

STANNIAN ANDRADITE FROM "DAVIB OST", SOUTH WEST AFRICA

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ABSTRACT

Green andradite garnet, containing up to 4.58% Sn in octahedral co-ordination, is described from an occurrence near Usakos, South West Africa. The andradite is believed to have formed from grossular as a result of pneumatolitic activity associated with nearby pegmatites. These garnets contain between 94.4 and 98.5% of the andradite molecule and are among the very few recorded natural garnets found to contain more than traces of Sn.

Nine andradite grains were analyzed and their physical and optical properties determined. Stepwise multilinear regression analysis was applied to the data, which *inter alia* show that the degree of replacement of Fe³⁺ by Sn is reflected by systematic variations in the value of refractive indices and unit-cell dimensions. Equations obtained by the regression analyses show the relationship of the Sn, Mn and Fe²⁺ in these garnets with unit-cell and refractive index values, and *vice versa*. The refractive index can in turn be predicted from unit-cell value, and calculated density, but these equations can only be applied within the range of the grains investigated.

INTRODUCTION

Synthetic tin-bearing germanate garnet has been reported by Geller *et al.* (1960), but the presence of tin in natural garnets, other than in trace amounts, is quite uncommon. Saksela (1951) described an andradite-grossular containing 1.4% SnO₂. Hellwege (1956) reported 0.3% SnO₂ in andradite from Pitkäranta. Dađák & Novák (1965) reported 1.07 to 1.36% SnO₂ in an andradite-grossular garnet from Plavno, Czechoslovakia, and Mulligan & Jambor (1968) described a green andradite containing 0.9% SnO₂ in skarns in the Cassiar District, British Columbia. In this paper a green andradite garnet, containing up to 5.8% SnO₂, is described.

GEOLOGIC SETTING

The stannian andradite has been identified

in a calc-silicate band occurring in the dominantly schistose succession of the Khomas Stage, Damara Formation on the farm 'Davib Ost' near Usakos, South West Africa (Fig. 1). 'Davib Ost' is situated to the north of the village of Usakos, and the tin-bearing garnet occurs approximately 1 km southwest of the precipitous slopes of the Erongo Mountains. The geology of this area has been described by Frommurze *et al.* (1942), who have shown that the highly folded Precambrian Damara metasediments of central South West Africa have suffered intrusions by two ages of granite, the older of which gave rise to numerous

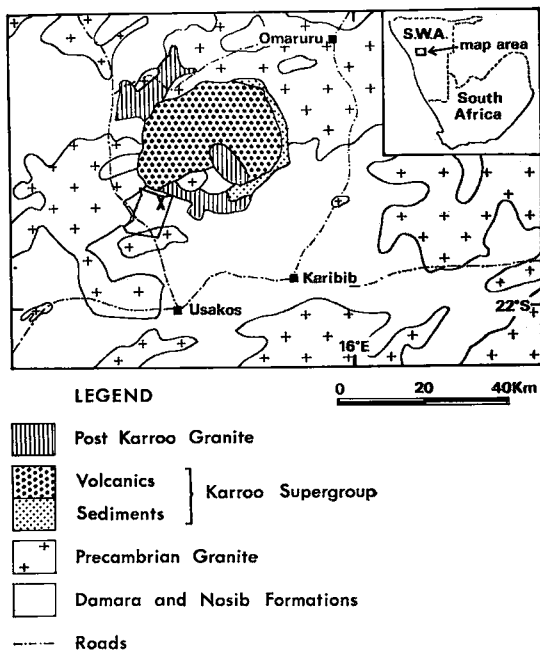


FIG. 1. Geological map of the area north of Usakos, S.W.A. The Sn-containing andradite occurrence is marked 'X' and the farm 'David Ost' is surrounded by a solid line. (Geology after 1: 1,000,000 map of S.W.A., Geol. Surv. S. Africa, 1963).

pegmatites, many of them containing cassiterite, tantalite, wolframite, tourmaline, and lithium minerals. On 'Davib Ost', stannian garnet occurs in metasediments within a triangular area covering some 500 square metres and defined by three intersecting pegmatite dykes each approximately 2-3 metres wide.

Apart from the pegmatites, outcrops are scarce, and attention was first drawn to the area by the presence of attractive green garnet crystals and aggregates among the surface rubble. In 1937 a trench, since filled in, was excavated to obtain more of the garnet, which was in demand as a semi-precious stone and as attractive mineral specimens, and it was found that the garnet-bearing horizon could be traced on strike for some 13 metres. Specimens obtained from the trench rubble and from the collection of Mr. E. Brusius of Usakos showed that the tin-bearing garnet occurs as encrustations of dodecahedral crystals up to 2 cm thick along the contact between a layer of massive granular vesuvianite and massive pink to cream-coloured grossular ($a = 11.87\text{\AA}$). It forms linings to drusy cavities within the vesuvianite layer and discrete crystals in small silicate-cemented breccia zones. Replacement of the massive grossular by the tin-bearing andradite is indicated by the development of wart-like 2 cm-high growths of green andradite, from the boundary between vesuvianite and grossular into the latter. Well-developed dodecahedral crystals of andradite are common in the rubble and range in size from microscopic dimensions to 0.5 cm.

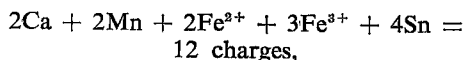
GENESIS

Grossular and vesuvianite associated with the andradite are presumed to have formed from calcareous metasediments by contact meta-

morphism associated with granite intrusion. Fe and Sn ions necessary for the growth of stannian andradite at the expense of grossular are most likely to be sought in later pneumatolytic emanations from nearby pegmatites. However, the juxtaposition of grossular and andradite without garnet of transitional composition remains unexplained and rather perplexing.

COMPOSITION

Qualitative electron microprobe analyses of the stannian andradite showed Ca, Fe, Mn, Sn, and Si to be the only cations present. Quantitative microprobe analyses of nine grains were carried out using a synthetic glass standard for the determination of Ca, Mn, and Sn, and an analyzed silicate mineral for the determination of Si and Fe. The acceleration potential used was 25 kV and the sample current $0.02\mu\text{A}$ on brass. The raw data were corrected for dead time, drift, absorption, fluorescence, and atomic number effects using the computer program of Beeson (1967). The results obtained are presented in Table 1. The major difference among the nine analyzed garnets is SnO_2 which ranges from 0.40 to 5.82 weight per cent. Unlike andradite analyses such as those reported by Deer *et al.* (1962), aluminum is conspicuous by its absence. Calculation of the mineral formulae on the basis of 12 oxygens was not possible, as the valence state of Fe could not be determined with the electron microprobe. Calculation to a total of 8 cations showed Si to be systematically slightly high. The cations Ca, Mn, Sn, Fe^{2+} , and Fe^{3+} were therefore calculated to total 5, and Si_5O_{12} stoichiometry was assumed. To divide Fe into ferrous and ferric, the following two equations were employed (M. H. Hey, personal communication):



as the 5 cations must equal 12 positive charges between them. Solving the above gives:

$$\text{Fe}^{3+} = 2 - 2\text{Sn},$$

assuming the Sn to be tetravalent and the Mn to be divalent. The calculated atomic proportions are given in Table 2.

PHYSICAL PROPERTIES

The majority of the andradite grains studied are green, but variations in shade are apparent, and gradations in colour from green to brown are present in single grains, which may show a

TABLE 1. RESULTS OF CORRECTED ELECTRON MICROPROBE ANALYSES OF NINE ANDRADITE GRAINS (wt. %)

Grain no.	1	2	3	4	5	6	7	8	9
CaO	30.43	30.78	31.37	30.70	32.21	31.47	30.99	31.07	31.09
FeO	2.37	2.12	3.06	1.97	1.68	3.02	2.78	1.36	4.26
MnO	0.57	0.09	0.12	0.14	0.10	0.52	0.78	0.59	0.07
Fe_2O_3	27.99	28.43	27.18	28.35	28.50	25.68	26.30	30.37	24.50
SnO_2	2.16	1.71	1.61	1.67	2.39	4.83	4.07	0.40	5.82
SiO_2	36.95	35.80	35.88	36.26	36.26	35.40	35.87	36.61	36.64
Total	100.07	98.93	99.22	99.09	101.14	100.92	100.79	100.40	102.38

TABLE 2. CALCULATED ATOMIC PROPORTIONS AND MOL PER CENT ANDRADITE, CALDERITE, AND SKIAGITE OF THE NINE GRAINS INVESTIGATED

Grain no.	Atomic Proportions					Si+O	Mol % and.	Mol % cald.	Mol % sklagite		
	Ca	Mn	Fe^{2+}	Fe^{3+}	Sn						
1	2.860	0.042	0.098	0.076	0.076	1.848	3	12	95.4	1.4	3.2
2	2.898	0.007	0.096	0.060	0.060	1.880	3	12	96.6	0.2	3.2
3	2.929	0.009	0.062	0.056	0.056	1.888	3	12	97.6	0.3	2.1
4	2.903	0.010	0.086	0.059	0.059	1.882	3	12	96.8	0.3	2.9
5	2.955	0.007	0.038	0.082	0.082	1.836	3	12	98.5	0.2	1.3
6	2.910	0.038	0.052	0.166	0.166	1.668	3	12	97.0	1.3	1.7
7	2.882	0.058	0.061	0.141	0.141	1.718	3	12	96.0	1.9	2.0
8	2.873	0.043	0.084	0.014	0.014	1.972	3	12	95.8	1.4	2.8
9	2.887	0.005	0.108	0.201	0.201	1.598	3	12	96.2	0.2	3.6

* Fe^{2+} replacing Ca ** Fe^{2+} in coupled substitution with Sn^{4+} , replacing Fe^{3+} . assumed Si and O.

TABLE 3. PHYSICAL CONSTANTS OF THE NINE GARNET GRAINS INVESTIGATED

Grain no.	$\alpha(\text{\AA})^*$	$D(\text{calc})$ g/cc	Refractive index*	Vickers micro-indentation hardness			Mohs' hardness (calc)	Reflectance (μ)			
				average	s.d.†	no. of determinations		435	550	590	626
1	12.0658(8)	3.895	1.875(3)	1445	114	5	7.28	8.5	15.0	8.2	1.0
2	12.0673(5)	3.883	1.880(2)	1345	72	7	7.14	8.5	15.0	8.5	1.0
3	12.0631(8)	3.881	1.884(2)	1536	107	3	7.50	8.5	15.0	8.2	1.0
4	12.0664(3)	3.881††	1.885(3)	1349	96	6	7.11	8.5	15.0	8.0	1.0
5	12.0694(8)	3.884	1.875(3)	1253	83	6	6.92	8.0	14.5	8.0	1.0
6	12.0741(9)	3.924	1.864(2)	1432	63	6	7.28	8.5	15.0	8.5	1.5
7	12.0721(8)	3.918	1.865(3)	1338	42	4	7.09	8.0	15.0	8.0	1.0
8	12.0577(8)	3.872	1.886(2)	1338	97	3	7.09	8.0	15.0	8.0	1.0
9	12.0860(4)	3.932	1.865(4)	1448	86	4	7.32	7.5	14.0	7.5	1.0

*Number in brackets refers to \pm value of last digit

†calculated estimate of standard deviation

††Experimentally determined value of 3.86 found by using the method of Jahns (1939)

zonal structure. One sectioned crystal was found to have a brown outer zone, followed by a green zone and an olive-coloured core. Higher tin contents are associated with greener crystals; for example, a grain having atomic proportions of 0.04 Mn and 0.01 Sn was dark yellowish brown 10YR4/2 (rock colour chart, Geol. Soc. Amer.), whereas a grain having 0.01 Mn and 0.20 Sn was moderate green 5G5/6. Grains showing colours intermediate between these two were found to correspond to moderate olive brown 5Y4/4, light olive brown 5Y5/6, pale olive 10Y6/2, and moderate yellowish green 5GY7/6. The association of green colour and increased tin content was also observed by Mulligan & Jambor (1968) in the garnets described by them.

In thin section the andradite is colourless to pale green, isotropic, and relatively free from inclusions. (However, microprobe analyses confirmed that tin-bearing inclusions are absent). Refractive indices of the nine analyzed grains were determined by the immersion method using sodium light (Table 3). Indices of the liquids were checked immediately after use with a Leitz-Jelley refractometer.

Reflectances of the same nine grains were determined on polished sections at four wavelengths using a Leitz Ortholux microscope fitted with an MPV photometer. Tungsten carbide, calibrated by the firm Carl Zeiss, Göttingen, was employed as a standard. The values obtained are listed in Table 3.

Hardness measurements were conducted on the nine analyzed grains by means of a Leitz Miniload hardness tester using a 30-second indentation period with a 25g weight. Mohs' hardness values were calculated from the Vickers hardness values using the formula of Young & Millman (1963). Both sets of hardness values are presented in Table 3.

The density of analyzed grain no. 4 was determined with Clerici solution using the method of Jahns (1939). The densities of all analyzed grains were calculated from their unit-cell parameters and chemical compositions using the for-

mula $D = (GN)/(10^{-24}AV)$, where G = gram formula weight in grams, N = number of formulas per unit cell, A = Avogadro's number, and V = cell volume. These results, together with the single experimentally-determined density, are shown in Table 3.

The nine analyzed grains were investigated using a 114.6mm Debye-Scherrer camera, Ni-filtered Cu radiation, and silicon as an internal standard. Theta values, corrected relative to the internal standard, were processed by means of a self-indexing and unit-cell refinement program (Appleman & Evans 1968). The unit-cell values appear in Table 3. Qualitatively, the nine diffraction patterns are similar, and only that of grain no. 9, being the richest in Sn, is given in Table 4.

DISCUSSION

The question as to which element is replaced by Sn in the andradite structure requires consideration. The possibility that the high-valence cations Ti, Zr, and Sn are present in tetrahedral coordination in natural and synthetic garnets has been considered by Milton *et al.* (1961) in their study of the zirconium garnet, kimzeyite, and by Geller *et al.* (1960) for synthetic garnet structures. These authors concluded that Sn is unlikely to enter the tetrahedral positions. On the other hand, Dadák & Novák (1965), as well as Ringwood (1955), favour the substitution of anionic complexes $(\text{SiO}_4)^{4-}$ by $(\text{SnO}_4)^{4-}$. However,

TABLE 4. X-RAY DATA OF GARNET GRAIN 9

hkl	d_{obs}	d_{calc}	I/I_0	hkl	d_{obs}	d_{calc}	I/I_0
220	4.270	4.2731	5 α	840	1.3515	1.3513	1 α
400	3.016	3.0215	9 α	842	1.3190	1.3187	4 α
420	2.702	2.7025	10 α	664	1.2887	1.2884	4 α
332	2.582	2.5768	2 α	10.4.0	1.1222	1.1222	4 α_1
422	2.466	2.4671	9 α	10.4.2	1.1035	1.1033	3 α_1
431	2.3691	2.3703	4 α	880	1.0686	1.0683	4 α_1
521	2.2075	2.2066	4 α	12.2.2	0.98008	0.98031	5 α_1
611	1.9617	1.9606	5 α	10.8.4	0.97950	0.98031	3 α_2
444	1.7444	1.7445	2 α	10.8.4	0.90087	0.90084	2 α_1
640	1.6753	1.6760	6 α	12.6.2	0.89122	0.89100	3 α_1
642	1.6142	1.6151	10 α	12.8.2	0.83038	0.83007	2 α_1
800	1.5109	1.5108	3 α		0.82999	0.83007	1 α_2
822	1.4263	1.4244	1 α	14.4.2	0.82243	0.82235	5 α_1
					0.82231	0.82235	3 α_2

TABLE 5. RESULTS OF STEPWISE MULTILINEAR REGRESSION ANALYSIS ON STANNIAN ANDRADITE

Chemistry in terms of physical properties		% Variance explained	Standard error of $x(y)$
EQUATION (with standard error of coefficients indicated)			
Sn	$= -44.5577 + (4.2057 \pm 0.9253)\alpha - (3.2556 \pm 0.8197)\eta$	97.1	0.0119
Fe ²⁺	$= -33.5916 + (2.4514 \pm 1.8506)\alpha + (2.1761 \pm 1.6393)\eta$	24.4	0.0238
Mn	$= 50.1253 - (3.6315 \pm 0.9412)\alpha - (3.3440 \pm 0.8337)\eta$	74.0	0.0121
Physical properties in terms of chemistry			
α	$= 12.0564 - (0.0948 \pm 0.0261)\text{Mn} + (0.1259 \pm 0.0088)\text{Sn} + (0.0404 \pm 0.0226)\text{Fe}^{2+}$	97.8	0.0015
η	$= 1.8878 - (0.1051 \pm 0.0447)\text{Mn} - (0.1360 \pm 0.0150)\text{Sn} + (0.0416 \pm 0.0387)\text{Fe}^{2+}$	94.9	0.0026
Physical properties in terms of physical properties and chemistry			
η	$= 2.4467 - (0.4132 \pm 0.1121)\rho + (0.0861 \pm 0.3110)\alpha$	90.0	0.0033

In this table Fe²⁺ refers to that replacing Ca

substitution of Si by Sn in the garnets we investigated is unlikely because Si values are already slightly in excess (Table 1). Furthermore, in these garnets Sn and total Fe show a good inverse correlation (-.93). Thus, the one clearly significant substitution is $\text{Sn} \rightleftharpoons \text{Fe}$, and $\text{Fe}^{2+}\text{Sn} \rightleftharpoons 2\text{Fe}^{3+}$ is most likely. Mulligan & Jambor (1968) also favour this type of substitution. As $\text{Fe}^{3+} + 2\text{Sn} = 2$, there must be in place of the 6-fold coordinated Fe³⁺ as many Fe³⁺ atoms as there are Sn—the rest of the Fe³⁺ and the Mn replacing Ca in 8-fold coordination (M. H. Hey, personal communication). Thus all Sn and an equal amount of the Fe³⁺ are assumed to occur in 6-fold coordination.

Attention is drawn to the purity of the andradite molecule in which the Sn and Mn ions occur, because Al is conspicuous by its absence, and only very little of the calderite ($\text{Mn}_3^{2+}\text{Fe}_3^{3+}\text{Si}_5\text{O}_{12}$) and skiagite ($\text{Fe}_3^{3+}\text{Fe}_3^{3+}\text{Si}_5\text{O}_{12}$) molecules are present (see Table 2). The garnet described by Mulligan & Jambor (1968) consists of 99.95% andradite molecule, although they did not take into consideration the presence of a small amount of calderite and skiagite. The purest andradite quoted by Deer *et al.* (1962, Table 15, anal. 2) consists of 94.2% andradite molecule, whereas our nine andradites contain between 95.4 and 98.5% of the andradite molecule, though the presence of some hydrogarnet is not ruled out in view of the slight excess in SiO₂ values.

Inspection of Tables 2 and 3 reveals that reflectance, micro-indentation, and Mohs' hardness values of the grains investigated do not seem to be affected perceptibly by variations in their chemical composition. However, trends of

variation are present between other physical properties and the chemical compositions of these andradites.

To put this on a more quantitative basis, a correlation matrix of the physical properties of unit cell value (a) and refractive index (n), as well as atomic proportions of the cations partaking in substitutions, *i.e.* Mn, Sn and Fe²⁺, was calculated for the nine grains. Only Fe²⁺ replacing Ca was considered. Sn contents correlate well with the physical properties of unit-cell size (.95) and inversely with refractive index (-.93). There is also a good inverse correlation between unit-cell size and refractive index (-.82).

Following the calculation of the correlation matrix, computerized stepwise multilinear regression analysis was applied to the data. The significant equations, shown in Table 5, were restricted to first-order equations so as to conform to the mixture law generally accepted for garnets (M. H. Hey, personal communication). The fits are, with a few exceptions, remarkably good, as can be seen from the high percentages of variance explained in most instances, and the low standard deviations obtained. The equations derived make it possible to relate the physical properties to the substituting ions. It should be emphasized, however, that these equations only apply to the range of compositions investigated here. Extrapolation to other compositions is not recommended before further data are available and the equations are suitably refined. We nevertheless have attempted some limited extrapolations (Table 6, column 5) fairly successfully.

In all the equations shown, the degree of accuracy can be estimated from two standard de-

TABLE 6. PROPERTIES OF SYNTHETIC ANDRADITE, Sn-BEARING ANDRADITES AND IDEAL ANDRADITE DEDUCED FROM THIS STUDY

Physical property	Synthetic andradite (Skinner 1956)	Low-tin andradite, Table 2, no. 8 (Numerical values from Table 3, no. 8)	High-tin andradite, Table 2, no. 9 (Numerical values from Table 3, no. 9)	Ideal andradite (this study)
a	12.048	12.0577 ± 0.0008	12.0860 ± 0.0004	12.056*
n	1.887 ± 0.002	1.886 ± 0.002	1.865 ± 0.004	1.888 ± 0.005*
$\rho(\text{calc})$	3.859 ± 0.001	3.872	3.932	3.851†

*Calculated from Table 5.

†Calculated from unit-cell value (*) and ideal chemical composition.

viations at the 95% confidence limit. For example, in the fourth equation:

Unit cell = $12.0564 - 0.0948 \times \text{at. prop. Mn} + 0.1259 \times \text{at. prop. Sn} + 0.0404 \times \text{at. prop. Fe}^{2+} \pm 2 \times 0.0015$. Thus, for example, for grain 1, $a = 12.0659 \pm 0.0030$, which is in excellent agreement with the experimentally-determined value of 12.0658 \AA . Most remarkable is the very strong effect of the small amount of Sn (with a range of only 0.187 atomic proportion, i.e. 4.27 weight %) on most of the physical properties of these otherwise almost pure andradite garnets.

Skinner (1956) reported on the physical properties of end-members of the garnet group, and, in view of the purity of the andradite molecule in the minerals under discussion, the values determined for high- and low-tin garnets are compared with those of Skinner (Table 6). In column 5 of Table 6, the physical properties of ideal 100% pure andradite as deduced from our observations, are compared with those predicted by Skinner (column 2). McConnell (1966), using the ionic radii of Ahrens, calculates for andradite $a = 12.037 \text{ \AA}$. Novak & Gibbs (1971), using the radii of Shannon & Prewitt (1969), calculate $a = 12.058 \text{ \AA}$. Our value of 12.056 \AA falls between that of Skinner (1956) and Novak & Gibbs (1971). The replacement of $2\text{Fe}_{\text{VI}}^{3+}$ by $\text{Sn}_{\text{VI}}^{4+} + \text{Fe}_{\text{VI}}^{2+}$, as proposed in this paper, leads to an increase in the value of a due to the larger ionic radii of $\text{Sn}_{\text{VI}}^{4+}$ (0.69) and $\text{Fe}_{\text{VI}}^{2+}$ (0.77) as compared to $\text{Fe}_{\text{VI}}^{3+}$ (0.645) (values of Shannon & Prewitt).

Fleischer (1937), by extrapolation of measurements on natural garnets, obtained 3.835 for the density of andradite, which differs from the value given by Skinner (1956), and from our calculated value (Table 6, column 5). However, our calculated value agrees closely with that of Skinner (1956).

ACKNOWLEDGMENTS

The authors wish to record their indebtedness to the following: Mr. Tony Marshall who drew attention to the tin-bearing garnet, Messrs. E. J. Poole and E. Brusius who made a visit to "Davib Ost" possible, and to Drs. I. Copelowitz and J. P. R. de Villiers who provided most valuable assistance in the mathematical treatment of the data presented. This paper is published by kind permission of Dr. R. E. Robinson, Director General, National Institute for Metallurgy, Johannesburg. They are also greatly indebted to Dr. M. H. Hey, British Museum, for many helpful comments which improved the manuscript. However, the authors assume full respon-

sibility for the methods used and opinions expressed in this paper.

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Manuscript received January 1975, emended March 1975.