New data of eskolaite, Zn-bearing chromite, willyamite and ullmannite from the Outokumpu mine, eastern Finland



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Abstract

Two massive sulphide ore samples from the Outokumpu mine, eastern Finland, were studied by ore microscopy and electron microprobe analysis. The main minerals are pyrrhotite, pentlandite, chalcopyrite, and sphalerite with accessory galena and molybdenite. The matrix contains euhedral crystals of homogeneous or zoned eskolaite with variation of Cr and Al. Zn–bearing-chromite, occuring in sulphide or silicate matrix, is mainly zoned with a clear variation between Fe and Mg+Zn and between Cr and Al. Very rare are willyamite and ullmannite as inclusions in sulphides. Previously unpublished electron microprobe analyses are presented of eskolaite, Zn-chromite, willyamite and ullmannite. The crystallisation equilibrium temperatures for eskolaite are estimated for the dark zones as ca. 600°C and for the light zones ca. 400°C. The chromite grains are zoned with high Zn contents derived from the Zn-bearing sulphide ore during cooling of the sulphides and metamorphism. The occurrence of willyamite and ullmannite suggests their crystallization below 550°C.

Key words: massive sulfide deposits, ore minerals, eskolaite, chromite, uraninite, willyamite, ullmannite, chemical composition, electron probe data, Proterozoic, Outokumpu, Finland

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I. Introduction

Eskolaite is a rare mineral. It was first observed in 1949 from Outokumpu mine, eastern Finland (60°44′ N latitude and 29°00′ longitude) and later characterized as a new mineral by Kouvo & Vuorelainen (1958). In the meantime it is described from five other localities worldwide. Milton & Chao (1958) and Milton & Narain (1969) found eskolaite as a major constituent in merumite, a complex mixture of several chromium minerals, in gravels of the Merume River, Guyana. The eskolaite from County Wicklow, Ireland is submicroscopic. It occurs around quartz grains and in the matrix of greywacke and could be only identified by XRD (Oppenheim et al., 1977). Forster (1960) described eskolaite in association with chromite from gold occurrences in the Lowveld, northeast Transvaal, South Africa. Cassedanne & Cassedanne (1980) found eskolaite as a rare component from the alluvium of the Chapada Diamantina in Bahia, Brazil. Karpenko & Tištšenko (1992) described the mineral from concentrates of core samples from the Belomor-Kuloiian plateau, Arkhangelsk region, Russia. Eskolaite was first analysed using wet chemical methods by Kouvo & Vuorelainen (1958). First electron microprobe analyses were published by von Knorring et al. (1986) and recently by Peltonen et al. (1996), all from the Outokumpu mine. The aim of this paper is mainly to study the chemical composition of eskolaite and its variation.

We will also present new analytical data of Zn-bearing chromite and previously unreported willyamite, ullmannite and uraninite from the Outokumpu ore. Zn-bearing chromite was first described by Thayer et al. (1964) from chromite dykes cutting diopside skarns (Vähätalo, 1953) from the Outokumpu mine. Later, Zn-bearing chromite was also found inside the sulphide ore body (Weiser, 1966, 1967).

In 1997, the senior author received two massive ore samples from Outokumpu mine of the Natural history museum of the University of Helsinki (B 6384 and B 6379) labelled as eskolaite, and eskolaite and cobalt pentlandite, respectively. The samples were studied by ore microscopy and electron microprobe (EMP) at the Federal Institute for Geosciences and Natural Resources, Hannover, Germany.

2. Analytical methods

Two polished sections of each sample were studied with a polarizing microscope Leica DMRB in reflected light in air and oil immersion (Standard Immersion Oil, n=1.5) and photographed with Kodak Professional film 5018 EPY.

The minerals were analyzed with a Camebax Microbeam EMP with 20 kV accelerating voltage, and 30 nA specimen current. The standards and X-ray lines for eskolaite and chromite were: Cr K α (eskolaite and chromite), Fe K α , Al K α , Mg K α (chromite), Zn K α (gahnite), Ni K α (bunsenite), Mn K α and Ti K α (pyrophanite), V K α (metal and vanadinite). The measuring times were in eskolaite 10 s for Cr and 20 s for other elements, in chromite 10 s for Cr, Al, Fe, Mg, and 20 s for other elements. The following X-ray lines and standards were used for sulphides and sulphosalts: Fe K α and S K α (synthetic pyrrhotite), Zn K α (sphalerite), Cu K α (chalcopyrite), Ni K α , Co K α , Cd L α , Se L α , Te L α (metal), Sb

L α (stibnite), As L α (synthetic galliumarsenide). The measuring time were for the main elements 10 s, for Sb, As, Se and Te 20 s, and for Cd in sphalerite 30 s. Raw data were corrected using the PAP program supplied by CAMECA. Detection limits of the analyzed elements were 0.05 wt.%. In total, 104 EMP analyses were carried out on the various types of ore minerals in sample B 6384 and sample B 6379.

3. Results

3.1. Description of the samples

Specimen B 6384 is a massive sulphide ore sample from the Outokumpu mine, Outokumpu. The main ore minerals are mainly coarse-grained intergrown pyrrhotite and chalcopyrite. All other observed ore minerals occur as inclusions in pyrrhotite and/or chalcopyrite. Conspicuous is the frequent occurrence of eskolaite. The grains are mainly euhedral single crystals up to several 100 µm across. Eskolaite is grey with a bluish tinge, especially in oil. The reflection pleochroism in air is weak, more noticeable in oil. The anisotropy is weak, but clearly recognizable, with blue colour in air and more brownish in oil. Internal reflections could not be observed. The majority of the crystals show, especially under oil immersion, a clear zoning with light bluish and darker brownish-grey colours (Fig. 1a-f). This zoning is also clearly seen in back-scattered electron images (Fig. 2a-f). Inclusions in eskolaite are small droplets of pyrrhotite and galena and needle-like grains of chalcopyrite. A droplet of ullmannite, intergrown with chalcopyrite, could be observed in one eskolaite grain. Cracks and cavities can be filled with fine-grained graphite. Some eskolaite grains show a marginal alteration, which can also start from cracks and catch inner parts of the crystals. Microprobe analyses of this material showed same elements as in eskolaite, but low totals. Presumably it is hydrous chromium oxide. In contrast to eskolaite only one chromite grain could be found in sample B 6384. It is a euhedral homogeneous single crystal 150 µm across without any inclusions and surrounded by silicate (Fig. 3a, 3b). Pentlandite is very common in the polished sections of sample B 6384 and occurs as two types. The first type consists of irregularly distributed subidiomorphic grains up to some hundred microns. The second type are flame-like exsolution lamellae on grain boundaries of pyrrhotite. Sphalerite is also very common as rounded xenomorphic grains up to 200 µm in size. Under the ore microscope sphalerite shows in oil immersion reddish internal reflections. The droplike grain of ullmannite, intergrown with chalcopyrite, occurs as inclusion in eskolaite. It is of white colour and shows very high reflectivity and weak anisotropy. Galena could also be detected as inclusions in eskolaite, chalcopyrite or silicate. Fine-grained lamellar graphite is very common occurring as aggregates in silicate, randomly on eskolaite and filling of the cracks in it. Very rare metamictic idiomorphic uraninite grains up to 50 µm across are surrounded by thucholite halo in the silicate matrix (Fig. 4). Uraninite has a low reflectivity and is in oil immersion of grey colour with a distinct brownish tinge.

The specimen B 6379 is a massive sulphide ore sample from the stope V22, Outokumpu mine. Coarse-grained pyrrhotite is the main ore mineral that includes all other ore minerals. Pentlandite is very common in the polished sections and occurs, similar to sample B 6384, as two types: as irregularly distributed anhedral grains up to some hundred microns and as typical flame-like exsolution lamellae on grain boundaries of pyrrhotite. Sphalerite is also very common. The xenomorphic grains up to 300 µm across occur as inclusions in pyrrhotite or on the boundary between pyrrhotite and silicate. Chalcopyrite occurs as lobate inclusions up to 150 µm in pyrrhotite or silicate. Galena occurs as up to 20 µm small single grains irregularly distributed in silicate. Very rare are drop-like grains of ullmannite up to 40 µm long as isolated inclusions in pyrrhotite (Fig. 5). Ullmannite is of white colour with a bluish tinge, showing high reflectivity and weak anisotropism. Similar to the optical properties of ullmannite are some up to 60 µm long needles in pyrrhotite or on the grain boundary between pyrrhotite and silicate (Fig. 6). The exact identification of these phases is only possible by microprobe analyses (Dobbe, 1991). The analyses (see below) showed that these grains are the cobalt analogue of ullmannite called willyamite, first described from Broken Hill, Australia (Pittman, 1893). According to our knowledge, this is the first description of willvamite from Outokumpu. Irregular graphite is commonly distributed as grains up to 50 µm across. Graphite sometimes contains small laths of molybdenite. Only one euhedral crystal of chromite, 200 µm across, could be observed as inclusion in pyrrhotite (Fig. 3c, 3d). The chromite grain is zoned and the inner part of the broken crystal is replaced by silicate. The chromite shows a bluish grey colour, low reflectivity, with light and dark strips and patches. The dark strips show a brownish tinge under oil immersion. They form on two sides of the broken crystal the outer zones whereas the two other sides are light strips and patches. Eskolaite could not be observed in sample B 6379. In the silicate matrix there are a few rounded metamictic grains of uraninite with a thucholite rich halo similar to sample B 6384.

3.2. Chemical composition of the ore minerals 3.2.1 Eskolaite

Sixteen grains of eskolaite of sample B 6384 were analyzed by microprobe. Six grains are homogeneous whereas the other ten are zoned. The homogeneous grains are very similar in their composition with a mean of 64.92 wt.% Cr, 3.14 wt.% V, and 0.28 wt.% Fe (Table 1). This corresponds to the general formula of $(Cr_{1.90}V_{0.09}Fe_{0.01})_2O_3$. Only two grains contain small amounts of Al (0.40 wt.%). Mg, Mn, Ni, Zn, and Ti could not be detected. This is in good agreement with the results of the wet chemical analysis by Kouvo and Vuorelainen (1958) who found 64.4 wt.% Cr, 3.11 wt.% V, and 0.38 wt.% Fe, corresponding exactly to the formula of the microprobe analyses. Most of the eskolaite grains show a clear zoning with variable light and dark parallel laths, stripes, or plates in idiomorphic orientation in the microphotographs (Figs. 1a-f), as well as in the BSE images (Fig. 2a-f). Figures 1a and 2a show a grain with a dark centre surrounded by darker zones and a broad light rim, whereas Figures 1b and 2b show a crystal with a dark centre



Fig. 1. Optical photographs of eskolaite sample B 6384 (plan polarized reflected light, oil immersion). a) Euhedral zoned eskolaite with inclusions of chalcopyrite (yellow) in chalcopyrite (yellow) – pyrrhotite (brownish pink) -matrix (see Fig. 2a). b) Eskolaite with internal euhedral zoning, surrounded by silicate. Small irregular grains of chalcopyrite (yellow) in silicate-filled cracks. On the lower edge of the eskolaite grain a micro-inclusion of galena (white) (see Fig. 2b). c) Partly zoned euhedral eskolaite with inclusions of pyrrhotite (brownhisch pink) and a small rim of silicate – graphite -mixture in pyrrhotite (brownish pink) – pentlandite -matrix (see Fig. 2c). d) Lobate grain of eskolaite with a euhedral zoned core in silicate matrix (see Fig. 2d). e) Euhedral zoned eskolaite in chalcopyrite (yellow) (see Fig. 2e). f) Euhedral homogeneous eskolaite with inclusions of pyrrhotite (brownish pink) intergrown with an anhedral zoned eskolaite in chalcopyrite matrix (yellow) (see Fig. 2f).



Fig. 2. Back-scattered electron images of eskolaite (sample B 6384). Grain numbers refer to analytical results listed in Table I. a) Euhedaral zoned eskolaite with inclusions of chalcopyrite (cpy) surrounded by pyrrhotite (po) and chalcopyrite (cpy) (grain 1). b) Zoned eskolaite with inclusions of chalcopyrite (cpy) and galena (gal) surrounded by silicate (black) (grain 2). c) Partly zoned euhedral eskolaite with inclusions of pyrrhotite (po), surrounded by a small rim of a mixture of silicate and graphite, in pyrrhotite (po) and pentlandite (pn). d) Lobate grain of eskolaite with a zoned core in silicate matrix (black). e) Euhedral zoned eskolaite in chalcopyrite (cpy). f) Euhedral homogeneous eskolaite with inclusion of pyrrhotite (po), intergrown with an anhedral zoned eskolaite in chalcopyrite (cpy) (grain 3).



Fig. 3. Zn-bearing chromite grains in Outokumpu ore. a + b) Homogeneous euhedral chromite in silicate gangue between pyrrhotite (brownish pink) and chalcopyrite (yellow). Sample B 6384 (Table 2, no. 1). a) oil immersion, b) backscattered electron image. c + d) Fractured euhedral zoned chromite in pyrrhotite (brownish pink). The inner part is replaced by pyrrhotite (brownish pink) and a mixture of silicate (black) and molybdenite (brown). Sample B 6379 (Table 2, no. 2, 3). c) oil immersion, d) backscattered electron image.

surrounded by several zones with variable brightness and a dark oscillatory rim. Some grains show a zoning only in parts of the crystal (Figures 1c + 2c, 1d + 2d). The light zones of the eskolaite consist only of Cr, V, and Fe similar to the homogeneous eskolaite. The darker zones are always characterized by noticeable amounts of Al (3.45 wt.%). In some analyses of the darker zones up to 0.77 wt.% Ti could be detected, Mg, Mn, Ni, and Zn could not be detected in the light or in the dark zones. In general, the following compositional ranges could be obtained: 58.90 – 66.29 wt.% for Cr, 1.94 – 7.01 wt.% for V, 0.18 – 1.30 wt.% for Fe, and 0 – 3.45 wt.% for Al. The core of the zoned crystal of Fig. 1f/2f has a composition of 65.67 wt.% Cr, 3.19 wt.% V, and 0.19 wt.% Fe, corresponding to the formula $(Cr_{1.90}V_{0.09}Fe_{0.01})_2O_3$. This is exactly the same composition as the measured homogeneous eskolaite of this sample. However, the rim of this zoned eskolaite contains only 60.64 wt.% Cr, 3.67 wt.% V, 0.29 wt.% Fe, but 2.96 wt.%



Fig. 4. Uraninite rimmed by a carbon rich halo beside chalcopyrite in silicate matrix (sample B 6384). a) oil immersion, b) back-scattered electron image in polished section.



Fig. 5. Ullmannite in pyrrhotite (sample B 6379, oil immersion).



Fig. 6. Willyamite (white) between pyrrhotite (brownish), sphalerite (grey) and silicate (black) (sample B 6379, oil immersion).

Al with the formula $(Cr_{1.72}Al_{0.16}V_{0.11}Fe_{0.01})_2O_3$. The composition of the core of the eskolaite grain of Fig. 1f/2f is similar to the homogeneous outer parts of the grains in Fig. 1c/2c and Fig. 1d/2d. The crystal of Fig. 1a/2a (Table 1, Anal. No. 1-5) shows several light and dark zones which correspond to a variation mainly of Cr and Al, whereas the concentration of V and Fe only in the core is lightly increased. The lowest value of Cr (58.90 wt.%), the highest of Al (3.45 wt.%) and a high value of V (4.43 wt.%) could be measured in the dark part of the zoned region of

the grain of Fig. 1c/2c. The formula corresponds to $(Cr_{1.67}Al_{0.19}V_{0.13}Fe_{0.01})_2O_3$. An unusually high content of V (7.01 wt.%) together with a high amount of Fe (0.94 wt.%) and 0.77 wt.% Al could be detected in the lightest part of the zoned region in Fig. 1d/2d suggesting that V and Fe can also substitute Cr. The zoning of the eskolaite is characterised by the co-variation of Cr and Al (e.g. Fig. 1a/2a, Anal. no. 1-5; Fig. 1b/2b, Anal no. 6-13). However, there is no consistent trend in the compositional changes from core to rim (e.g. Fig. 1a/2a, Fig. 1f/2f).

Table I	. Selected e	lectron mi	icroprobe a	nalyses of e	eskolaite.									
Anal.no.		2	3	4	5	9	7	8	6	10	11	12	13	14
						W	eight per cent	t						
$Cr_{2}O_{3}$	86.69	89.97	89.76	94.86	92.12	90.98	89.04	96.89	91.37	94.11	92.47	95.94	92.55	94.17
, M_O,	2.35	4.73	3.29	n.d.	1.32	2.30	5.90	n.d.	4.17	2.17	3.23	n.d.	3.64	n.d.
ر م آ	8.56	5.16	5.04	5.55	5.89	5.47	5.03	2.89	4.37	3.23	4.04	4.06	4.30	5.40
Fe,O	1.39	0.70	0.79	0.53	0.97	0.59	0.40	0.20	0.34	0.30	0.33	0.28	0.31	0.43
TiŌ	0.70	n.d.	1.28	n.d.	n.d.	0.73	n.d.	n.d.	n.d.	0.25	0.25	n.d.	n.d.	n.d.
Totaľ	99.66	100.56	100.16	100.94	100.30	100.07	100.37	99.98	100.25	100.06	100.32	100.28	100.80	100.00
						ator	nic proportio	SUC						
ŗ.	1.719	1.751	1.767	1.881	1.828	1.798	1.724	1.938	1.785	1.861	1.815	1.912	1.803	1.882
AI	0.069	0.137	0.096		0.039	0.068	0.170		0.122	0.064	0.094		0.106	
$^{\wedge}$	0.172	0.102	0.101	0.112	0.118	0.110	0.099	0.058	0.086	0.065	0.080	0.082	0.085	0.100
Fe	0.026	0.010	0.012	0.008	0.014	0.011	0.007	0.004	0.007	0.006	0.006	0.006	0.006	0.008
Τï	0.013		0.024			0.014				0.005	0.005			
n.d.: not (letected													
no. 1-5: g	rain 1 (sampl	e B 6384, Fi	ig. 2a), 1 cent	er, 5 outer ri.	В									

3.2.2. Chromite

The chromite of sample B 6384 contains 35.76 wt.% Cr. 19.92 wt.% Fe, 10.15 wt.% V. 4.51 wt.% Zn, and 2.00 wt.% Mn, but no Al, Mg, Ni, or Ti. This corresponds to the calculated formula $(Fe_{0.77}Zn_{0.15}Mn_{0.08})_{1.00}$ $(Cr_{1.53}V_{0.44}Fe_{0.03})_{2.00}O_4$ (Table 2). The content of Cr and Zn is lower and Fe and Mn higher than in the zoned chromite of sample B 6379. More conspicuous are the very high content of V and lack of Al and Mg. A similar composition with a little lower amount of V was described by Weiser (1966) from chromite dikes from Outokumpu (see Vähätalo, 1953, page 39).

The chromite crystal in sample B 6379 (Fig. 4c, 4d) shows light and dark areas with sharp boundaries as al-

 Table 2. Electron microprobe analyses of chromite.

Analysis no.	1	2	3
	weight p	oer cent	
Cr ₂ O ₃	52.27	68.74	54.63
Al_2O_3	n.d.	n.d	13.59
V ₂ O ₃	14.93	0.37	0.37
Fe ₂ O ₃	1.00	0.80	0.11
FeO	24.73	16.43	12.92
MgO	n.d.	5.14	7.96
MnO	2.57	1.26	0.83
ZnO	5.62	6.97	8.72
Total	101.12	99.71	99.13
	atomic pro	oportions	
Cr	1.529	1.967	1.450
Al			0.537
V	0.443	0.011	0.010
Fe ³⁺	0.028	0.028	0.003
Fe ²⁺	0.766	0.498	0.362
Mg		0.277	0.398
Mn	0.081	0.039	0.024
Zn	0.153	0.186	0.216

n.d.: not detected

no. 6-13: grain 2 (sample B 6384, Fig. 2b), 6 center, 13 outer rim 14: grain 3 (sample B 6384, Fig. 2f), homogeneous eskolaite

no.

1: homogeneous chromite (sample B 6384)

2: zoned chromite (light in BSE), (sample B 6397)

3: zoned chromite (dark in BSE), (sample B 6397)

ready seen under the ore microscope. The light zones contain higher Cr (47.03 wt.%) and Fe (13.34 wt.%) contents than the darker zones (38.15 wt.% Cr and 10.12 wt% Fe, respectively). The light zones in BSE images are free from Al whereas the dark zones contain up to 7.19 wt.% Al. The Mg content of the dark areas is with 4.80 wt.% only slightly higher than the content in the light zones (3.10 wt.%). The Zn content of the chromite is 5.60 wt.% in the light and 7.00 wt.% in the dark zones. This is in good agreement with observations by Weiser (1966, 1967; Table 3) on chromite grains from the so-called parallel ore body (Vähätalo, 1953). The chromite also contains small amounts of Mn, which is with 0.98 wt.% slightly higher in the light zones than in the dark ones (0.64 wt.%). Both types of zones have only small amounts of V (0.25 wt.%). The calculated structural formula for the light zones is $(Fe_{0.50}Mg_{0.28}Zn_{0.18}Mn_{0.04})_{1.00}$ $(Cr_{1.97}Fe_{0.02}V_{0.01})_{2.00}O_4$ and for the dark areas $(Mg_{0.40}Fe_{0.36}Zn_{0.22}Mn_{0.02})_{1.00}(Cr_{1.45}Al_{0.54}V_{0.01})_{2.00}O_4.$

3.2.3. Uraninite

Euhedral chromite grains surrounded by a thucholite halo discovered in the specimen B 6384 are similar to those described by Wetherill et. al (1962) as uraninite inside thucholite balls. Uraninite has in average (9 analyses) 63.77 wt.% U, 20.81 wt.% Pb and 0.08 wt.% Th, 0.34 wt.% Fe, 0.33 wt.% Cu, 0.12 wt.% Bi, and 13.34 wt.% O. The age estimates obtained for the uraninite are U²³⁸/Pb²⁰⁶ 1815 Ma, U²³⁵/Pb²⁰⁷ 1850 Ma, and Pb²⁰⁷/Pb²⁰⁶ 1885 Ma.

3.2.4. Sulphosalts and Sulphides

Willyamite could only be found in sample B 6379. The two grains contain 23.07 respectively 21.47 wt.% Co, 2.63 respectively 2.70 wt.% Ni and 0.84 respectively 4.92 wt.% Fe. One grain also contains 0.59 wt.% Zn. The Sb content of 57.69 resp. 54.19 wt.% is partly substituted by traces of As (0.26 - 0.30 wt.%) and Te (0.15 - 0.25 wt.%). The content of S lies at 15.10 respectively 16.01 wt.%. The formulae of the two grains

are $(Co_{0.83}Ni_{0.10}Fe_{0.03}Zn_{0.02})_{0.98}(Sb_{1.01}As_{0.01})_{1.02}S_{1.00}$ and $(Co_{0.75}Ni_{0.10}Fe_{0.18})_{1.03}(Sb_{0.92}As_{0.01})_{0.93}S_{1.03}$ (Table 4, no. 3, no. 4).

Ullmannite of sample B 6384 contains, apart of the main elements Ni, S, and Sb, small amounts of Co (2.77 wt.%) and traces of Fe (0.40 wt.%) and Cu (0.34 wt.%) substituting Ni and 0.37 wt.% As substituting Sb. The calculated formula is (Ni_{0.86}Co_{0.10} Fe_{0.02}Cu_{0.01})_{0.99}(Sb_{0.99}As_{0.01})S_{1.00} (Table 4, no. 1). Ullmannite of sample B 6379 is characterised by small amounts of Fe (2.07 wt.%) and Co (2.63 wt.%) substituting for Ni and 0.30 wt.% As substituting for Sb. This corresponds to the formula (Ni_{0.87}Co_{0.09}Fe_{0.08})_{1.04} (Sb_{0.98}As_{0.01})_{0.99}S_{0.97} (Table 4, no. 2).

Pyrrhotite of sample B 6384 contains between 0.40 and 0.53 wt.% Ni, but no Co. The Ni content of pyrrhotite with 0.33 - 0.38 wt.% is slightly lower in sample B 6379.

The analysed grains of pentlandite of sample B 6384 have a very homogeneous composition with a mean Co content of 10.25 wt.% (Table 4, no. 5) and the general formula $(Ni_{4.10}Fe_{3.63}Co_{1.35})_{9.08}S_{7.92}$. Pentlandite grains of sample B 6379 have Co contents between 12.40 and 13.64 wt.% which are significantly higher than those in sample B 6384 (see Table 4). The Fe content varies between 24.89 and 25.78 wt.% depending on the content of Co. The Ni content is very constant of around 28.51 wt.%. This leads to the general formula of $(Fe_{3.50}Ni_{3.78}Co_{1.78})_{9.06}S_{7.94}$.

Sphalerite of sample B 6384 contains between 5.63 and 5.94 wt.% Fe, traces of Co (0.32 wt.%) and in some grains traces of Cu (0.25 wt.%), but no Cd. Sphalerite of sample B 6379 contains between 5.92 and 8.14 wt.% Fe and always traces of Co up to 0.35 wt.%, but no other significant elements, especially no cadmium. The average formula is $(Zn_{0.90}Fe_{0.11})_{1.01}S_{0.99}$.

The measured grains of chalcopyrite of sample B 6384, including the inclusions in eskolaite, contain only Cu, Fe and S in stoichiometric composition CuFeS₂. All four measured grains of chalcopyrite of sample B 6379 also have a stoichiometric composition. Only one grain contains 0.23 wt.% Ni.

			-	,				,							
Anal.no.	1	2	3	4	5	9	7	8	9	10	11	12	13	14	15
							weight pe	ar cent							
Cr_2O_3	57.00	53.93	57.15	58.17	45.01	44.28	45.16	44.57	43.26	52.03	59.19	64.01	54.32	57.58	50.57
Al_2O_3	10.75	5.66	11.46	7.70	21.54	19.46	20.02	13.33	23.42	15.24	9.48	4.06	11.97	2.85	7.42
V_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.45	4.58
$\mathrm{Fe_2O_3}$	0.74	14.23	0.11	4.45	0.17	5.35	2.89	15.53	0.46	n.d.	n.d.	3.09	0.86	4.59	6.76
FeO	22.02	7.58	18.16	13.98	16.26	9.35	12.75	4.26	13.60	17.50	18.14	13.55	15.77	18.15	17.33
MgO	5.00	13.43	5.97	8.00	5.77	10.97	7.85	15.02	7.29	4.89	5.37	8.20	6.45	4.52	5.67
MnO	n.d.	n.d.	n.d.	1.32	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.16	n.d.	2.14	1.93
ZnO	4.41	5.16	7.18	6.04	11.32	9.22	11.32	7.64	11.97	10.34	7.86	5.82	8.83	5.71	5.65
Total	99.92	99.99	100.03	99.66	100.07	98.63	99.99	100.35	100.00	100.00	100.04	99.89	98.20	99.99	99.91
							atomic prof	portions							
Cr	1.546	1.420	1.537	1.574	1.165	1.130	1.161	1.125	1.100	1.392	1.614	1.753	1.497	1.628	1.391
AI	0.435	0.223	0.460	0.311	0.831	0.740	0.768	0.502	0.889	0.608	0.386	0.166	0.481	0.120	0.304
A	ı	١	١	١	ı	١	١	١	ı	ı	ı	١	ı	ı	0.128
Fe^{3+}	0.019	0.357	0.003	0.115	0.004	0.130	0.071	0.373	0.011	ı	ı	0.081	0.022	0.124	0.177
Fe^{2+}	0.632	0.211	0.517	0.400	0.445	0.252	0.347	0.105	0.366	0.495	0.523	0.393	0.450	0.543	0.504
Mg	0.256	0.662	0.303	0.409	0.281	0.528	0.381	0.715	0.350	0.247	0.271	0.424	0.328	0.241	0.294
Mn	ı	ı	ı	0.038	ı	١	١	ı	ı	ı	ı	0.034	ı	0.065	0.057
Zn	0.112	0.127	0.180	0.153	0.274	0.220	0.272	0.180	0.284	0.258	0.201	0.149	0.222	0.151	0.145
n.d.: not de	stected														

Table 3. Selected electron microprobe analyses of zoned Zn-chromite (Weiser, 1966).

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Table 4. Liecti	on microprobe	e analyses of st	upilides.				
Analysis no.	1	2	3	4	5	6	7
			weight per	cent			
Fe	0.40	2.07	0.84	4.92	26.06	25.78	24.99
Со	2.77	2.63	23.07	21.47	10.25	12.40	13.64
Ni	23.60	24.15	2.63	2.70	30.94	28.95	28.44
Cu	0.34	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	n.d.	n.d.	0.59	n.d.	n.d.	n.d.	n.d.
S	15.15	14.71	15.10	16.01	32.50	32.81	32.78
As	0.37	0.30	0.26	0.30	n.d.	n.d.	n.d.
Te	n.d.	n.d.	0.15	0.23	n.d.	n.d.	n.d.
Sb	56.89	56.32	57.69	54.19	n.d.	n.d.	n.d.
Total	99.52	100.18	100.33	99.82	99.75	99.94	99.85
			atomic propo	ortions			
Fe	0.015	0.078	0.032	0.182	3.632	3.586	3.481
Co	0.100	0.094	0.833	0.754	1.354	1.634	1.799
Ni	0.858	0.870	0.095	0.095	4.102	3.832	3.768
Cu	0.011						
Zn			0.019		0.001		
S	1.008	0.970	1.003	1.034	7.912	7.948	7.952
As	0.011	0.008	0.007	0.008			
Te			0.003	0.004			
Sb	0.997	0.978	1.008	0.921			

 Table 4. Electron microprobe analyses of sulphides.

n.d.: not detected

1: ullmannite (sample B 6384); 2: ullmannite (sample B 6379); 3 and 4: willyamite (sample B 6379); 5: pentlandite (sample B 6384)

6: pentlandite, lowest Co content, (sample B 6579); 7: pentlandite, highest Co content, (sample B 6379)

4. Discussion and conclusions

The analyses of eskolaite grains of the present study and from previous studies are plotted in Fig. 7 in a ternary Cr_2O_3 - V_2O_3 -Fe₂O₃ diagram and in the Cr_2O_3 -V2O₃ XY-diagram. The present analysis points overlap the first analysis point of Kouvo and Vuorelainen (1958) and the points of von Knorring et al. (1986), but only partly overlap the analyses of Peltonen et al. (1996), which seem to have higher V_2O_3 contents. All the analyzed grains are from the Outokumpu ore body and its wall rocks, but from different mines. In the studied samples eskolaite occurs within the massive sulphide ore or in the tremolite skarn rocks rich in chromian skarn minerals (von Knorring et al. 1986). The grains analyzed by Peltonen et al. (1996) were taken from two drill core intersections of the Keretti mine, showing most of the eskolaite grains on the borders of the sulphide ore body in quartz rich wall rocks. The eskolaite grains from Keretti mine have exceptionally high V_2O_3 contents suggesting higher vanadium whole rock contents in the wall rocks than inside the massive sulphide ore. The eskolaite grains of this study occur together with silicates as inclusions in massive sulphides. The zoned eskolaite grains have trapped inclusions of chalcopyrite and pyrrhotite and veinlets and inclusions of silicates (Fig. 1a-f, 2a-f). The trapped sulphide inclusions suggest an ear-



Fig. 7. Ternary and XY-diagram of the eskolaite: triangles, this study; dot, Kouvo & Vuorelainen (1958); diamonds, von Knorring et al. (1986); crosses, Peltonen et al. (1996).

ly formation of eskolaite in high temperature. Peltonen et al. (1996) consider, however, eskolaite as a metamorphic mineral that has formed in a pressure of 3-5 kb and temperature of ca. 580 – 640°C.

Eskolaite is isostructural with corundum, hematite and karelianite. The experimental studies of the systems eskolaite-corundum and eskolaite-hematite have shown a complete solid solution at high temperatures (>1100°C). With decreasing temperatures the solid solution field breaks up to form a miscibility gap, and the natural eskolaite and corundum have only small amounts of Al and Cr, respectively (Barks & Roy, 1972; Chatterjee et al., 1982). According to these experimental studies, eskolaite contains about 25 mol.% Al₂O₃ at 580°C, which decreases to a few percent close to 200°C. The pressure dependence of the solvus is very small allowing the use of eskolaite composition as a geological thermometer. The maximum Al₂O₃ content of the analyzed eskolaite grains is 5.9 wt.% (Table 1, anal. no. 7, Fig. 2 b) corresponding approximately to an equilibration temperature of 430°C. However, the same analysis also shows 5.0 wt.% V_2O_3 . If this is added to Al₂O₃, the crystallization temperature is ca. 600°C. The zoned grains of eskolaite reflect changes in the crystallization temperatures. The light zones (Fig. 1a-f, 2a-f) in the rim, showing the lowest Al contents (Table 1, anal. no. 4, 8, 12, 14, Figures 1a/2a, 1b/2b and 1f/2f), correspond to the lowest temperatures of crystallization at around 400°C. Finally, the eskolaite grains have been hydrothermally replaced by silicates. The relationship between hematite and eskolaite is probably similar, because in nature eskolaite has only low contents of Fe₂O₂. In the Outokumpu sulphide ore and skarns, eskolaite is the only existing mineral of this group reflecting the high Cr content. Chromium has distributed in several phases including chromite, eskolaite, uvarovite, chrome-diopside and chromian tremolite (von Knorring et al., 1986). Both the sulphide ore and the skarns have undergone one or several metamorphic-metasomatic events (polymetamorphism). According to Treloar et al. (1981), the garnet-cordierite thermometry in the Outokumpu area gives $600 \pm 50^{\circ}$ C (P=3.5 ± 1 kb). Olivine-spinel thermometry gives a temperature of 630 - 640°C (Peltonen et al., 1996). These temperatures are in the field of the monosulphide solid solution and high enough to enable extensive diffusion and vapour activity between the sulphide, silicate and oxides phases.

Primary magmatic chromian spinel phases have crystallized before the sulphide melt, and they have changed their composition near the cooling sulphides (Fig. 8). This explains the formation of the homogenous Zn rich chromite, in which part of the 2⁺ valence elements have been replaced by Zn originally present in sphalerite of the sulphide ore (Table 2, anal. no. 1, Fig. 4a, 4b). Liipo et al. (1995) also suggest that the large amount of Cu-Co-Zn-Au ore is the source of the Zn in the chromite. The zoned Zn-bearing chromite represents a further metasomatized variation with high Zn in the core and increasing Fe, Al and Mg contents in the rims due to reaction with surrounding silicates (Table 2, anal. no. 2 and 3, Fig. 4c, 4d). Von Knorring et al. (1986) list several types of chromite from diopside-tremolite skarns, chromite dykelets crosscutting the skarns, from a chromite band in uvarovite-tremolite skarn, in dolomite, with uvarovite and enclosed in uvarovite crystals.

Ullmannite and willyamite form a solid solution NiSbS-CoSbS (Dobbe, 1991). In the Hultebo deposit, Tunaberg, Bergslagen, central Sweden, cobaltian willyamite is rimmed by willyamite indicating a later crystallisation of willyamite. Dobbe (1991) suggest that the crystallization of ullmannite is followed by cobaltian ullmannite and willyamite solid solution during cooling of the hydrothermal solution. Bayliss (1969) synthesized solid solutions in the cubic (Ni,Co)SbS series at 550°C, but not the end member willyamite CoSbS. Dobbe (1991) assumes a miscibility gap in ullmannite-willyamite series below 550°C, similar to that of gersdorffite-cobaltite. In the present study, the grains of ullmannite and willyamite in the sulphide ore samples of Outokumpu are not intergrown with each other, and no conclusions of their mutual crystallization sequence can be done.

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Fig. 8. Ternary and XY-diagram of Zn-bearing chromite: triangles, this study; dot, Thayer et al. (1964); diamonds, Weiser (1966, 1967).

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