_0 = 10.01$ Å and $c_0 = 3.28$ Å which agree well with the values of Hiller and Wegener (1960). The powder pattern for γ-NiSe is given in Table 4 together with that for millerite. The mineral is trigonal and its powder pattern very similar to that of millerite except that the d-values for

Table 5. X-ray powder data for Ni_3Se_4 and $Ni_3(Se,S)_4$ from Kuusamo, NE-Finland compared with those for polydymite. Camera diametre 114.59 mm, Cu/Ni radiation.

	Polydymite ASTM 8—106			Ni$_3$ (Se, S)$_4$ Kuusamo			Ni$_3$Se$_4$ Kuusamo		
hkl	I	d		I	d		I	d	
111	20	5.50		mw	5.60		mw	5.75	
220	40	3.34	$a_0 =$ 9.48 Å	mw	3.40	$a_0 =$ 9.65 Å	mw	3.52	$a_0 = 9.94$ Å
311	90	2.85		vs	2.90		ms	3.00	
222	—	—		w	2.79		ms	2.87	Z = 8
400	90	2.36		vs	2.41		vs	2.48	
422	30	1.941		v	2.00		—	—	V = 982.1 Å³
511, 333	90	1.820		s	1.86		m	1.905	
440	100	1.674		vs	1.706		vs	1.755	$D_{calc.} =$
531	10	1.600		—	—		—	—	6.62 g/cm³
026	10	1.499		—	—		—	—	
533	50	1.444		—	—		—	—	
540	—	—		vw	1.50		—	—	
622	—	—		—	—		w	1.498	
444	60	1.369		vw	1.395		w	1.434	
711, 551	20	1.330		vw	1.355		—	—	
642	30	1.269		f	1.29		—	—	
731, 553	80	1.232		vw	1.255		vw	1.293	
800	70	1.185		vw	1.21		—	—	
660, 822	10	1.117		—	—		—	—	
751, 555	70	1.095		—	—		—	—	
662	—	—		—	—		w	1.149	
840	60	1.055		vw	1.078		w	1.11	
842	—	—		f	1.055		—	—	
911, 753	5	1.041		—	—		—	—	
664	5	1.010		—	—		—	—	
931	50	0.994		—	—		—	—	

γ-NiSe are invariably somewhat bigger. The powder pattern shows the mineral to be isotype with millerite which has a space group R3m.

The powder data for cubic Ni_3Se_4 resemble those for tyrrelite and also for polydymite very closely. For the sake of comparison the d-values and intensities of polydymite, of a $Ni_3(Se,S)_4$ variant with about 63 mole per-cent of polydymite component and of Ni_3Se_4 are given in Table 5. The Table shows that the length of the a-axis increases from polydymite towards Ni_3Se_4 with increasing Se-content reaching a = 9.94 Å at Ni_3Se_4.

The space group for the cubic Ni_3Se_4 is obviously the same as that for tyrrelite, i.e. Fd3m. The mineral can be considered as the nickelian analogue of bornhardite (Ramdor, 1955) which has only a slightly longer a-axis than Ni_3Se_4.

The density of the cubic Ni_3Se_4 i.e. 6.62 g/cm³ has been obtained by calculation based on the assumption that it is structurally similar to tyrrelite. The density for tyrrelite is 6.6 g/cm³, as reported by Robinson and Brooker (1952).

NOMENCLATURE

The facts presented above suggest the existence of five new nickel selenide minerals. The β-NiSe mineral is named in honour of the late Dr. J. J. Sederholm, the former Director of the Geological Survey of Finland, in recognition of his unique and fundamental contribution to Pre-Cambrian geology. The name sederholmite should be applied to hexagonal β-NiSe phase from the stoichiometric NiSe composition to the point at which β-NiSe changes into monoclinic Ni_3Se_4 phase.

The monoclinic Ni_3Se_4 mineral is named after the late Dr. W. W. Wilkman as an appreciation of his great contribution to geological knowledge about Finland, and the name wilkmanite is proposed to be used for a mineral the composition of which falls within the range of $Ni_{0.82}Se — Ni_{0.7}Se$.

For the ortho-rhombic $NiSe_2$ mineral the name kullerudite is suggested in honour of Dr. Gunnar Kullerud, Carnegie Institution of Washington, Geophysical Laboratory, in recognition of Dr. Kullerud's valuable contributions to mineralogy.

The γ-NiSe mineral is named in honour of the late Dr. Eero Mäkinen, the former President of the Outokumpu Co. as an acknowledgement of his great merit in geology and mineralogy, as well as of his achivements in the Finnish mining industry.

The name trüstedtite is proposed for the spinel type Ni_3Se_4 mineral in honour of the late Dr. O. Trüstedt in recognition of his pioneering work in the development of prospecting methods which in 1910 led to the discovery of the Outokumpu deposit.

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REFERENCES

DERRIKS, J. J. & VAES, J. F. (1955) The uranium deposit of Shinkolobwe. Publ. A., U. Nat., P/1105, (Conf. 8), pp. 94—128.

GORDON, S. G. (1925) Proc. Acad. Nat. Sci. Phila. 77 p. 317.

GRØNVOLD, R. & JACOBSEN, E. (1956) X-ray and magnetic study of nickel selenides in the range NiSe to $NiSe_2$. — Acta chem. Scand. 10, p. 1440.

HERZENBERG, R and AHLFELT, F. (1935) Zentr. Mineral. Geol. p. 277.

HILLER, JOH. -E. und WEGENER, W. (1960) Untersuchungen im System Nickel-Selen. N. Jb. Miner., Abh, 94 Festband Ramdohr. pp. 1147—1159.

JONG, W. F. de and WILLEMS, H. W. V. (1928) Die Verbindungen $FeSe_2$, $CoSe_2$ und $NiSe_2$. Z. anorg. allg. Chem., 170, p. 241.

KLEMM, DIETRICH D. (1962) Die Synthesen der Mischkristallreichen NiS_2 — $NiSe_2$ und CoS_2 — $CoSe_2$ und ihre Beziehung zum natürlichen Auftreten der Mineralien Vaesit — Blockit und Catterit — Trogtalit. N. Jb. Miner., Mh. 2, pp. 32—44.

KULLERUD, G. and DONNAY, G. (1958) Natural and synthetic ferroselite. A roentgenographic mimesis of rammelsbergite. Geochim. et Cosmochim. Acta. Vol. 15, pp. 73—79.

LEVI, G. R. ed BARONI, A. (1935) Strutture ed alterazioni di struttura di NiS e di NiSe. A. Z. Krist. Vol. 92, pp. 210—215.

MACHATSCHKI, F. and STRADNER, E. (1952) Ein Selenid-Mineral vom Spinelltyp. Anzeiger, 89, p. 211.

RAMDOR, P. (1955) Vier neue natürliche Kobaltselenide vom Steinbruch Trogtal bei Lautenthal, Harz. Monatsh. Mineral. pp. 133—142.

ROBINSON, S. G. and BROOKER, E. J. (1952) A cobalt-nickel-copper selenide from the Goldfields District, Saskatchewan, Am. Mineral. Vol. 37, pp. 542—544.