Uvarovite* and grossular from the Fengtien nephrite deposits, eastern Taiwan

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ABSTRACT. Uvarovite and grossular, the former comparatively rare, occur along the serpentinite-graphite schist contact in the Fengtien area, on the eastern slope of the Central Range of Taiwan. Uvarovite occurs as small emerald-green euhedral crystals on diopside-fels with dodecahedral crystal forms and many other modifications. Its refractive index is 1.782, specific gravity 3.702, and unit cell edge 11.912 Å. Chemical and probe analyses give average Cr2O3 contents of 11.60 wt. %; spectrographic analysis shows significant enrichment in Cr, Be, Co, Y, Sb, and La over grossular. Associated minerals include nephrite, diopside, tremolite asbestos, zoisite, and clinozoisite. Grossular is reddish-brown; large crystals, dodecahedral in form often modified by trapezohedrons, are associated with diopside, idocrase, and calcite. n =1.746, SG = 3.636, and a = 11.866 Å. Structurally and chemically it is quite near the grossular end member. Grossular is considered to be formed from pneumatolysis associated with the intrusion of ultramafic rocks, whereas uvarovite is a replacement product of relict chromite in the original ultramafic rocks where migration of elements such as silicon and calcium from wall rocks are prominent.

UVAROVITE is a member of the ugrandite series and is the rarest of the six end members of the garnet family. The pure uvarovite end member has not been recorded in natural minerals; in fact the natural garnet that has been called 'uvarovite' always contain a considerable amount of the grossular and andradite molecule. Garnets with uvarovite as the dominant molecule are of restricted occurrence and are found chiefly in serpentinite, often in association with chromite (Chakraborty, 1968), and in metamorphosed limestones and skarn ore-bodies (Deer *et al.*, 1963). The best-known occurrences are those in Outokumpu, north Karelia, Finland (von Knorring, 1951), and in the Bushveld Complex, South Africa (Frankel, 1959).

The brilliant emerald-green uvarovite was found a few years ago in the Fengtien nephrite deposits (fig. 1), about 20 km south of the city of Hualien, eastern Taiwan. A brief account on the mode of occurrence and physical properties of the material has already been reported (Huang and Yeh, 1978; Lee *et al.*, 1978); however, chemical composition, trace-element chemistry, and some other properties are not given. Recently, the present writers examined further specimens from this area, and an attempt has been made to deal with the physical and optical properties in more detail, particularly with full chemical and trace element analyses of the uvarovite in comparison with grossular from the same area.



FIG. 1. Sketch map showing the location of the Fengtien nephrite deposits in relation to the serpentinites.

Geologic setting

The strata exposed in the area consist mainly of the Tananao schists and serpentinites. The Tananao schist is of late Palaeozoic and/or Mesozoic age with graphite schist predominant and intercalates with thin lenses of chlorite schist, talc schist, and

^{*} See note on p. 37.

crystalline limestone in places (Yen, 1954; Ho, 1975; Huang and Yeh, 1978). The graphite schist consists mainly of quartz, sericite, chlorite, graphite, microcline, albite, and calcite, with small amounts of biotite, sphene, and apatite. Schistosity which strikes nearly E.-W. and dips 20-30° to the north is well developed. Small-scale folding and faulting, trending NE-SW or nearly E.-W., is common.

Serpentinites in this area are layered in form and occur as sills intruding into the graphite schist. At present nine serpentine layers are recognized in the area, up to about 40 m in thickness and hundreds of square metres in extent (Tan et al., 1981). The contacts between the serpentinites and the schists are generally concordant; a metasomatic zone which consists of nephrite, diopside-fels, garnets, tremolitic asbestos, epidote, zoisite, and clinozoisite is commonly observed at each contact. Under the microscope, the massive, dark-green serpentinite consists chiefly of antigorite with accessory relict chromite, magnetite, and pyroxene. Crysotile both clino- and ortho-, and lizardite also exist in minor amounts. Ribbon and stockwork structures caused by cross-fibre tremolitic asbestos veinlets are common. Some serpentinites that are composed mainly of lizardite reveal distinct mesh texture, suggesting the protolith of the serpentinites in this area to be ultramafic igneous rock as peridotite or pyroxenite.

Mode of occurrence

Uvarovite is so far known in Taiwan only at the Fengtien nephrite deposits, while grossular has been found at many other places in the island. The distribution and mineral associations of the uvarovite and grossular in the Fengtien area are dissimilar in certain respects. Although they occur more or less in the same zones of contact, they are not associated with each other. The mode of occurrences of the uvarovite and grossular in the Fengtien nephrite deposits are illustrated separately in figs. 2 and 3.

The occurrence of uvarovite is quite restricted, and so far it is only found at S-3, I-1, and I-2 adits in this mining area. Uvarovite is scattered as individual dodecahedral crystals or as small irregular patches in the contact zones of graphite schist with serpentinites, in association with tremolitic nephrite, diopside, tremolitic asbestos, quartz, zoisite, and clinozoisite. The uvarovite crystals are small in size, generally 0.1 to 0.7 mm in diameter. Under a microscope, euhedral, pale-green to green uvarovite crystals with dark chromite cores are frequently observed, showing its close genetic relationship with relict chromite.

Grossular is found in diopside-grossular veins in serpentinite near the contact zones, in association



FIG. 2. Cross-section of the metasomatic zone occurs at S-3 adit, Fengtien mining area.

with diopside, idocrase, and calcite. It is pale-brown to reddish-brown in colour and translucent to transparent. The crystals are generally dodecahedral, often modified by trapezohedra. The grain size of the euhedral to subhedral grossular crystals is much larger than that of the uvarovite; diameters up to 2 cm or more are common.

Results and discussions

X-ray diffraction data. Table I records X-ray powder diffraction data for representative uvarovite and grossular samples obtained using a Diano X-ray powder diffractometer. Diffraction data for natural uvarovite have been published previously by Frankel (1959) and for synthetic uvarovite by Skinner (1956). The X-ray data of the Fengtien uvarovite are quite different from those of grossular



FIG. 3. Sketch map showing the occurrence of diopsidegrossular-idocrase vein in serpentinite.

from the same area, but closely resemble those for uvarovite from the Bushveld Complex, South Africa (Frankel, 1959). Fairly complete and continuous variation in d spacings occurs within this ugrandite series, because of the Cr^{3+} substitution. The d spacings of the Fengtien uvarovite are intermediate between those of synthetic grossular and uvarovite. The unit cell dimensions were calculated by taking the average values obtained from the (420), (642), and (800) reflections. The values are listed in Table III, and will be discussed later.

Chemical analyses and formulae. Chemical analyses of the uvarovite and grossular are presented in Table II. They were obtained on carefully handpicked material in a Perkin Elmer model 503 atomic absorption spectrophotometer using the procedure of Medlin *et al.* (1969). The structural formulae, calculated on the basis of a total cation

balance of +24, are also given. It is evident that a considerable deficiency in Si is present in both varieties of the Fengtien garnets. Some Al and Ti ions, if available, are assumed to fill the tetrahedral positions. Al, Cr, and Fe³⁺ ions are placed in octahedral positions, while the remaining divalent metal ions, Fe²⁺, Mn, Mg, and Ca, are situated in the interstices within the Si-Al network. The small amount of Na is neglected, as it probably arises from traces of impurites. The number of ions in the octahedral positions is usually close to 2.0; for uvarovite and grossular the calculated ion ratios in octahedral sites are Al: Cr = 5:3 and Al: $Fe^{3+} =$ 9:1 respectively. It means that about one-tenth of the Al, 0.185, is substituted by Fe³⁺ in octahedral sites in grossular. In uvarovite more than one-third of the Al, 0.733, is substituted by Cr with only small Fe³⁺ substitution. The intersticial ions are usually

TABLE I. X-ray powder diffraction data for uvarovites and grossular

1		2		3		4		
d (Å)	Ι	$d(\text{\AA})$	I	d (Å)	I	d(Å)	Ι	hkl
_				_		4.24	15	220
		_		_		3.205	6	321
2.973	55	2.975	m	2.981	52	2.999	70	400
2.655	100	2.659	S	2.666	100	2.684	100	420
2.529	5	2.535	w	2.541	8	2.557	20	332
2.423	15	2.428	m	2.433	23	2.449	55	422
2.328	11	2.301	m-w	2.337	16	2.352	25	431
2.167	10	2.173	m-w	2.175	12	2.191	15	521
2.099	2	_		2.104	3			440
1.926	15	1.931	m	1.933	20	1.946	20	611
1.876	1	1.885	m-w	1.884	4	1.896	10	620
_						1.845	8	541
1.714	8	1.719	m-w	1.719	7	1.732	8	444
1.645	18	1.654	m	1.652	17	1.664	25	640
1.586	32	1.594	s	1.591	36	1.603	25	642
1.483	8	1.499	m-w	1.488	8	1.500	10	800
1.460	2	_		1.467	2	1.477	6	741
1.419	1	_		1.420	1	1.432	8	653
_		_		_		1.414	6	822
1.326	7	1.335	m	1.331	9	1.341	15	840
1.294	10	1.304	m	1.299	12	1.309	15	842
1.264	7	1.274	m	1.269	6	1.279	15	664
1.198	1	1.2058	w	1.2037	3	1.211	8	844
1.1017	10	1.1140	m	1.1048	9	1.1142	15	10.4.0
1.0826	7	1.0922	m	1.0862	8	1.0955	15	10.4.2
1.0479	4	1.0575	m	1.0506	6	1.0607	8	880

1. Grossular from Fengtien, eastern Taiwan.

2. Uvarovite from the Bushveld Complex, Transvaal, South Africa. (Analyzed by J. J. Frankel, sample No. 7.)

3. Uvarovite from Fengtien, eastern Taiwan.

4. Synthetic uvarovite (ASTM Card no. 11-696).

w = weak m = medium s = strong

 TABLE II. Chemical analyses and formulae of uvarovite and grossular from Fengtien

	Uvarovite	Grossular
SiO ₂	34.02	36.82
TiO ₂	0.88	0.00
$Al_2\bar{O}_3$	15.48	22.09
Cr_2O_3	11.63	0.00
$Fe_2O_3^*$	2.48	4.25
MnO	1.93	0.63
MgO	0.50	0.13
CaO	32.37	35.72
Na ₂ O	0.18	0.17
K ₂ Õ	0.00	0.00
H_2O^+ †	0.52	0.18
Total	99.98	99.99

Ti	0.053	3 000	0.000 3.00
Al	0.236) 5.000	0.180
Al	1.219)	1.815
Cr	0.733	2.000	0.000 2.000
Fe ³⁺	0.048	}	0.185)
Fe ²⁺	0.100	ו	0.060
Mn	0.130		0.041
Mg	0.059	3.053	0.015 } 3.048
Ca	2.764		2.932
Na	0.028]	0.025

* Total Fe as Fe₂O₃.

Grossular

Andradite

 \dagger H₂O⁺ = weight loss from 110 to 1100 °C.

60.9

2.4

close to 3.0; it is evident that Ca, 2.932, constitutes the main intersticial ion of grossular, while much more substitution of Fe^{2+} , Mn, and Mg for Ca is seen in the uvarovite.

90.8

9.2

The mole percentage end members were calculated on the basis of total cation numbers = 2 in the octahedral sites. The results are listed in Table II. It shows that the Fengtien uvarovite is mineralogically an isomorphous mixture of end members with a $Uv_{36.7}Gro_{60.9}And_{2.4}$ composition, while grossular has a composition of $Gro_{90.8}And_{9.2}$. The compositions established by the determinative diagrams of Winchell (1958) using refractive index n = 1.782, specific gravity SG = 3.702 and unit cell edge a = 11.912 Å for uvarovite is $Uv_{40}Gro_{60}$ and n = 1.746, SG = 3.646 and a = 11.866 Å for grossular is $Gro_{90}And_{10}$. They are quite consistent with each other.

 TABLE III. Physical properties of uvarovites and grossular

	1	2	3	4
Refractive index	1.734	1.746	1.782	1.860
Specific gravity	3.594	3.646	3.702	3.848
Unit cell edge (Å)	11.851	11.866	11.912	12.000

1. Synthetic end member grossular (Skinner, 1956).

2. Grossular from Fengtien, eastern Taiwan.

3. Uvarovite from Fengtien, eastern Taiwan.

4. Synthetic end member uvarovite (Skinner, 1956).

Physical properties Table III gives the physical data of uvarovites and grossulars. Uvarovite is deep-green to emerald-green in colour and translucent to opaque. The crystals are small, generally less than 0.7 mm in diameter, and with dodecahedral crystal form. Under the binocular microscope euhedral uvarovite crystals with dark chromite cores are commonly observed. Uvarovite is green to pale-green under a single nicol, and the green colour becomes deeper towards the chromite core. It is always anisotropic, with pale grey to grey interference colour. A typical sectorial extinction which probably results from the sector twins of the uvarovite crystals is often marked; distinct sector twins composed of six pyramids with vertices meeting at the centre of the crystal can be observed occasionally.

The specific gravity of the uvarovite measured by pyknometry is 3.702, slightly larger than that of the grossular, 3.646, but is rather smaller than the value, 3.848, for an ideally pure uvarovite. The differences in specific gravity are obviously due to variations in Cr_2O_3 content, and partly due to variations in the amount of iron.

The refractive indices of the uvarovite and grossular measured by immersion method are 1.782 and 1.746 respectively; both are lower than the value 1.860 for the uvarovite end member indicating a linear relationship between refractive index and Cr_2O_3 content in the ugrandite series.

The unit cell dimensions of the uvarovites and grossulars calculated from X-ray diffraction data are 11.912 and 11.866 Å respectively; both are within the value 12.000 Å for the uvarovite end member and 11.851 Å for the grossular end member (Skinner, 1956). Again this is related to the Cr^{3+} content, because the replacement of Al^{3+} (ionic radius 0.67 Å) by Cr^{3+} (0.755 Å) in octahedral co-ordination must expand the lattice of grossular as the composition approaches that of uvarovite.

Trace element chemistry. In an attempt to characterize the differences in the trace elements content between uvarovite and grossular, semi-quantitative emission spectrographic analyses for twenty-six minor and trace elements were made on the Fengtien garnets. Table IV lists the results for

 TABLE IV. Semi-quantitative spectrographic analyses, in ppm, for minor and trace elements in warovite and grossular, Fengtien

	Uvarovite	Grossular	
Ag	5	1.5	
Au	<1	<1	
В	500	100	
Ba	< < 5	<5	
Be	>>>1000	2	
Bi	< 0.1	< 0.1	
Cd	300	30	
Co	500	< < < 0.2	
Cr	>>>5000	50	
Cu	< < 0.5	<<<0.5	
Ge	0	< 0.1	
In	200	100	
La	>1000	100	
Мо	< < < 0.2	< < < 0.2	
Nb	<5	<5	
Ni	30	0.8	
Pb	< < 0.5	< < 0.5	
Sb	>10000	< 100	
Sc	30	10	
Sn	0	0	
Sr	200	500	
v	200	400	
W	< 20	< 20	
Y	100	0.2	
Zn	5000	500	
Zr	1	1	

representative samples. Generally, uvarovites are significantly enriched in Cr, Be, Co, Y, Sb, and La over grossulars, relatively enriched in Ni, Cu, Cd, Zn, B, Ag, Sc, and In, and impoverished in Sr, V, Ba, and Ge; Au, Bi, Mo, Nb, Sn, W, and Zr show no significant change. The factors resulting in variations in elemental abundances between uvarovite and grossular may be due to ion substitution and occlusion of chromite during mineral growth, although the uvarovite samples were carefully selected to exclude under a binocular microscope any black stain of chromite. Some tremolite and the serpentine mineral lizardite, which occur close to the S-3 adit, with mesh texture and blackish-green appearance also exhibit a very high abundance in Be, Cr, and Sb. This result shows that the minor and trace elements in the uvarovite could have been contributed by the relict chromite and the hydrothermal solution derived from the serpentinites.

Beryllium (ionic radius 0.41^{IV} Å) is concentrated

in uvarovite (> 1000 ppm) relative to grossular (2 ppm) and apparently replaces the silicon ion (0.40 Å). Chromium (0.755 Å) is enriched in uvarovite (11.63 %) relative to grossular (50 ppm). It apparently replaces Al ions in octahedral site. The other elements are thought to replace octahedral cations or exist among the intersticial ions.

Other data pertinent to the structure of uvarovite

Zoning in uvarovite. Uvarovite crystals with a black chromite core were analysed with an automated ARL-SEMQ electron microprobe to obtain information on inter-element relationships in the sectioned uvarovite crystals. Groups of crystals were embedded in epoxy and ground to expose the centres of crystals. An accelerating potential of 20 kV, beam diameter 2-5 μ m, specimen current 0.01 μ A on brass, counting interval 20 seconds were used as operating conditions. For all elements, count readings were corrected for matrix effects using Bence-Albee data reduction method. Synthetic compounds and natural minerals such as chromite, diopside, rhodonite, and wallastonite were used as standards.

TABLE V. Zoning of uvarovite

	R1		R3	CR	Core
			105		
SiO ₂	39.35	38.78	39.58	38.38	26.32
TiO ₂	1.17	0.96	1.11	1.02	0.73
Al ₂ Õ ₃	12.03	11.62	10.75	9.72	11.69
Cr_2O_3	10.30	11.36	11.83	12.86	20.13
FeŌ	1.56	1.46	1.52	1.60	9.05
MnO	1.00	1.01	0.84	0.77	1.90
MgO	0.10	0.02	1.68	1.02	0.03
CaO	34.28	34.44	33.62	33.92	24.91
Total	99.79	99.65	100.93	99.29	94.76

Table V lists the results of chemical analyses from outer rims of the crystal R1, R2, and R3 towards the rim of the core CR and the centre of the core. They show that Cr, Fe, and Mn are enriched in the core region where Si, Ca, and Ti concentrations are low. Al and Mg concentrations fluctuate slightly throughout the entire region. Cr and Fe contents increase towards the centre region but the variation is not significant until the rim of the core region is reached. Si, Ca, and Ti concentrations also change abruptly at the core region. The total major chemical constituents of the core amounted to only 94.76 %, indicating that it may contain other minor and trace elements. This might be the reason why uvarovite in the Fengtien area is enriched in minor and trace elements (Table IV).



FIG. 4. Scanning electron micrographs of uvarovite crystals on a matrix of diopside and tremolitic asbestos from S-3 adit, Fengtien. Showing the occurrence of euhedral uvarovites intergrown with tremolitic asbestos (A) and with diopside beneath (A and B). Euhedral uvarovites showing cube and tetrahexahedron (C, centre); dodecahedron and hexoctahedron (D, centre); trapezohedron (D, upper right); cube and tetrahexahedron (D, lower right). Some uvarovites have been deeply etched.

Occurrence and morphology of uvarovite under scanning electron microscope. The fine structure, morphology, and association of the uvarovites are illustrated in scanning electron micrographs in fig. 4. Emerald-green euhedral uvarovite crystals are intergrown with white elongate tremolitic asbestos and pale-green prismatic diopside crystals. The crystal forms of uvarovite are mainly modified dodecahedra (see fig. 4).

The origin of uvarovite and grossular

Although geological and mineralogical studies of the Fengtien nephrite deposits have been carried out by many investigators in the past (Huang, 1969; Tan *et al.*, 1978; Lee and Yui, 1980; Tan *et al.*, 1981), the mechanism of serpentinization and the mineralization of the deposits is still inadequately understood. The present study provides some information on the paragenesis of the deposits.

The authors' belief is that both uvarovite and grossular were formed at the early stage of mineral-

ization; however, field evidence and chemical data reveal that the two species of garnets have formed in different ways. Grossular resulted from pneumatolysis associated with the intrusion of ultramafic rocks, whereas uvarovite is evidently a replacement product of the relict chromite which is the main opaque mineral in the original ultramafic rocks.

From the chemical composition of uvarovite, its formation requires the addition of Ca and Si; these elements may be provided partly by the hydrothermal solutions which are rich in these elements, and partly derived from the wall rocks during the process of serpentinization, since the serpentinization of the ultramafic rocks in the Fengtien area was accompanied by the migration of such elements as Si, Al, and Ca, from the schist and the ultramafic rocks (Yui and Lee, 1980).

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[Editor's note added in proof. On the basis of the end-member molecules given in Table II the mineral described in this contribution as uvarovite is, in fact, chromian grossular.]