

KARELIANITE, A NEW VANADIUM MINERAL

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ABSTRACT

A new vanadium mineral, vanadium sesquioxide, has been identified in boulders derived from the Outokumpu ore body. Electron probe analysis gives the formula as  $(V_{1.82}Fe_{0.08}Cr_{0.07}Mn_{0.03})O_3$ . The mineral is isostructural with hematite, eskolaite and corundum (space group  $R\bar{3}c$ ). The name karelianite, after the region of Finland in which the Outokumpu mine is situated, is proposed for the pure end member,  $V_2O_3$ .

A second isometric vanadium oxide, containing approximately 63%  $V_2O_3$  has been found closely associated with karelianite. This mineral appears to be a spinel of the type (Mn, Fe) (V, Cr, Fe) $_2O_4$  but with the available evidence, the possibility of a  $\gamma$ - $Fe_2O_3$  type structure and the identification of this mineral with the previously described mineral, coulsonite, cannot be excluded.

INTRODUCTION

The following notes are the result of a field study and a microscopical investigation of the Outokumpu-type ore boulders found to the south-east of the Outokumpu ore field. This research, carried on at the Exploration Department of the Outokumpu Company, was undertaken in the hope of establishing the source of the boulders. In the course of the work, two new oxide minerals were found by Y. Vuorelainen which had not previously been identified. The mineral grains obtained from polished sections were large enough for a diffraction study using a standard 57.3 mm powder camera, which showed one mineral to be anisotropic and to have spacings almost identical with those of vanadium sesquioxide (hexagonal). The powder diffraction pattern of the second mineral approximated to that of magnetite and suggested a spinel structure. A qualitative x-ray fluorescence analysis of a small amount of the first mineral confirmed the presence of vanadium.

For the sake of clarity and in anticipation of subsequent results the two minerals will be referred to as sesquioxide and "spinel" respectively, although as shown later, the use of the second term requires confirmation.

OCCURRENCE

The ore boulders studied have been derived from the Outokumpu ore body described by Vähätalo (1953). The deposit lies within the Karelian schist belt, and the ore field is underlain mainly by mica schists, quartzites, black schists and some dolomite associated with skarn rocks and thick bodies of ultramafic ophiolites. The mica schist comprises the wall rock of the complex. The few granite dikes intruding the Outokumpu

complex originate from the Maarianvaara granite on the northwestern side. As noted by Vähätalo (1953), the Outokumpu ore is situated in the tectonic disturbance zone of quartzite, so that the country rock consists of quartzite.

Routine polished section and *x*-ray examinations showed that the minerals are closely associated with pyrrhotite, whereas chalcopyrite and pyrite occur as accessory constituents. The largest grains exceed 0.3 mm (sesquioxide) and 0.1 mm ("spinel"). The sesquioxide is normally crystallized in prismatic form and is commonly surrounded by the "spinel." In such cases the "spinel" is usually anhedral but exhibits development of crystal forms in separate grains. Pyrite, pyrrhotite and chalcopyrite have been found as inclusions in the sesquioxide crystals. Figure 1 is a photomicrograph showing both oxides.

The three main types of Outokumpu ore, disseminated, normal and brecciated, have been described by Vähätalo (1953). The vanadium minerals have been observed in boulders representing the first two of these ore types. The quantity is greatest in the sulfide veins running

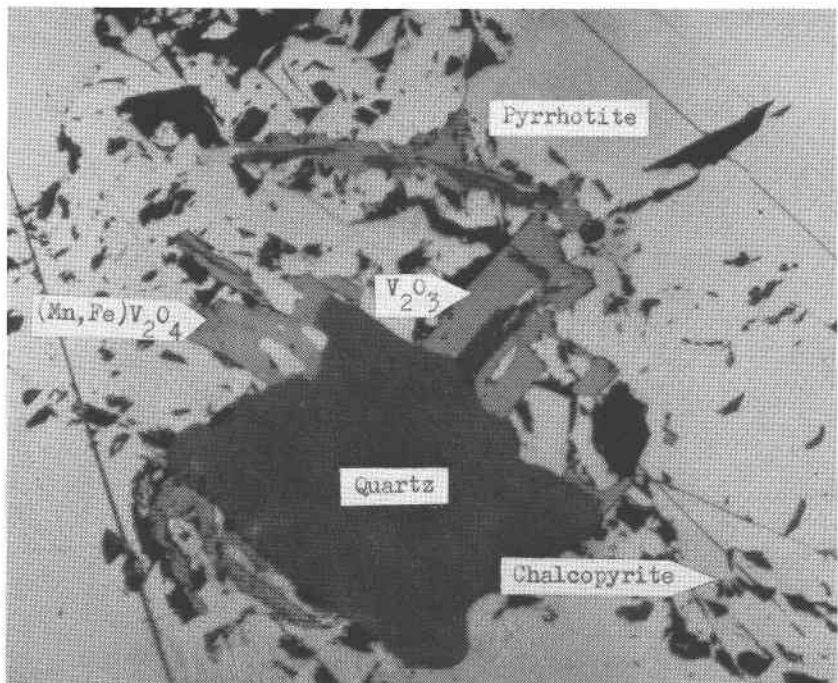


FIG. 1. Photomicrograph of a polished surface showing the  $V_2O_3$  mineral and intergrown "spinel"; Hovila boulder, Outokumpu, Finland ( $\times 100$ ).

through the disseminated ore. Characteristically, the minerals have commonly crystallized as a thin coating on the quartz, yellowish tremolite or on other gangue minerals. Graphite has been observed in all specimens that are rich in gangue. Pyrite is a persistent mineral throughout but is quantitatively less important than pyrrhotite. It most commonly occurs as a fine-grained granular mass. Eskolaite ( $\text{Cr}_2\text{O}_3$ ) was not found associated with these vanadium minerals, although it may be noted that chemical analyses of eskolaite (Kouvo and Vuorelainen, 1958) include approximately 4%  $\text{V}_2\text{O}_5$ .

The occurrence of graphite, the presence of quartzite in one half of a boulder, and the abundance of sphene in some specimens are interpreted as indicating the vicinity of the ore contact. Cobaltian pentlandite appears to be closely associated with these vanadium minerals. As noted earlier (Kouvo *et al.* 1959), the siegenite member of the  $\text{M}_3\text{S}_4$  type structure has been found to be the product in the secondary alteration, when the pentlandite structure has disappeared. This is also the case in the boulders studied, in which the primary pentlandite lattice was only identified in the lamellae formed by exsolution, thus providing evidence that the boulders are of natural occurrence and not the result of recent mining from the main ore body.

The mineral associations, the excellent development of the crystal forms in separate grains and the observed inclusions suggest a primary origin of the vanadium minerals. They have been found so far only in boulders derived from the Outokumpu ore, but more intensive investigations would doubtless result in their discovery within the main ore body.

#### DESCRIPTIONS

This information is necessarily incomplete because of the small grain size of the minerals and may require subsequent revision. It is believed, however, that enough new information will be presented to serve as an aid to future systematic microscopical observations.

*Sesquioxide.* The grains of this mineral are large enough to be observed under a binocular microscope. Conchoidal fracture pieces are black in color. In powdered form the material differs from eskolaite (light green) and hematite (reddish brown) in being black. In polished section the sesquioxide is brownish olive gray and weakly pleochroic. It is strongly anisotropic with polarization colors reddish brown to gray. No internal reflections have been observed. The standard etch reactions are:  $\text{HNO}_3$  (1:1) positive;  $\text{HCl}$  (1:1),  $\text{FeCl}_3$  (20%),  $\text{KCN}$  (20%),  $\text{KOH}$  (40%) and  $\text{HgCl}_2$  (5%) negative. The microhardness (Vickers,  $\text{M}_{\text{H}50}$ ) was found

to be 1790 kg/mm<sup>2</sup> (Mohs scale 8–9). The reflectivity in air is 18–19% (green and orange).

“*Spinel*.” The “spinel” grains were too small to be viewed under the binocular microscope. In polished section this mineral is isotropic and dark gray in color. Internal reflections have not been observed. The reflectivity in air for green light is 15–16% and for orange light 13–14%. It differs from magnetite in being darker in color and non-magnetic. It is softer than chromite; the measured Vickers microhardness was found to be 644 kg/mm<sup>2</sup> (Mohs scale 5–6).

The behavior of the spinel with reagents varied according to whether the grains were isolated or intergrown with sesquioxide. The intergrown material showed a negative reaction to the following reagents: HCl (1:1), FeCl<sub>3</sub> (20%), HgCl<sub>2</sub> (5%), KOH (40%) and KCN (20%). A positive reaction was obtained with HNO<sub>3</sub> (1:1). The isolated grains, however, were negative to all the above reagents.

#### CHEMICAL COMPOSITION

Specimens from ten ore boulders were analysed for trace elements at the Outokumpu Company spectrochemical laboratory at Pori. Considerable variation was found in the vanadium content (0.001–0.02% V). The samples richest in vanadium were selected for further examination: Hovila (rich in chalcopyrite) 0.01% V; Hovila (rich in pyrrhotite) 0.02% V; Alikäytävä 1, 0.02% V.

The analyses of individual grains were carried out with the electron probe microanalyser. The instrument used (Long, 1958; Agrell and Long, 1959) was equipped with scanning facilities (Cosslett and Duncumb, 1956; Duncumb, 1959) that allow an image to be formed on the screen of a cathode ray tube, showing, on a magnified scale, the distribution of a selected element over the surface of the specimen. In addition to providing qualitative information about the association of different elements in the specimen, the scanning image also serves as a means of positioning the electron probe at a particular point in the surface for quantitative analysis.

Figure 2 shows photographs of the scanning images obtained with a polished section in which the sesquioxide and the “spinel” are intergrown. In the three photographs the spectrometer has been set successively to select V K<sub>α</sub>, Fe K<sub>α</sub> and Mn K<sub>α</sub>. A comparison with the reflected light photograph indicates that the manganese is primarily associated with the spinel phase. The spotted appearance of these pictures is due to the fact that each x-ray quantum detected by the proportional counter separately brightens the cathode ray tube at one point. When the number of quanta

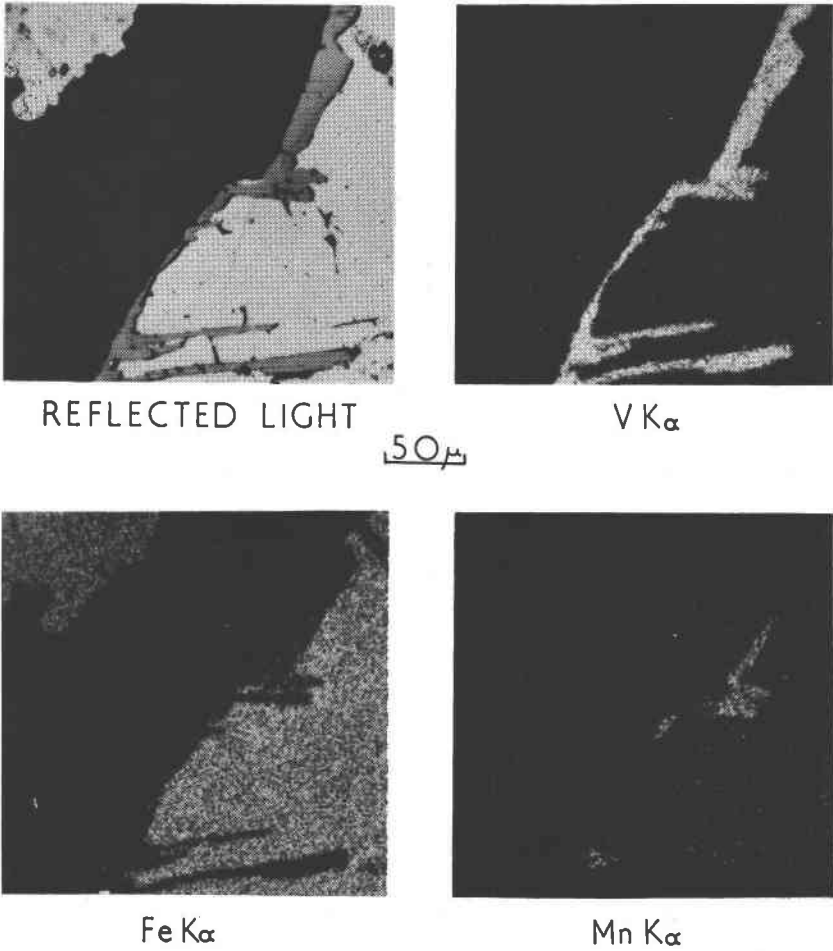


FIG. 2. Photomicrograph and  $x$ -ray scanning images showing intergrown  $V_2O_3$  (mid-gray in reflected-light picture) and "spinel" (dark gray).

contributing to any given area of the picture is small, statistical variations of the number become apparent. Some quanta of continuous or "white" radiation are also detected, and the effect of these is to produce a background of bright points in the picture even when the concentration of the element to which the spectrometer is set is zero. This background imposes a limit on the minimum concentration that can be detected in a given period, both in the case of scanning pictures and in quantitative determinations with the stationary probe.

Several determinations of the composition were made with the electron

probe stationary on 1–2  $\mu$  diameter areas of the two oxide phases. Comparison of the measured intensities of the lines V  $K_{\alpha}$ , Cr  $K_{\alpha}$ , Mn  $K_{\alpha}$  and Fe  $K_{\alpha}$  gave, after correction for the effects of absorption and secondary fluorescence, the results shown in Table 1. Pure metals were used as standards. Complete resolution of the V  $K_{\beta}$  and the Cr  $K_{\alpha}$  lines was not possible with the spectrometer used and the necessary correction to the measured intensity of the Cr  $K_{\alpha}$  line was determined experimentally with the aid of the standards.

The results of several determinations at different points in the sesquioxide were consistent, but successive measurements on the "spinel" gave somewhat erratic results, apparently due to the presence of small inclusions visible only under a high power oil immersion objective. These inclusions have not been identified, but the results in Table 1 were ob-

TABLE 1. ELECTRON PROBE ANALYSES OF INTERGROWN SESQUIOXIDE AND "SPINEL"

Sesquioxide		"Spinel"	
V <sub>2</sub> O <sub>3</sub>	92.9 ± 2.5%	V	43 ± 3% ≡ 63% V <sub>2</sub> O <sub>3</sub>
Cr <sub>2</sub> O <sub>3</sub>	3.7 ± 0.5%	Cr	3.2 ± 0.5% ≡ 4.8% Cr <sub>2</sub> O <sub>3</sub>
MnO	1.5 ± 0.5%	Mn	17 ± 1.5% ≡ 21.9% MnO
Fe <sub>2</sub> O <sub>3</sub>	4.1 ± 0.5%	Fe	5.9 ± 0.5% ≡ 7.6% FeO
Total	102.2%	Total	97.3%

tained from an area believed to be free from them. The small concentration of manganese in the sesquioxide has been calculated as MnO, since it is unlikely that Mn<sub>2</sub>O<sub>3</sub> will be taken up in the rhombohedral V<sub>2</sub>O<sub>3</sub> lattice (Montoro 1940).

The difference between the intergrown and isolated "spinel" grains in their reaction to 1:1 HNO<sub>3</sub> suggests a possible compositional variation. Direct comparisons were made with the electron probe which showed a difference in the V:Cr ratio. The vanadium content falls to 36 ± 3% in the isolated spinel grains, while an approximately complementary rise of the chromium content from 3% to 11% occurs.

Only very small variations in the V:Cr ratio were observed between intergrown and isolated grains of the sesquioxide.

#### CRYSTALLOGRAPHY

The crystal structures of spinels and sesquioxides are well known and it has been possible to make useful correlations between the diffraction data of the Outokumpu oxides and synthetic compounds. Powder patterns of the natural minerals were obtained using filtered copper and iron radiation and 114.6 mm powder cameras with silicon as a standard. According

TABLE 2. COMPARATIVE X-RAY POWDER DATA FOR THE NATURAL  $V_2O_3$  MINERAL FROM OUTOKUMPU, FOR VANADIUM SESQUIOXIDE AND FOR HEMATITE

hkl	$V_2O_3$ Mineral Outokumpu		Vanadium Sesquioxide ASTM 1-1293		Hematite ASTM 6-0502	
	d(Å)	I	d(Å)	I	d(Å)	I
102	3.67	70	3.65	60	3.68	70
104	2.71	90	2.70	80	2.69	100
110	2.49	80	2.47	60	2.51	80
006	2.33	1	2.32	2		
113	2.20	20	2.18	20	2.20	70
202			2.03	2	2.07	10
204	1.84	25	1.83	25	1.837	70
116	1.70	100	1.69	100	1.691	80
121			1.61	2	1.634	10
108					1.596	40
212	1.58	1	1.57	3		
214	1.47	20	1.47	25	1.484	70
300	1.44	40	1.43	30	1.451	80
208			1.33	10	1.348	20
119						
1.0.10	1.32	5			1.309	40
220	1.25	5	1.24	4	1.255	30
306	1.22	1	1.22	2	1.224	10

to Zachariasen (1928) the symmetry of  $V_2O_3$  is rhombohedral ( $D5_1$ ,  $Z=2$ ), with the space group  $D_3^6d$  ( $R\bar{3}c$ ). Comparative powder diffraction data are given in Table 2.

The powder pattern is almost identical with those of vanadium sesquioxide and hematite, although the observed spacings are slightly larger than those for pure  $V_2O_3$ . The data give lattice dimensions of  $a=4.99$  Å and  $c=13.98$  Å.

The oxide phase of the ternary system Fe-V-O has been studied by Mathewson *et al.* (1932). The x-ray powder spacing data for  $FeV_2O_4$  spinel ( $Fd\bar{3}m$ , type H11;  $Z=8$ ) given by them are presented in Table 3 together with the measured data for the natural isotropic oxide from Outokumpu. The vanadium mineral coulsonite (Dunn, 1937; Dunn and Dey 1937) is usually described as  $\gamma-(Fe,V)_2O_3$  (isom.) and identical in structure with maghemite,  $\gamma-Fe_2O_3$ . Additional unidentified lines were present in the powder pattern of the "spinel" but some lines which should have resulted from a  $\gamma-Fe_2O_3$  structure were absent.

The identification of the mineral coulsonite rests on etch tests and only qualitative chemical data are available. It is clear that a single crystal and electron probe studies of this mineral and of the Outokumpu "spinel" are necessary in order to provide reliable structural assignments.

TABLE 3. COMPARATIVE X-RAY POWDER DATA OF NATURAL VANADIUM SPINEL, SYNTHETIC  $\text{FeV}_2\text{O}_4$  AND MAGNETITE

Vanadium spinel Outokumpu		$\text{FeV}_2\text{O}_4$ Mathewson <i>et al.</i>		Magnetite ATSM 11-614	
d(Å)	I	d(Å)	I	d(Å)	I
4.88	15			4.85	40
4.14	2				
2.99	40	3.000	m	2.966	70
2.84	1				
2.55	100	2.560	vs	2.530	100
2.44	2			2.419	10
2.12	25	2.110	m	2.096	70
1.72	1	1.725	m	1.712	60
1.63	40			1.614	85
1.50	60	1.494	vs	1.483	85
1.35	1			1.327	20
1.29	2			1.279	30
1.28	1			1.264	10
				1.2112	20
1.13	1	1.218	m	1.1214	30
1.10	15	1.096	s	1.0922	60
1.06	1	1.052	m	1.0489	40
		0.998	w		
0.982	B	0.970	s	0.9890	10

## NOLANITE

A third oxide was found, in some cases intimately associated with the sesquioxide, but also as separate grains. This mineral was pure gray, strongly anisotropic and moderately pleochroic. The x-ray powder pattern indicates nonlanite ( $\text{Fe}^{2+}_{2.5} \text{V}^{3+}_{1.7} \text{V}^{4+}_{4.5} \text{O}_{16}$ ), described by Robinson *et al.* (1957) from Beaver Lodge, Saskatchewan. The crystals were too small to allow a separation. This oxide was easily distinguished from the other oxides described in this paper.

## NOMENCLATURE

Electron microprobe analyses and the crystallographic data obtained suggest the existence of a new vanadium mineral,  $\text{V}_2\text{O}_3$ , isostructural with hematite, eskolaite and corundum. The name karelianite, after the region of Finland in which the Outokumpu mine is situated, is proposed for this mineral, the name to be applied to the pure end member. The mineral *karelinite* described in 1858 by Hermann has been shown to be a mixture of bismuth minerals (Palache *et al.*, 1944).

The second mineral, isometric manganese-iron-vanadium-chromium



oxide, found intimately associated with karelianite, is considered to be an open question. It is suggested that it may correspond with the artificial compound  $\text{FeV}_2\text{O}_4$ , thus being a natural vanadium spinel.

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