Tin-containing andradite from Plavno mine in the Krušné Hory Mts., Czechoslovakia

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Summary. Stannian andradite occurs with pyroxene and carbonates, with blende and pyrite as accessories in a skarn deposit in the Plavno mine, Krušné Hory Mts., NW. Bohemia. The green crystals are rhombic dodecahedra up to 3 cm in size. Sp. gr. 3·78; *n* 1·879; *a* 12·079 ± 0·002 Å. Quantitative chemical and spectrographic analyses are given; the composition is $(Ca_{2\cdot96}Mg_{0\cdot04}Mn_{0\cdot02})_{3\cdot02}$ $(Fe^{3+}_{1\cdot79}Al_{0\cdot18})_{1\cdot97}$ $(Si_{2\cdot95}Sn_{0\cdot04})_{2\cdot99}O_{12}$. The content of tin ($SnO_2$ 1·07 %) is isomorphously bound in the lattice, and according to crystallochemical calculations the entrance of tin into the garnet lattice is most probably due to substitution of SnO_4^{4-} for SiO_4^{4-}. The presence of tin in the andradite shows that this element was already present in the metasomatic solutions during the process of skarnization.

IN the course of an investigation of the Ni–Co–Bi formation in the Plavno mine, Krušné Hory Mts., Erzgebirge, NW. Bohemia, one of the authors found in the skarn deposit a green garnet resembling uvarovite. Spectrographic analysis, however, revealed the presence of a considerable amount of tin, and the authors identified the mineral as andradite rich in tin.

Garnets of andradite–grossular composition rich in tin are scarce. A higher content of tin has been detected only in andradite from the cassiterite–polymetallic deposit Pitkäranta (M. Saksela, 1951); the content of tin in this garnet is similar to that in the andradite from Plavno. As will be shown, andradite from Plavno mine occurs in a skarn body in the absence of any other tin minerals. Optical investigation also proved that the garnet contains no inclusions of tin-minerals; the tin must therefore be present in the garnet lattice, which is very interesting from the viewpoint of the geochemistry of this element and the explanation of its bonding is important for the general discussion of tin distribution in silicates.

Occurrence. Stannian andradite occurs as a very abundant component of the approximately 2 m thick skarn body, which was crossed by the north-bound crosscut in the deposit Plavno at a depth of 330 m. The skarn body follows the contact of the 'rudohorská' (Ore Mts.) granite of the Vykmanov massif and mica schists of the Jáchymov series. The occurrence described is one of the three blind skarn bodies that were discovered in the Plavno mine by mining works. This skarn and its geological position is discussed by J. Chrt and J. Strnad (1964). In addition to andradite, the skarn contains pyroxene and carbonates. In contrast to other skarn lenses in the Plavno mine (M. Kvaček and F. Novák, 1963), the skarn with tin-containing andradite is very poor in minerals of the sulphide stage; blende and pyrite were found only as accessories. The presence of reddish-brown blende was ascertained by spectrographical analysis. In addition to Zn and considerable amounts of Fe and Cd traces of Cu, In, Mn, Sn, Pb, Ag were detected.

In thin sections the mineral is present in the form of light-green aggregates of crystals. The cores of the larger individuals are usually isotropic, with no variations in colour. The crystal margins display growth zones differing in colour sharply one from another. These marginal parts display also a strong anomalous anisotropy; small crystals are penetrated by a dense irregular network of cracks and some marginal parts are slightly comminuted (see fig. 1). Inclusions in garnet are scarce; calcite and pyroxene were observed, in the larger crystals only. Neither in the polished nor in the thin sections were there any inclusions that resembled in their properties cassiterite or any other mineral of tin.

Physical properties. Andradite participates in the skarn body as almost monomineralic aggregates of individual euhedral crystals up to 3 cm in size (fig. 2). The crystals are dark grass-green to black-green, bounded by simple crystal forms {110}; some individuals exhibit subparallel growths.

The specific gravity determined by suspension method in Clerici solution is 3·78. The specific gravity calculated on the basis of chemical composition and the unit-cell dimension is slightly higher, reaching 3·798.

The refractive index was determined by the minimum deviation method as n 1·879; B. J. Skinner (1956) gives n 1·887 for pure synthetic andradite. With isomorphous substitution of the grossular component this refractive index decreases rapidly (according to Skinner the refractive index for pure grossular is 1·734). The unit-cell dimension of the garnet was determined by the back-reflection method (Cu-K_α, λ 1·5418 Å) as a 12·079±0·002 Å.

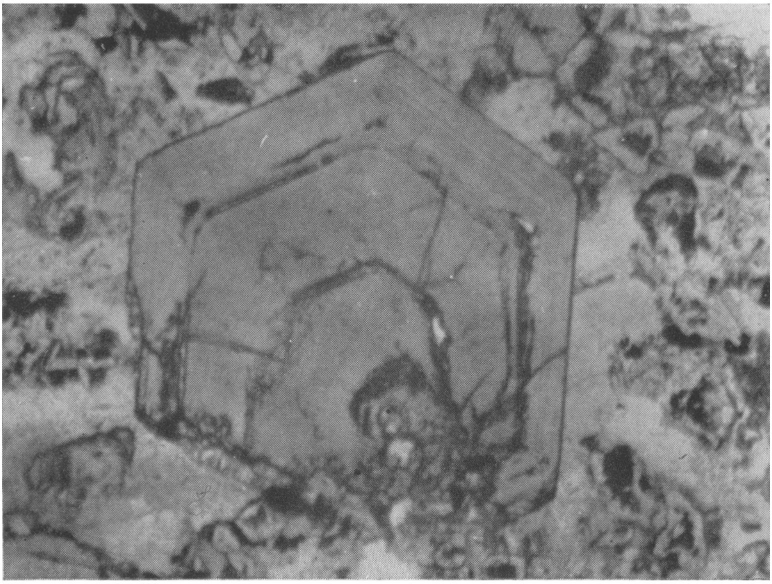

FIG. 1. Zonal crystal of andradite. ×90.

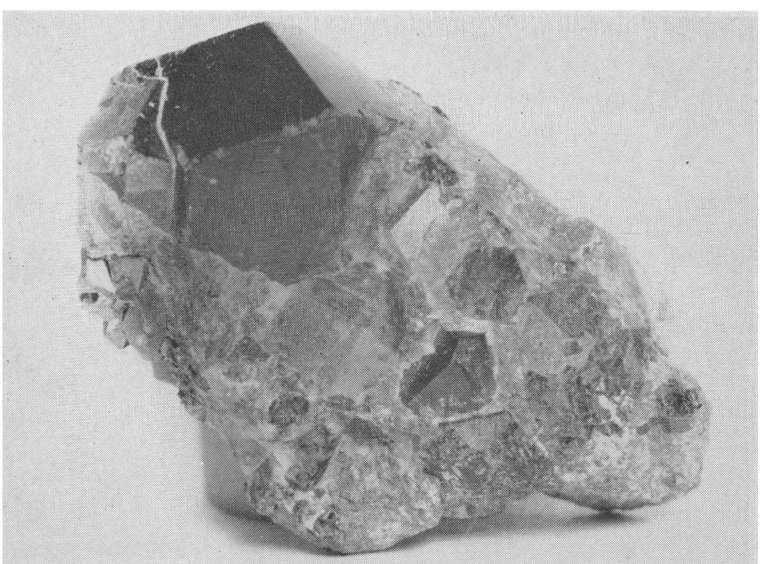

FIG. 2. Stannian andradite crystals.

These values indicate that we are concerned here with an almost pure andradite end-member of the garnet group. The value of the unit-cell dimension is even higher than the values given for the garnet ternary diagrams, e.g. by A. Sriramadas (1957), H. Winchell (1958),

TABLE I. Unit-cell dimensions of some andradites

Plavno, Czechoslovakia	$12{\cdot}079 \pm 0{\cdot}002$ Å	V. Dadák and F. Novák
Not given	12·07	M. Fleischer 1937
Obří důl, Czechoslovakia	$12{\cdot}060 \pm 0{\cdot}004$ $12{\cdot}057 \pm 0{\cdot}003$	V. Dadák and F. Novák
Synthetic andradite	12·048	B. J. Skinner 1956
	12·04	G. Menzer 1929
Alatal, Piedmont, Italy	$12{\cdot}026 \pm 0{\cdot}003$	V. I. Mikheev 1957
Dobšiná, Czechoslovakia	$12{\cdot}001 \pm 0{\cdot}007$	V. Bouška *et al.* 1962

V. Bouška *et al.* (1962); most of them consider *a* 12·048 Å pertaining to andradite to be the maximum value for garnets. The higher value of the unit-cell dimension is undoubtedly caused by the admixture of tin. The unit-cell dimensions of some andradites from other localities are summarized in table I.

TABLE II. Quantitative chemical analysis and atomic ratios of tin-containing andradite from Plavno mine. Anal. P. Novotný

		Recalc. after deducting insoluble		Ions per 12 oxygen	
CaO	32·90 %	32·86 %	Ca	2·96	3·02 ΣRO
MgO	0·28	0·28	Mg	0·04	
MnO	0·32	0·32	Mn	0·02	
Fe_2O_3*	28·28	28·25	Fe	1·79	1·97 ΣR_2O_3
Al_2O_3	1·85	1·85	Al	0·18	
K_2O	0·09	—	—		—
Na_2O	0·00	—	—		—
SnO_2	1·07†	1·07	Sn	0·04	2·99 ΣRO_2
SiO_2	35·42	35·37	Si	2·95	
				a 12·079 Å	
				n 1·879	
Total	100·21	100·00			

* Total iron as Fe_2O_3.

† Another sample, analysed by J. Mrázek, gave 1·36 % SnO_2.

Chemical composition, crystallochemical formula, and discussion of Sn-*content*

The chemical composition of the garnet from Plavno mine is given in table II, where the crystallochemical formula on the basis of the general structural formula $R_3^{2+} R_2^{3+} Si_3O_{12}$ is also given. The garnet is composed mainly of andradite 89·7 % with a little isomorphous admixture of grossular 6·4 % and with negligible amounts of pyrope (0·9 %) and spessartine (0·7 %) components. The small excess of 0·8 % CaO is most probably due to calcite, which has been detected by optical investigation in fine veinlets in the garnet.

In the interpretation of the crystallochemical formula there are some difficulties in connexion with the position of Sn^{4+}. According to published data the isomorphous substitution of tin in silicates is very limited and for the most part substitution of Fe^{2+} by Sn^{4+} is assumed (ionic radii after L. H. Ahrens, 1952; Sn^{4+} 0·71 Å, Fe^{2+} 0·74 Å), sometimes also substitution of Ca^{2+} by Sn^{2+} (ionic radii after Ahrens Sn^{2+} 0·93 Å, Ca^{2+} 0·99 Å), see K. Rankama and Th. Sahama (1950), H. Borchert and J. Dybek (1959). Later, A. E. Ringwood (1955) and S. T. Badalov (1957) presumed in garnets originating at higher temperatures the substitution of anionic complexes $(SiO_4)^{4-}$ by $(SnO_4)^{4-}$. In the present case, the substitution of Fe^{2+} by Sn^{4+} can be excluded, and according to crystallochemical calculations R^{2+} displays a little excess, while of there is a little deficiency of Si, which speaks in favour of the entrance Sn into the anionic complex $(SiO_4)^{4-}$. On this assumption the crystallochemical formula of andradite from Plavno mine may be expressed: $(Ca_{2\cdot96}Mg_{0\cdot04}Mn_{0\cdot02})_{3\cdot02}(Fe^{3+}_{1\cdot79}Al_{0\cdot18})_{1\cdot97}(Si_{2\cdot95}Sn_{0\cdot04})_{2\cdot99}O_{12}$. However, the possibility of a substitution of Fe^{3+} by Sn^{4+} cannot be excluded, since the ionic radii are rather similar (ionic radii after Ahrens: Fe^{3+} 0·64 Å, Sn^{4+} 0·71 Å). Such a heterovalent substitution requires a compensation of the valency by some univalent cation, perhaps alkali, in the position of RO.

In addition to the components detected by chemical analysis, the presence of Cu, Ti, and Zn in insignificant amounts (of the order 0·0X %) and Ga, Ge, and In in traces has been ascertained by spectrographic analysis.

Occurrence and distribution of tin in garnets

There are very few records of the presence of tin in garnets: M. Saksela (1951) found 1·44 % SnO_2 in an andradite with 36·6 % grossular from Pitkäranta; H. Hellwege (1956), 0·32 % in andradite from the Omelyanov mine, Pitkäranta; S. T. Badalov (1957), 0·13 % in a grossular with 9·1 % andradite; A. S. Dudykina (1959), an average of 0·014 % in 21 stannian garnets from various skarns; and H. Hellwege (1956), 0·0103 % in grossular from a granite pegmatite at Truninasca, Val Bandasca, Switzerland.

It will be seen that all the tin-rich garnets are andradites or grossulars; in other garnets the content of tin detected was never more than 0·01 % and in most of them Sn is not detectable (A. S. Dudykina, 1959). This speaks in favour of the possibility that Sn replaces Ca in garnets and is therefore associated with members of the garnet group rich in Ca. We must bear in mind that the entrance of tin into the garnet lattice requires a sufficient amount of tin in the solutions from which the garnets are formed, as well as relatively high temperatures of origin. These conditions are maintained particularly in the formation of tin-bearing polymetallic skarns (e.g. Pitkäranta) and in some quartz-granite dykes (S. T. Badalov, 1957), where there are garnets of mostly andradite and grossular composition.

The tin content in andradite varies considerably within one locality: Plavno 1·07–1·36 % SnO_2, Pitkäranta 0·32–1·44 % SnO_2. This variation may be due to non-uniform distribution of tin in the garnet crystals, which display distinct zonal structure (Plavno and Obří důl in Czechoslovakia). The distinct zonal development of andradite crystals witnesses substantial changes in the ore-forming solutions. The higher content of tin in andradites from Plavno indicates an increased supply of tin by ore-forming solutions as early as the skarnization stage. After the end of the skarnization process, the supply of tin went on and in the following cassiterite–sulphidic stage cassiterite originated first, followed by stannite, while a certain part of the tin was deposited in the lattice of other skarn minerals (pyroxenes, &c.) and sulphides (blende, chalcopyrite, &c.), see F. Novák, 1964, M. Kvaček and F. Novák 1963. The question of tin distribution in skarn garnets and other silicates will be studied further by the authors.

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