A new occurrence of uvarovite from northern Karelia in Finland.

(With Plate XV.)

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I N 1929 Väyrynen¹ discovered a chalcopyrite-bearing pyrrhotine deposit at the village of Luikonlahti, 30 km. NW. of the Outokumpu mine. This occurrence is associated with a complex of serpentine, quartzites, phyllites, dolomites, and diopside-tremolite-rocks, together with penetrating granites, aplites, and pegmatites. The rock association thus closely resembles that of the Outokumpu ore-field.

In 1947, during a geological excursion to north Karelia, under the direction of Professor Eskola, the writer collected material from Luikonlahti mine containing large amounts of uvarovite. Two main types of uvarovite-bearing rocks are represented:

- 1. A glassy, dark-grey quartzite, impregnated with excellent tiny crystals of pyrrhotine and irregular aggregates of uvarovite.
- 2. A pyrrhotine ore with diopside and uvarovite.

Although lacking the brilliant emerald-green colour of the Outokumpu uvarovite-rocks these types are nevertheless more impressive in that the uvarovite occurs as a true 'rock-forming' mineral.

The main interest naturally attaches to the composition and properties of the uvarovite, and it is with these mineralogical and chemical aspects that the following investigation is mainly concerned. For comparative purposes a uvarovite garnet from Outokumpu has also been investigated.

Petrographical characters of the uvarovite-bearing rocks.

The three main rock types employed in the investigation were:

- 1. Quartzite, with pyrrhotine and uvarovite, from Luikonlahti.
- 2. Pyrrhotine ore, with uvarovite and diopside, from the same locality.
- 3. Quartzite, with uvarovite, diopside, tremolite, calcite, and some pyrrhotine, from Outokumpu.

¹ H. Väyrynen, On the geology and tectonics of the Outokumpu ore field and region. Bull. Comm. Géol. Finlande, 1939, no. 124.

1. In hand-specimen the quartzite from Luikonlahti is a glassy, dark grey unstratified rock impregnated with tiny (1-2 mm.) crystals of pyrrhotine and small aggregates of uvarovite up to 10 mm. in diameter. Under the microscope, quartz as irregular grains, usually with undulating extinction, is seen to be the main constituent. Uvarovite occurs in aggregates following the boundaries between the quartz grains (pl. XV, fig. 1) and is almost invariably slightly anisotropic. Pyrrhotine forms perfect six-sided crystals, many of which contain a tiny central inclusion of quartz. In addition to these main constituents very subordinate amounts of diopside, radiating fibrous tremolite, and calcite are also present.

2. The uvarovite-bearing pyrrhotine ore from Luikonlahti is somewhat variable in constitution, but usually contains approximately equal amounts of pyrrhotine, uvarovite, and diopside; in certain specimens, however, the silicates may predominate. The uvarovite forms patches up to 1 cm. in diameter.

Under the microscope two generations of uvarovite can be distinguished. The garnet of the first generation is normally partly decomposed and may be represented only by very fine-grained aggregates of diopside and tremolite containing fringed relict grains of uvarovite. The shapes of the original crystals can, however, be clearly recognized under crossed nicols. Uvarovites of the second generation are fresh and contain no inclusions. They occur sometimes as perfect crystals, with only the edges altered (pl. XV, fig. 2) and often surround partly decomposed uvarovites of the first generation. Both isotropic and anisotropic types of uvarovite have been observed and in a few cases excellent zoning occurs (pl. XV, fig. 4). Very often the central part of the garnet crystal only is anisotropic and zoned.

The diopside forms well-developed crystals and is almost always twinned. Sphene is quite abundant, usually in cracks, and tremolite has also been identified. Chalcopyrite is a fairly common constituent in some specimens, and, more rarely, molybdenite has also been found.

3. The specimen from Outokumpu, taken for comparison, is a glassy quartzite with fine-grained diopside-tremolite bands containing scattered grains of uvarovite and chromite. Excellent crystals (110) and (112) of uvarovite with striated faces, up to 1.5 cm. in diameter, occur in pockets of coarse-grained calcite, and are associated with irregular patches of pyrrhotine, which may show small inclusions of uvarovite.

Under the microscope it is apparent that the uvarovite normally occurs in a groundmass of quartz, diopside, tremolite, and calcite. In this case also two generations of uvarovite can be distinguished. The earlier generation, which appears to have developed from chromite, is often isotropic and contains cracks, and inclusions of calcite (pl. XV, fig. 5). The second generation forms more massive crystals, is usually anisotropic, and is devoid of chromite relicts. The original crystal boundaries of the first-generation uvarovite can be clearly recognized under crossed nicols, and these ghost-like uvarovites are invariably seen to be surrounded by fresh uvarovite of the second generation (pl. XV, fig. 6).

Grains of chromite in various stages of alteration are abundant in the uvarovite, and chromite is also found independently as well-preserved crystals. In certain cases, cracks in the chromite are filled with uvarovite, diopside, tremolite, and calcite (pl. XV, fig. 5). Finally, chromite occurs as inclusions in uvarovite either in the form of rounded and perforated crystals and irregular grains or as a dust-like product.

Chemical investigation.

Chemical analyses were carried out on carefully separated and handpicked material from the three specimens, and the results are given in table I. In each case 0.5 gram of substance was used. Chromium was determined volumetrically, and aluminium in the usual manner by difference from the sesquioxides.

Menzer¹ has shown that the cubic unit cell of garnet contains eight molecules of composition $R_3^{2+}R_2^{3+}[SiO_4]_3$. Accepting, as a basis for calculation, the presence of 96 oxygen atoms in a unit cell, it is possible to calculate (from the chemical analyses) the corresponding numbers of atoms of the other elements present. These results are given in table II.

These analyses represent isomorphous mixtures of uvarovite and grossular with some and radite. In the garnets from Luikonlahti the proportion of uvarovite to grossular is about 1:1 as against a proportion of 3:1 in the new analysis of uvarovite from Outokumpu.

The Cr_2O_3 content of the analysed uvarovites ranges from 12.25 to 22.60 %, and the corresponding Al_2O_3 content from 12.00 to 5.34 %. The iron content is fairly low in all cases. Compared with previous analyses of uvarovite from Outokumpu, viz. analyses 4 and 5, the main difference lies in the chromium and aluminium contents.

¹ G. Menzer, Die Kristallstruktur der Granate. Zeits. Krist., 1928, vol. 69, pp. 300-396. [M.A. 4-111.]

				1.	2.	3.	4.	э.
SiO_2	•••	•••		38.68	38·4 0	37.31	35.88	36.79
Al_2O_3	•••			12.00	10.77	5.34	1.13	1.93
Cr_2O_3				12.25	14.97	$22 \cdot 60$	27.04	27.54
Fe_2O_3	•••		•••	2.47	1.89	0.30	$2 \cdot 46$	0.41
MnO			•••	n.d.	n.d.	0.12	0.03	
MgO				0.20	0.48	0.25	0.04	0.50
CaO				34.04	33.08	34.25	33.31	32.74
ign.		•••		0.20	0.40	0.10	0.18	
							•	
				99.84	99.99	100.30	100.07	99.91

TABLE I. Chemical analyses of uvarovite. 0

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1. Uvarovite in pyrrhotine-quartzite, Luikonlahti, Finland. Analyst: O. von Knorring.

2. Uvarovite in pyrrhotine-diopside ore, Luikonlahti, Finland. Analyst: O. von Knorring.

3. Uvarovite in diopside-tremolite skarn, Outokumpu, Finland. Analyst: O. von Knorring.

4. Uvarovite in uvarovite-tremolite-tawmawite-pyrrhotine vein, Outokumpu, Finland. Analyst: L. Lokka (in P. Eskola, 1933)¹.

5. Uvarovite in quartzite, Outokumpu, Finland. Analyst: L. H. Borgström.²

TABLE II. Number of atoms (0 = 96) in unit cell of uvarovite.

		1	2	3	Theoretical
0	 •••	96	96	96	96
Si	 	24.33	24.28	$24 \cdot 14$	24
Al	 •••	8.88	8.00	4 ·08	
Cr^{3+}	 •••	6.08	7.46	11.56	
Fe^{3+}	 •••	1.16	0.90	0.14	_
		16.12	16.36	15.78	16
Mn	 			0.18	
Mg	 	0.18	0.45	0.24	
Ca	 ••••	22.93	$22 \cdot 40$	23.73	
		23.11	22.85	$24 \cdot 15$	24

The diopside from sample no. 2 was analysed, mainly as a check for chromium, and the Cr₂O₃ content was found to be very small indeed, less than 0.01 %. The composition of this diopside is shown in table III: together with an analysis of chrome-diopside from Outokumpu for comparison.

¹ P. Eskola, On the chrome minerals of Outokumpu. Compt. Rend. Soc. Géol. Finlande, 1933, no. 7, pp. 26-44. [M.A. 6-46.]

² L. H. Borgström, Uwarowit från Kuusjärvi. Geol. För. Förh. Stockholm, 1901, vol. 23, pp. 560-563.

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		1.	2.
SiO ₂		53.20%	52.84%
Al_2O_3		0.76	1.04
Cr_2O_3		0.00x	0.44
FeO	•••	6.06	2.52
MgO	•••	15.59	17.26
CaO		24.70	25.44
H_2O			0.88
		100.31	100.42

TABLE III. Chemical analyses of diopside.

1. Diopside in uvarovite-pyrrhotine ore, Luikonlahti, Finland. Analyst: O. von Knorring.

2. Diopside in diopside skarn, Outokumpu, Finland. Analyst: E. S. Tomula (in P. Escola, 1933, loc. cit.).

Determination of the refractive index and specific gravity of the analysed uvarovite garnets.

Ford,¹ Fleischer² and others have shown that the optical and physical properties of a garnet are directly dependent on its chemical composition. In the case of uvarovite, however, exceptionally few cases are known in which the chemical composition, refractive index, and specific gravity have been determined on the same specimen. It is desirable, therefore, to obtain all possible physical data for the three analysed uvarovite garnets. According to Ford the calculated refractive index for an ideal uvarovite is 1.870, a value which is based on only one determination.

Anomalous birefringence introduces certain difficulties in refractive index determination on uvarovite and, in addition, the analysed material was too brittle to make prisms. The indices were, therefore, determined by the immersion method in sodium-light using phenyldiiodoarsine with methylene iodide. The results of these determinations are listed in table IV. When the maximum values obtained are plotted against the corresponding Cr_2O_3 content (fig. 1) an almost perfect linear relationship is seen to exist between the refractive index and chemical composition of uvarovite, despite small differences in the iron content. It is apparent from these results that the value 1.870 for uvarovite, as quoted in textbooks, is too high. The specific gravity of the analysed uvarovites were

¹ W. E. Ford, A study of the relations existing between the chemical, optical and other physical properties of the members of the garnet group. Amer. Journ. Sci., 1915, ser. 4, vol. 40, pp. 33-49. [M.A. 2-37.]

² M. Fleischer, The relation between chemical composition and physical properties in the garnet group. Amer. Min., 1937, vol. 22, pp. 751-759. [M.A. 7-109.]

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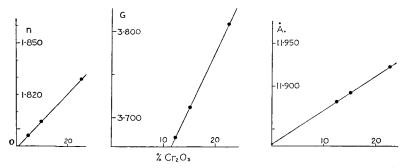


FIG. 1. Variation of the refractive index, specific gravity, and edge of unit-cell dimensions with chromium content.

determined by means of a pyknometer, using toluene as displacement liquid. The results are compiled in table IV, again showing a linear relationship.

TABLE IV. X-ray, optical, and specific gravity data for uvarovite.

		Mol. wt.	a.	Sp. gr.	n.
Luikonlahti no. 1		 470.2	11·881 Å	3.676	1.796
Luikonlahti no. 2		 $472 \cdot 4$	11.892	3.712	1.798 - 1.804
Outokumpu no. 3		 487.6	11.922	3.809	1.821 - 1.829
Outokumpu (Menzer)	•••	 $495 \cdot 2$	11.950	3.802	1.8516

X-ray study of the analysed uvarovites.

According to Stockwell¹ the first X-ray study on garnet (an almanditespessartine) was made by Nishikawa in 1917 and, later, Menzer (loc. cit.) carried out a complete investigation of the six main garnet species. Subsequently Stockwell pointed out that a linear relationship exists between the edge length (a) of the unit cell and the chemical composition within the garnet group. In the case of the material under investigation two garnet molecules are involved, viz. uvarovite and grossular. In order to obtain a complete picture of the comparative relationship between these garnet molecules, the edge lengths of the analysed uvarovites and of a pink grossular from New Mexico were determined.

In fig. 1 the dimensions of a so obtained are plotted against the Cr_2O_3 content of the uvarovites. The four points of the corresponding garnets all lie almost exactly on a line. Menzer (loc. cit.) obtained somewhat higher values of a both for grossular and uvarovite, but in spite of

¹ C. H. Stockwell, An X-ray study of the garnet group. Amer. Min., 1927, vol. 12, pp. 327-344. [M.A. 3-433.]

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this, a line through the values obtained by Menzer, is almost parallel to the former. There can, therefore, be little doubt concerning the existence of a linear relationship between the edge length of the unit cell and the chemical composition of the garnets, as Stockwell has pointed out.

General considerations.

The most significant features of the geology and genesis of uvarovites from Luikonlahti and Outokumpu are their association with serpentine intrusions. Thus the source for the element chromium seems to be determined. However, very little is known concerning the active mode of introduction of chromium into the various uvarovite-bearing rocks. The present investigation provides some evidence on this problem.

Uvarovite has undoubtedly been formed in different ways and during various stages of metamorphism. In specimen no. 2, from Luikonlahti (containing uvarovite, diopside, and pyrrhotine) the first-generation uvarovite was apparently formed at the same time as the associated skarn minerals, and probably as one of the first as it appears to precede diopside, tremolite, and the other silicates. It must be assumed in this case that the chromium was introduced from the associated ultrabasic rocks. The second-generation uvarovite developed during the deposition of pyrrhotine, the chromium metasomatism being connected with the ore genesis. The uvarovite from the Luikonlahti quartzite is also associated with pyrrhotine and must be similar in genesis to this later type.

In the material from Outokumpu the first generation of uvarovite is undoubtedly a replacement product of the chromite, whereas the second generation is again intimately connected with the formation of ore minerals.

Eskola (loc. cit.) states that the skarn-mineral association is connected with the dolomites in Outokumpu. He also describes a peculiar occurrence of dolomite containing chromite, which association has, however, been found only in one place, whereas chromite-free dolomites have been observed quite frequently.

On the assumption that dolomites containing chromite have reacted during a stage of metamorphism with silica in the presence of water, the following reaction could occur:

 $Dolomite + chromite + SiO_2 + H_2O \rightarrow tremolite + diopside + uvarovite.$

Eskola mentions that the chromite is unevenly distributed in the dolomite, an observation which is in good agreement with the uneven distribution of chromium in the skarn. The aluminium content in uvarovite, tremolite, and diopside is partly derived from aluminium-bearing chromite and partly from aluminium present in the rock itself. If the chromite in dolomite is of a hydrothermal origin, formed before or during the process of serpentinization, the skarn-mineral association, including uvarovite and also the ore with the second-generation uvarovite, must have formed *after* the serpentinization. A similar origin for uvarovite could be applied to the Luikonlahti locality.

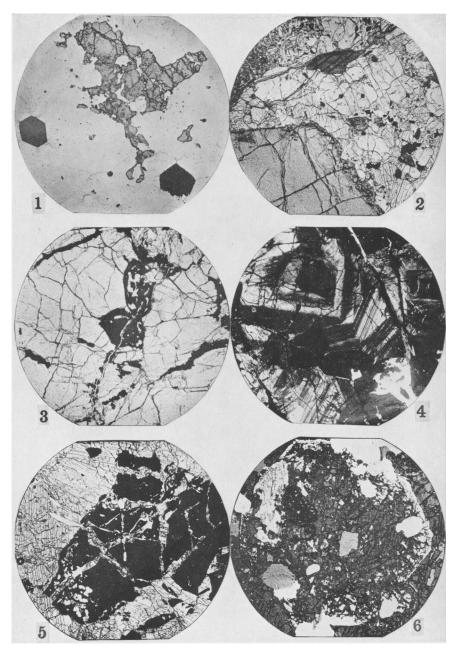
The chemical investigation has shown that the composition of uvarovites from the same locality may vary to some extent. The refractive indices, specific gravities, and unit-cell dimensions, determined on the analysed chrome garnets are directly dependent on the chemical composition.

Acknowledgements.—Thanks are due to Messrs. T. F. Johnston and Mr. W. L. Wilson of this department for their technical assistance during the course of the investigation. The writer is indebted to Mrs. Toini Mikkola of the Geological Survey of Finland in Helsinki for determination of the refractive indices of the analysed uvarovites. A special expression of gratitude is due to Professor W. Q. Kennedy for all the aid and encouragement he has given me throughout the work.

EXPLANATION OF PLATE XV.

Photomicrographs of uvarovite from northern Karelia, Finland.

- Fig. 1. Uvarovite in glassy quartzite from Luikonlahti; the opaque mineral is pyrrhotine. $\times 19.$
- FIG. 2. Uvarovite-diopside skarn from Luikonlahti. Euhedral uvarovite in a groundmass of diopside, tremolite, and sphene. The opaque minerals are pyrrhotine, chalcopyrite, and molybdenite. $\times 19$.
- FIG. 3. A large uvarovite crystal with typical cracks and patches of pyrrhotine. $\times 19.$
- FIG. 4. As in fig. 3. Crossed nicols. $\times 19$.
- FIG. 5. Large chromite crystal, with cracks infilled by uvarovite, diopside, and tremolite, in tremolite base. $\times 19$.
- FIG. 6. Euhedral uvarovite crystal of the first generation with included chromite relicts, surrounded by second-generation uvarovite. Crossed nicols. $\times 19$.



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