

## ESKOLAITE, A NEW CHROMIUM MINERAL

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### ABSTRACT

A new mineral was discovered at the Outokumpu mine in Finland. Its formula is  $(Cr_{1.90}, V_{0.09}, Fe_{0.01}) O_3$  from chemical analysis. X-ray studies of single crystals and powders, as well as optical examination in reflected light, show the mineral to be isostructural with  $Cr_2O_3$ , the crystal structure of which, determined by Zachariasen (1928), has type  $D5_1$  and space group  $R\bar{3}c$ . The cell dimensions are not measurably affected by the substitution of  $Fe^{+++}$  and  $V^{+++}$  for  $Cr^{+++}$ . The habit ranges from long prismatic to platy.

The new mineral was found by Yrjö Vuorelainen, and it is named in honor of Professor Pentti Eskola of the University of Helsinki.

### INTRODUCTION

The compounds  $Fe_2O_3$ ,  $Cr_2O_3$  and  $Al_2O_3$  are isostructural, having the hematite structure. The end members of the series have been synthesized in the laboratory, but  $Cr_2O_3$  has not been found in nature.

The oxide of trivalent chromium,  $Cr_2O_3$ , is known by many names because of its color: green oxide of chromium, chrome ocher, ultramarine green, green cinnabar, green rouge etc. The known physical and chemical properties of this chromium compound are summarized by Udy (1957). The data given include the melting point (about  $2435^\circ C.$ ), the boiling point ( $3000^\circ C.$ ), the heat capacity, the magnetic, thermal expansion, and oxygen expansion data, the heat content and the entropy, the thermal conductivity, resistivity and emissivity, the index of refraction (2.5), and the chemical properties. X-ray powder data for pure  $Cr_2O_3$  are given by Jay and Wilde (1947), and by Swanson, Gilfrich, and Ugriinic (1955). The Curie point has been reported to be  $305^\circ K.$  and  $320^\circ K.$  by different investigators. Greenwald and Smart (1950) have found a change in crystal structure at  $318^\circ K.$  which first becomes apparent as a very slight broadening of the 422 reflection. At  $307^\circ K.$  the line is a distinct doublet, and the separation increases rapidly as the temperature is lowered.

A complete series of solid solutions formed between  $Cr_2O_3$  and  $Fe_2O_3$  has been described by Hamelin (1950). In addition, the formation of  $Cr_2O_3$  in chromium spinel in heating experiments has been discussed by Karyakin, Pyatikop and Sukharevskii (1956, 1957). Hamelin (1950) has pointed out that the presence of aluminum favors the formation of spinels.

### OCCURRENCE

The mineral later identified as the natural counterpart of the artificial compound  $Cr_2O_3$  was first observed by Yrjö Vuorelainen in the

summer of 1949 at the Outokumpu mine, Finland. The mineral characteristically occurred in fresh, well developed hexagonal prisms and plates, 1–5 mm. in size (Fig. 1), in chromium-bearing tremolite skarn.

The geology of the Outokumpu mine is described by Veikko O. Vähätalo (1953). Although the Outokumpu ore is a copper ore consisting of about one million tons of metallic copper, there are in the ore field, according to Eskola's estimation (Eskola, 1953), about seven million tons of metallic chromium in the numerous serpentine and skarn rocks. In an earlier work he (Eskola, 1933, p. 43) describes a number of

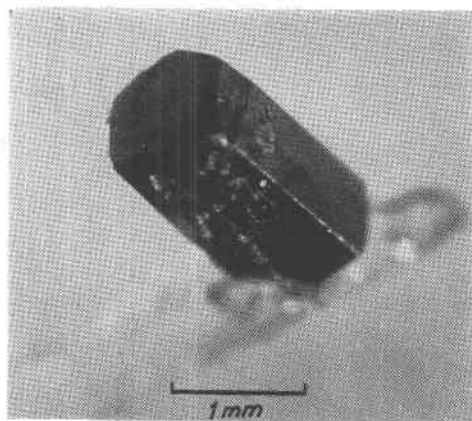


FIG. 1. Crystal of eskolaite from Outokumpu, Finland. Photo: W. S. Starks.

chromium-bearing minerals in different rocks associated with serpentine-rock, which is itself very poor in chromium and only seems to contain chromite in the form of pigment-like secondary products. The other chrome-bearing minerals and rocks are: (1) fuchsite in quartzite, which also contains streaks and patches of chrome-diopside and -tremolite, and uvarovite; (2) the latter three minerals, especially diopside, forming skarn deposits associated with dolomite; (3) chromite in dolomite; (4) picotite, kämmererite, and chromite in anthophyllite-cordierite rock; (5) uvarovite and tawmawite with some chromite in quartzose copper sulfide ore, and finally (6) the most remarkable occurrence of veins composed of uvarovite, tawmawite, chrome-tremolite with sulfides, mostly pyrrhotite, and also containing chrome-diopside and chromite. The chromite, as well as all the other chromium-bearing minerals of this locality, is in all probability of hydrothermal origin. The occurrence of chromium at Outokumpu illustrates the ability of this element to migrate and to take part in metasomatic replacements.

The specimens most abundant in the new chromium mineral were as follows:

1. Chromium-bearing tremolite skarn, rich in calcite, from contact with the ore. Mineral habit: long hexagonal prisms (up to 5 mm.). Associated minerals: pyrrhotite, pentlandite, chalcopyrite, chromium tremolite, uvarovite, tawmawite, calcite, and talc.

2. Quartzite from the foot wall of the ore. The specimen is from a cavity in a vein of milky quartz. Mineral habit: long prismatic (up to 1.5 mm.). Associated minerals: uvarovite, chromium bearing tremolite, calcite, and pyrite (pentagonal dodecahedron).

3. Veins of pyrrhotite. Mineral habit: platy (up to 6-7 mm.). Associated minerals: pyrrhotite, chromium-bearing tremolite, and chromium tourmaline. In some cases the mineral occurs as thin sheets on the surface of quartz.

4. Skarn ore rich in pyrrhotite. Mineral habit: short prismatic. Associated minerals: chromium-bearing tremolite, uvarovite, chromium tourmaline, chromium spinel, pyrrhotite, pyrite (octahedron), and chalcopyrite.

5. Chlorite seams. Mineral habit: thin platy. Associated minerals: chlorite, pyrite, chalcopyrite, pyrrhotite, and chromium spinel.

The mineral has not been found to occur with chromium diopside.

A further sample, weighing about eight kilos, was selected for separation. The concentration of the new mineral from rock samples was done by means of standard techniques. A Denver-Wilfley laboratory concentration table was adapted for treating the crushed sample. The heavy fraction was cleaned with bromoform, and then leached with a large quantity of hot hydrochloric and nitric acid to remove the soluble sulfides. The residue was further divided by centrifuging in Clerici solution. The heavy portion was passed through the Frantz isodynamic separator at the highest magnetic flux available to isolate the new mineral from the other constituents of higher magnetic susceptibility, especially from the abundant chromium spinel. The sample that was analyzed was determined by grain counts to contain less than 1% impurity, principally chromium spinel and tremolite.

Subsequent spectrographic, x-ray, and chemical analyses of the final sample of 1.5 grams established the mineral to be a new anhydrous chromium oxide expressed by the formula  $\text{Cr}_2\text{O}_3$ .

#### PHYSICAL AND OPTICAL PROPERTIES

The new mineral is lustrous black in color in crystals, and light green in finely divided material.

The specific gravity of  $5.18 \text{ gm.cm.}^{-3}$  was obtained by using an ASE Torsion-Type Balance and suspension in toluene and in bromoform. The determinations were made on a number of grains weighing between 6 and 20 mg. The grains were too small to guarantee high accuracy and from the invariable presence of tiny inclusions and cavities it might be inferred that the values would tend to be too low. A measured specific gravity of 5.215 is given for pure  $\text{Cr}_2\text{O}_3$  (Donnay, et al., 1954).

The absorption is so strong that in thin sections the mineral is opaque. In fragment mounts the thin grain edges are dark green with evident anisotropism, and with pleochroism from emerald green to olive green. It was not found to be pleochroic in polished sections.

On polished surfaces the mineral is gray. It is usually euhedral and strongly anisotropic with polarization colors as follows:

1. In air	Nicols completely crossed:	gray blue greenish gray
	Nicols not completely crossed:	dark violet blue light greenish gray
2. In oil	Nicols completely crossed:	gray brownish gray
	Nicols not completely crossed:	brownish gray greenish gray

Internal reflections are emerald green (also on borders against gangue). A clear red glint can be seen at the edges of small holes, which give a green reflection from the bottom.

Tests with chemical reagents gave the following results:

1:1	$\text{HNO}_3$	neg.	Aq. reg.	neg.
1:1	HCl	neg.	$\text{CrO}_3 + \text{HCl}$	neg.
20%	$\text{FeCl}_3$	neg.	HF	neg.
20%	KCN	neg.	70% $\text{HClO}_4$	neg.
40%	KOH	neg.	$\text{KMnO}_4$	neg.
5%	$\text{HgCl}_2$	neg.		

The microhardness (Vickers) was found to be about  $3200 \text{ kg/mm}^2$  (cassiterite:  $1900\text{--}2000 \text{ kg/mm}^2$  and chromite:  $1800 \text{ kg/mm}^2$ ).

The reflectivity in air as compared to that of hematite is:

	green	orange	red
eskolaite	22%	21%	20%
hematite	(26%)	(25%)	(21%)

A photomicrograph of a polished surface of the mineral is shown in Fig. 2.

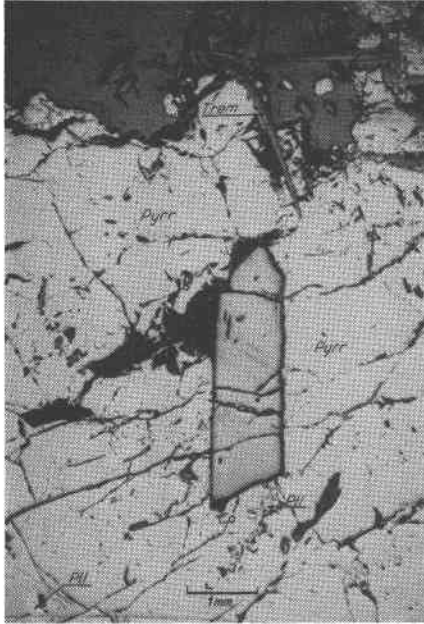


FIG. 2. Photomicrograph of a polished surface of eskolaite,  $\text{Cr}_2\text{O}_3$ , from Outokumpu, Finland. Pyrrhotite—Pyrr; chalcopyrite—Cp; pentlandite, PH; tremolite—Trem; and carbonate—Crb. Photo: Erkki Halme.

#### CHEMICAL COMPOSITION

A chemical analysis was made by Mr. Jorma Kinnunen, on material containing less than 1% impurities, mainly chromium spinel and tremolite. Results are given in Table 1.

The mineral sample was decomposed by means of  $\text{Na}_2\text{O}_2$  fusion in an Alsint crucible (pure alumina). Chromium+vanadium were titrated with ferrous ammonium sulphate using diphenyl amine sulfonate as indicator. Vanadium was titrated after removal of chromium by means of a mercury cell. Iron was separated from chromium and vanadium in alkaline carbonate solution and determined photometrically by means of salicylic acid. Aluminum, manganese, magnesia, silica, copper, and nickel were estimated spectrographically.

The above figures represent an average corresponding to the chemical composition of all samples collected. It seems reasonable to assume that for solid solutions the lattice constants and specific gravity would vary as a function of chemical composition from grain to grain. Small inclusions and cavities in grains were found to cause differences which overlapped the possible real differences in specific gravity between the

TABLE 1. CHEMICAL ANALYSIS OF ESKOLAITE FROM OUTOKUMPU, FINLAND  
Analyst: Jorma Kinnunen

	Weight per cent	Number of moles multiplied by 10,000
Cr <sub>2</sub> O <sub>3</sub>	94.13 ± 0.20	6191
Fe <sub>2</sub> O <sub>3</sub>	0.55	34
V <sub>2</sub> O <sub>3</sub>	4.58	305
Al <sub>2</sub> O <sub>3</sub>	0.19*	18
MgO	0.03*	7
MnO	0.03*	4
SiO <sub>2</sub>	0.20*	33
H <sub>2</sub> O (total)	0.10	
Total	99.81	

\* Based on a spectrographic analysis: O.X Al, Si (about 0.1)  
O.OX Mg, Mn (about 0.02)  
tr. Cu, Ni

Formula: (Cr<sub>1.90</sub>, V<sub>0.09</sub>, Fe<sub>0.01</sub>) O<sub>3</sub>.

grains. On the other hand the specific gravities of Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> are very close together. The determinations on the lattice dimensions did not show any remarkable differences. The total quantity of this mineral available for study was quite limited and did not allow several chemical analyses. A semiquantitative recast of the analysis on a different sample did not show any serious differences.

#### CRYSTALLOGRAPHY

The mineral usually forms in hexagonal prisms and thick plates, and gives a green streak. The calculated density obtained from the analysis given in Table 1 and from the cell dimensions given in Table 3, is 5.218 gm.cm.<sup>-3</sup>

Powder patterns were obtained using filtered copper, iron, and chromium radiation. The data for the interplanar spacings were calibrated with a silicon standard mixed with the sample. The results are given in Table 2, column 2, together with the data for synthetic Cr<sub>2</sub>O<sub>3</sub> and hematite.

The structural identity of the new mineral with the synthesized Cr<sub>2</sub>O<sub>3</sub> and hematite is evident. The *x*-ray powder pattern of hematite is similar, but it differs chiefly in having *d*-spacings corresponding to a larger unit cell than those of both the chromium compounds, although small differences in intensities were also noted. Intensity measurements were made by the flat-plate reflection method of the diffractometer.

In addition to the powder diffraction patterns shown in Fig. 3, the

TABLE 2. COMPARATIVE POWDER DIFFRACTION DATA FOR SYNTHETIC  $\text{Cr}_2\text{O}_3$  (SWANSON, GILFRICH AND UGRINIC, 1955), FOR ESKOLAITE, AND FOR HEMATITE (HARCOURT, 1942)

<i>hkl</i>	$\text{Cr}_2\text{O}_3$		Eskolaite		Hematite	
	<i>d</i> (Å)	I	<i>d</i> (Å)	I	<i>d</i> (Å)	I
01 $\bar{1}$ 2	3.633	74	3.630 ± .024	96	3.66	1
1014	2.666	100	2.665 ± .011	97	2.69	7
1120	2.480	96	2.479 ± .009	94	2.51	4
0006	2.264	12	2.269 ± .008	w	—	—
1123	2.176	38	2.174 ± .007	48	2.18	2
2022	2.048	9	—	—	—	—
0224	1.816	39	1.8146 ± .0034	58	1.835	3
1126	1.672	90	1.6746 ± .0039	100	1.68	5
1018	—	—	1.6139 ± .0032	w	—	—
21 $\bar{3}$ 2	1.579	13	1.5782 ± .0030	w	1.58	0.5
2134	1.465	25	1.4656 ± .0024	32	1.485	1
30 $\bar{3}$ 0	1.4314	40	1.4331 ± .0019	47	1.44	2
1.0. $\bar{1}$ .10	1.2961	20	1.2971 ± .0025	12	1.30	0.5
22 $\bar{4}$ 0	1.2398	17	1.2440 ± .0014	w	1.255	0.3

single crystal photographs were taken with Cu  $K\alpha$  radiation on the Buerger precession camera using the crystal shown in Fig. 1. These studies establish that the diffraction aspect is  $R^*c$ . All dimensions obtained from these films are given in Table 3. The morphology of the crystals obeys the rhombohedral lattice criterion, as the prism is  $\{11\bar{2}0\}$  rather than  $\{10\bar{1}0\}$ , and  $\{11\bar{2}3\}$  is observed, not  $\{11\bar{2}1\}$ . The forms  $\{01\bar{1}2\}$  and  $\{1014\}$  should be dominant, however, and their absence is anomalous.

The cell edges were also calculated from the *d*-values  $3.630 \pm .001 \text{ \AA}$  (01 $\bar{1}$ 2) and  $2.479 \pm .001 \text{ \AA}$  (11 $\bar{2}$ 0) obtained by means of a Norelco high-

TABLE 3. COMPARISON OF CRYSTAL DATA OF ESKOLAITE,  $\text{V}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$  AND  $\text{Fe}_2\text{O}_3$  (DONNAY ET AL., 1954)

	$\text{V}_2\text{O}_5$	$\text{Cr}_2\text{O}_3$	Eskolaite		$\text{Fe}_2\text{O}_3$
			powder data	single crystal data	
Lattice dimensions					
<i>a</i> 0	4.933 kX	4.94 kX	4.958 ± .002 Å	4.973 ± .015 Å	5.025 kX
<i>c</i> 0	13.940 kX	13.57 kX	13.60 ± .01 Å	13.57 ± .04 Å	13.735 kX
<i>c/a</i>	2.826	2.748	2.743	2.730	2.733
Cell volume	—	—	289.45 Å <sup>3</sup>	290.6 Å <sup>3</sup>	—
G	5.04	5.25	5.218	5.20	5.25

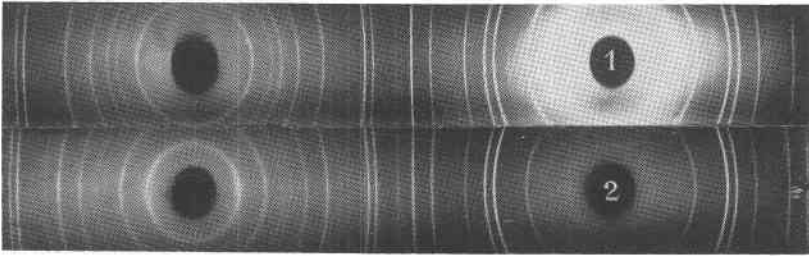


FIG. 3. Comparison of  $x$ -ray powder photographs: (1) eskolaite from Outokumpu, Finland; (2) hematite. Cr-radiation, V filter.

angle  $X$ -ray Spectrometer and using the sample mounting technique suggested by Holland (Holland et al., 1955).

The crystallographic data of eskolaite are given in Table 3 together with those of  $\text{Cr}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ , and  $\text{Fe}_2\text{O}_3$ .

#### NOMENCLATURE

On the evidence adduced above, the existence in nature of a chromium oxide corresponding in composition to  $\text{Cr}_2\text{O}_3$  and isostructural with hematite and corundum, is proposed.

The mineral is named in honor of Professor Pentti Eelis Eskola of the University of Helsinki in recognition of Professor Eskola's many fundamental contributions to mineralogy and petrology during the past half century.

By analogy with hematite and corundum, the name eskolaite should be appropriate for the pure end member.

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NOTE: A second occurrence of eskolaite is reported on page 1203 of this issue.



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