

# Geochemistry and EPR of cassiterites from the Iberian Hercynian Massif

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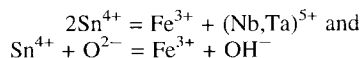
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## Abstract

This paper is based on microprobe analysis (Ta, Nb, Fe, Mn, Ti, W, Sn) and Fe<sup>3+</sup> EPR spectra of cassiterite samples from 14 tin deposits from the Iberian Hercynian Massif. The interpretation of microprobe data, atomic ratios (Fe+Mn)/(Nb+Ta), and Fe<sup>3+</sup> EPR spectra reveal that the coupled substitution: 3Sn<sup>4+</sup> = (Fe,Mn)<sup>2+</sup> + 2(Nb,Ta)<sup>5+</sup> is dominant in cassiterites from pegmatites, and high-temperature quartz veins and in the dark zones of cassiterites.

The mechanisms:



are dominant in those from medium–low temperature quartz veins and in the light zones of cassiterites.

KEYWORDS: cassiterite, trace elements, Fe<sup>3+</sup> EPR spectra, coupled substitutions.

## Introduction

THE Hercynian Belt in Europe is an important metallogenic province for tin, tungsten, gold and uranium. In the Spanish part of the belt there are numerous Sn and W mineralizations (about 200 occurrences), with north-south extension from Galicia to Andalusia, located in the inner part of the Iberian Hercynian Belt. The main tin mineral is cassiterite which is found in different genetic types of deposits: disseminations in granites, pegmatites, aplites, quartz veins and stockworks, and in alluvial placers derived from all these. Most deposits were discovered in the vicinity of major

lineaments and fault zones (Carvalho, 1977) located either inside granitic rocks or in the surrounding metamorphic rocks. The genetic linkage with granites is well accepted although the temporal relationship between granitization and mineralization has not been determined exactly. Some authors (Ribeiro, 1968) have proposed the association of these tin-bearing granites with the older aluminous-alkaline series ('Older Granites', Westphalian) and others (Conde *et al.*, 1971; Thadeu, 1973) with the calcalkaline granites ('Younger Granites'). There are not sufficient data to prove all this but in any case the tin mineralizations are mainly Autunian.

On the other hand, cassiterite is a mineral with variable chemical and physical features due to the different conditions of formation. It presents a wide range of chemical composition (minor and trace elements, such as Fe, Ti, Nb, Ta, Mn, W, Zr, etc.), colour (from black to colourless through intermediate zones with yellow, orange, brown, red, etc.), crystal morphologies, and number, shape and distribution of solid micro-inclusions (Wang, 1985; Murciego *et al.*, 1987). Microprobe analysis of this mineral (Bahezre *et al.*, 1961; Hall and Ribbe, 1971; Rémond, 1973; Clark *et al.*, 1976; Florov *et al.*, 1980; Izoret *et al.*, 1985; Giuliani, 1987; Murciego, 1990) shows that the optical zonation seems to correspond to a compositional zoning: light zones are rather chemically pure while the dark zones are enriched in minor and/or trace elements, commonly Fe, Mn, Ti, Nb and Ta. However, some authors (Schneider *et al.*, 1978; Moore and Howie, 1979) have pointed to the lack of correlation between chemical and optical zonation. The discussion still continues.

Otherwise the substitution mechanisms of tin in the cassiterite lattice by minor and trace elements, as well as the correlation between chemical composition and crystal genesis, have been the target of several studies, some of these elements being considered indicators of physical and chemical conditions of formation (Dudykina, 1959; Stevenson and Taylor, 1973). The relationship between crystallization conditions and the presence of different Fe<sup>3+</sup> paramagnetic centres, as well as their charge compensation mechanisms, may be studied by EPR (Electron Paramagnetic Resonance) (Calas and Cottrant 1982; Ruck *et al.*, 1989).

Numerous data sets obtained from the application of different techniques in the study of cassiterite show that it is possible to establish the relationship between the physicochemical variables, impurity distribution, zonations and genetic conditions of crystallization. The aim of this work is the application of some techniques (optical microscopy, microprobe analysis, EPR, IR) to cassiterites from ores of different genetic types in the Iberian Hercynic Belt, in order to better define their features and the substitution mechanisms of tin by other trace elements.

### Experimental

**Sample location.** The cassiterite samples are from different types of tin deposits from Galicia to Extremadura along the metallogenic province of the Iberian Massif. Fourteen of these cassiterite deposits have been sampled (Fig. 1): Penouta (Orense) and Golpejas (Salamanca), dissemination type in albitic granite; Las Navas (Cáceres) and S.M. Sando, Barquilla, La Fregeneda (Salamanca) in pegmatites

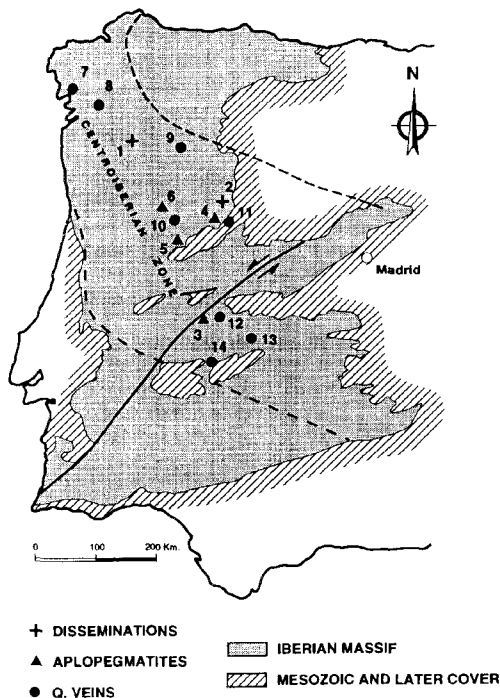


FIG. 1. Sample location map of cassiterites from selected tin deposits, Iberian Massif, Spain. 1: Penouta; 2: Golpejas; 3: Las Navas; 4: S. M. Sando; 5: Barquilla; 6: La Fregeneda; 7: S.Finx; 8: Sultana; 9: Calabor; 10: Lumbrales; 11: Teba; 12: El Gejo; 13: El Serranito; 14: La Parrilla.

and aplites with Li minerals and high-temperature quartz veins; S. Finx (La Coruna), Sultana (Orense), Calabor (Zamora), Lumbrales (Salamanca), Teba (Cáceres), El Gejo (Salamanca), El Serranito (Cáceres) in quartz veins; La Parrilla (Cáceres) in quartz veins with scheelite. A summary description of these deposits is shown in Table 1. In agreement with references cited in Table 1 some cassiterites belong to high-temperature deposits: Golpejas, Penouta, Las Navas, S.M. Sando, Barquilla and La Fregeneda; the other cassiterite samples belong to mesothermal and epithermal deposits.

**Microprobe analysis.** Chemical analyses were performed in a SX-50 CAMECA electron microprobe from Nancy I University (France). The analyses were carried out at 20 kV using a sample current of 20 nA and beam diameter of 1–2  $\mu\text{m}$ . The following elements were analysed: Sn, Ti, Fe, Mn, Nb and Ta. Analytical lines, standards, counting time in seconds and detection limits are: Sn (SnO<sub>2</sub>, L $\alpha$ , 20 s), Ti

TABLE 1. Summary of the cassiterite deposits

Deposit	Type	Mineralogy	Geological setting	Referenccs
Penouta (Orense) 1	Dissem. and Q-veins	Q + musc + ab	Albitic granite	Mangas (1987)
Golpejas (Salamanca) 2	Dissem. and Q-veins	Q + musc + ab Q + amblygonite	Albitic granite and CEG	Mangas (1987)
Las Navas (Cáceres) 3	Pegmatites	Q + musc + fd.K + lepidol. + spodum	Leucogranite and CEG	Marconet and Gagny (1984)
S. M <sup>a</sup> Sando (Salamanca) 4	Pegmatites	Q + fd.K + musc + tourm	CEG and 'older granites'	Gonzalo and Gracia (1985)
Barquilla (Salamanca) 5	Pegmatites and aplites	Q + musc + ab montebrasite	CEG	Murciego (1990)
La Fregeneda (Salamanca) 6	Q-veins and Pegmatites	Q + fd.K + musc Q + musc + ab + lepidol + spodum	CEG CEG	Mangas (1987)
S. Finx (La Coruña) 7	Q-veins	Q + musc + fd.K + tourm	Migmatites and granites	Mangas (1987)
Sultana (Orense) 8	Q-veins	Q + arsenopy	CEG	Gonzalo and Gracia (1985)
Calabor (Zamora) 9	Q-veins and stockworks	Q + musc + arsenopy	CEG	Ramirez (1979)
Lumbrales (Salamanca) 10	Q-veins	Q + fd.K + musc + fluorite + chlorite	Migmatites	Murciego (1990)
Teba (Cáceres) 11	Q-veins and stockworks	Q + musc + tourm + arsenopy	CEG	Mangas (1987)
El Gejo (Salamanca) 12	Q-veins	Q + musc + tourm arsenopy	'Older granites'	Gonzalo and Gracia (1985)
El Serranito (Cáceres) 13	Q-veins	Q + musc + arsenopy	CEG	Gonzalo and Gracia (1985)
La Parrilla (Cáceres) 14	Q-veins	Q + musc + tourm + arsenopy + scheel	CEG	Gumiel and Pineda (1981)

musc: muscovite; ab: albite; fd.K: K-feldspar; lepidol: lepidolite; spodum: spodumene; arsenopy: arsenopyrite; tourm: tourmaline; scheel: scheelite

CEG (Complejo Esquistograuváquico, Greywacke Schist Complex; Precambrian/Cambrian metamorphic rocks, which consist mainly of sandy slates, greywackes with lesser amounts of banded slates and intercalated quartzitic conglomerates).

The number in the first column relates to the localities shown in Fig. 1.

(FeTiO<sub>3</sub>,  $L\alpha$ , 60 s, 125 ppm), Fe (Fe<sub>2</sub>O<sub>3</sub>,  $L\alpha$ , 40 s, 250 ppm), Mn (MnTiO<sub>3</sub>,  $K\alpha$ , 60 s, 150 ppm), Nb (LiNbO<sub>3</sub>,  $L\alpha$ , 80 s, 170 ppm), Ta (LiTaO<sub>3</sub>,  $L\alpha$ , 100 s, 285 ppm).

*EPR spectra (Electron Paramagnetic Resonance Spectra).* EPR powder spectra have been recorded in the X band between 0 and 4000 Gauss, at room temperature, with a field modulation frequency of

100 kHz and the Te 102 cavity of the Bruker spectrometer. All spectra were made with derivative curves of absorption lines and recorded with samples of the same weight (100 mg) and at the same operating conditions (microwave frequency 9.79 GHz, field modulation intensity 10 Gauss for peak to peak, and time constant 100 ms); only gain is different in some spectra.

## Results

The cassiterite samples exhibit a wide range of colours (black, dark brown, red brown, light brown, orange, green, yellow, and even colourless). These colours may be present in a single crystal with variable distribution patterns (in zones, patches, speckled). Colour is homogeneous (black or dark brown) in cassiterites belonging to the high-temperature deposits (pegmatites and catathedral veins: Las Navas, La Fregeneda, Golpejas and S. M. Sando), while different colours are present in cassiterites from epithermal and mesothermal veins. The crystal habit is bipyramidal with the common {111} form, and a small development along the *c* axis is common in cassiterites from high-temperature deposits, while in the epithermal and mesothermal deposits the crystal habit is prismatic; the elongation ranges from 2 to 3. Faces of the tetragonal pyramid {111}, {101} and {100} are typical, and those of the dipyrmaid {231} and the ditetragonal prism {120} are subordinate. Transmitted light microscopy reveals the existence of a zoning pattern: alternating clear and dark zones of variable position, periodicity, width and lateral continuity.

In single crystals, zoning is well developed in some directions and it is not present in others. Colourless rings or patches surrounding micro-inclusions have been commonly observed in low to medium-temperature deposits. Variable kinds of twinning are common in all the crystals studied.

Marked pleochroism, ranging from red-brown tones along Ne to light brown along No is present in cassiterites from pegmatites and high-temperature veins, while very weak pleochroism is manifested only as a certain change in colour intensity, and is shown by cassiterites from low and medium-temperature deposits.

The reflected light microscopy shows that the cassiterite samples contain numerous micro-inclusions of different minerals. They are distributed randomly, along the twinning and growth planes. The sizes range between some few microns and 1 mm. Columbite inclusions are constantly found in cassiterite crystals from pegmatites and high-*T* veins, and columbite and ilmenorutile in samples from low-*T* and medium-*T* veins.

**Chemistry.** Analytical results by microprobe (atomic wt.%) are presented in Table 2. Tantalum was recorded above the detection limit in the pegmatite and high-temperature quartz-vein deposits only, and reaches a maximum of >6% in some pegmatite deposits. Titanium occurs in cassiterites of all deposits reaching a maximum average of >3.38% in quartz-vein deposits, and grading to <0.1% in pegmatitic and high-temperature deposits. Tungsten is detectable only in cassiterites associated with W-

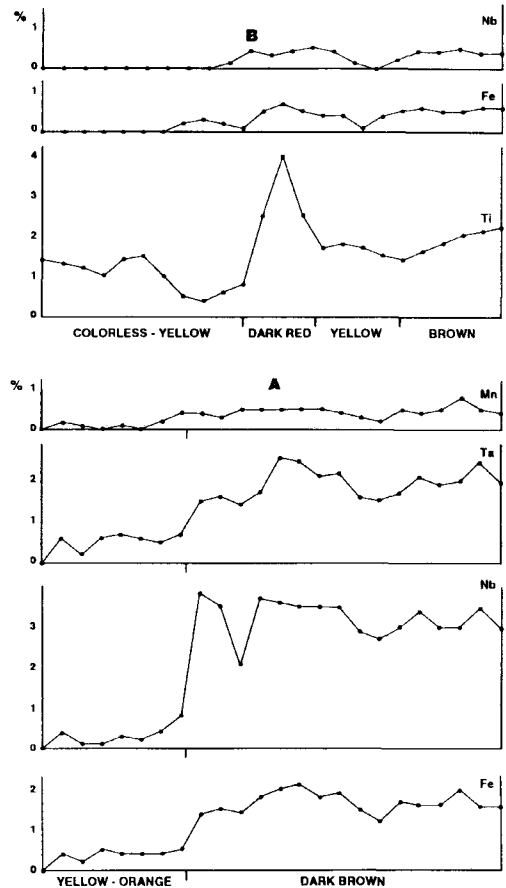


FIG. 2. Fe, Mn, Nb, Ti and Ta cassiterite contents (atomic wt.%) vs. colour in the Golpejas deposit (A) and Teba deposit (B).

containing minerals (i.e. La Parrilla deposit, maximum content 0.4%). Concentration curves of the elements Fe, Nb, Ta, Mn and Ti vs. colour (Fig. 2) reflect the zoning of impurity elements across some crystals.

**EPR.**  $\text{Fe}^{3+}$  EPR spectra of cassiterite samples are shown in Fig. 4. These spectra patterns can be grouped into: (a) Spectra with I, SN, Sd1 and Sd2 paramagnetic centres; mainly samples from quartz-vein deposits. (b) Spectra with the above centres besides the Sd3 paramagnetic centre; samples from pegmatites and of dissemination type. The comparative study of  $\text{Fe}^{3+}$  EPR spectra of dark and clear zones of the Sultana deposit (quartz-vein type) shows marked differences between both (Fig. 5).

TABLE 2. Microprobe analysis of cassiterite samples (atomic wt.%, average of 50–60 points analysed)

Deposit	Zone	Ti	Ta	Nb	Fe	Mn	Sn
Penouta	D	0.58	1.32	0.81	1.11	0.12	95.93
	L	0.02	0.11	0.22	0.32	0.02	99.14
Golpejas	D	0.01	1.76	2.68	1.56	0.43	93.26
	L	0.01	0.53	0.27	0.41	0.03	98.64
Las Navas	D	0.01	2.42	2.39	0.05	1.06	93.85
	L	0.01	0.47	1.17	0.02	0.19	98.06
S. M <sup>a</sup> Sando	D	0.41	0.96	0.87	0.92	0.02	96.85
	L	0.37	0.10	0.28	0.20	0.02	99.01
Barquilla	D	0.45	1.91	2.85	2.16	0.02	92.32
	L	0.38	0.23	0.97	0.62	0.01	97.68
La Fregeneda	D	1.64	1.02	1.51	1.86	0.03	93.84
	L	0.48	0.11	0.19	0.37	0.01	98.80
S. Finx	D	0.85	0.01	0.26	0.38	0.01	98.47
	L	0.34	0.01	0.06	0.10	0.01	99.48
Sultana	D	1.11	0.01	0.22	0.18	0.01	98.46
	L	0.90	0.01	0.08	0.09	0.01	98.91
Lumbrales	D	1.24	0.01	0.64	0.42	0.01	97.66
	L	0.93	0.01	0.11	0.12	0.01	98.81
Calabor	D	0.41	0.01	0.11	0.18	0.01	99.27
	L	0.26	0.01	0.03	0.04	0.01	99.65
Teba	D	1.97	0.01	0.41	0.50	0.01	97.11
	L	0.78	0.01	0.11	0.10	0.01	98.95
El Gejo	D	0.88	0.01	0.06	0.07	0.01	98.90
	L	1.73	0.35	1.02	0.87	0.02	95.98
El Serranito	D	0.88	0.03	0.30	0.38	0.01	98.37
	L	3.38	0.01	0.20	0.19	0.01	95.92
La Parrilla	D	1.12	0.01	0.05	0.09	0.01	98.73

D: dark; L: light

### Discussion and conclusions

Several studies on cassiterite geochemistry from different metallogenic environments have found systematic variations in chemical composition (Stevenson and Taylor, 1973; Schneider *et al.*, 1978; Moore and Howie, 1979; Dulski *et al.*, 1982; Wang, 1988; Möller *et al.*, 1988; Murciego, 1990). The cassiterite structure (rutile type) allows the entrance of different cations as impurities in substitution for Sn<sup>4+</sup>, in variable proportions up to 14 wt.% oxides (Murciego, 1990). This is due to crystallochemical similarities (radius, electronegativity) compared with Sn<sup>4+</sup> (radius) in octahedral coordination. Substituting cations mainly are the following: Fe<sup>2+</sup> (0.77), Fe<sup>3+</sup> (0.645), Mn<sup>2+</sup> (0.67), Mn<sup>3+</sup> (0.65), Nb<sup>5+</sup> (0.64), Ta<sup>5+</sup> (0.64), Ti<sup>4+</sup> (0.605), W<sup>4+</sup> (0.66), W<sup>6+</sup> (0.60) (in brackets: effective ionic radii after Shannon, 1976). Microprobe analysis reveals that minor and trace element contents of cassiterite show a distinct relationship to the environment of formation. Thus, Nb and Ta have

been suggested as favouring a pegmatitic (high-temperature) environment and Ti as favouring a lower-temperature environment (Stevenson and Taylor, 1973).

The Spanish cassiterites examined support the above general trends with both Nb and Ta reaching highest concentrations in the pegmatitic and high-temperature veins. Niobium occurs in cassiterites of all deposits, reaching a maximum average greater than 2% in the pegmatite deposits and grading to less than 0.5% in the quartz-vein deposits.

The microprobe data reflect the physico-chemical conditions of mineral formation. The dominance of Nb over Ta is observed in all cassiterites analysed. After Möller *et al.* (1988) this fact may be explained as the result of the higher natural abundance of Nb over Ta and the increased tendency of Nb<sup>4+</sup> to enter in a disordered rutile structure while Ta prefers the pentavalent state.

Different coupled substitutions in cassiterite have previously been suggested (Calas and Cottrant, 1982; Izoret *et al.*, 1985; Möller *et al.*, 1988; Ruck *et al.*,

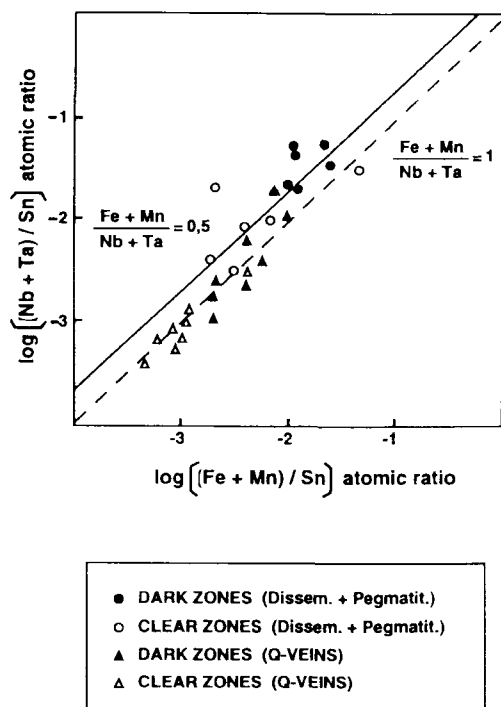
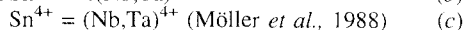
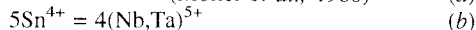
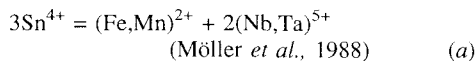
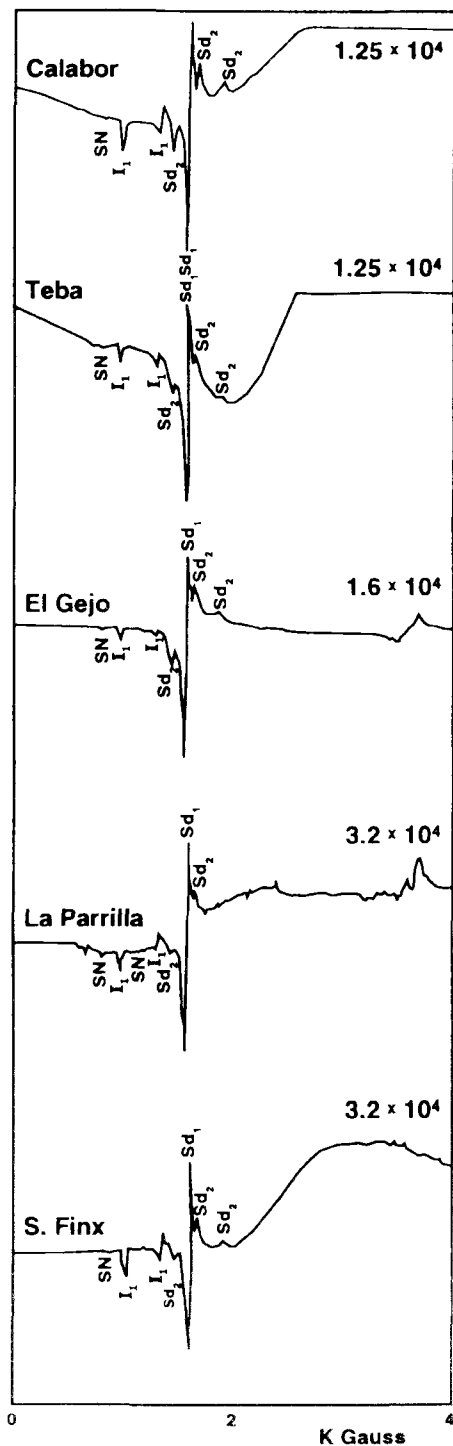


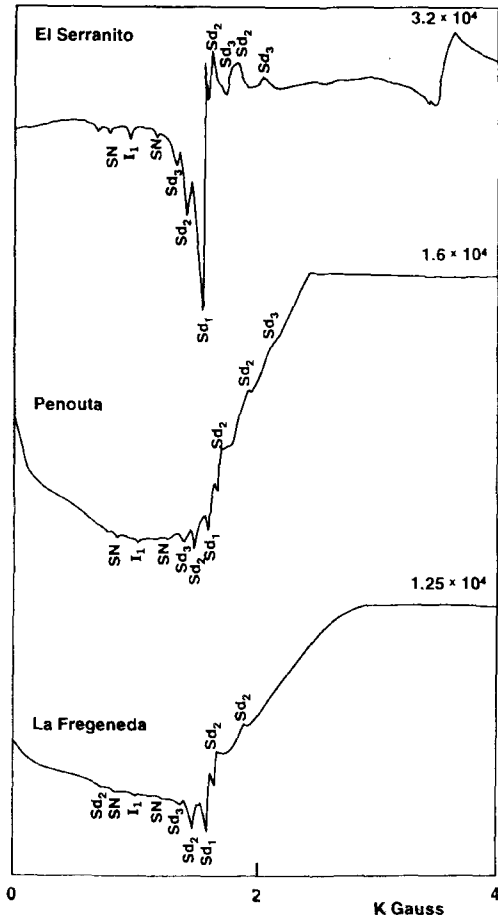
FIG. 3.  $\log (\text{Nb}+\text{Ta}/\text{Sn})$  vs.  $\log (\text{Fe}+\text{Mn}/\text{Sn})$  in cassiterites.

1989). The aim of this paper is to discuss the replacement mechanisms of  $\text{Sn}^{4+}$  by Fe, Mn, Nb and Ta on the basis of the analytical results from microprobe and  $\text{Fe}^{3+}$  EPR spectroscopy.  $(\text{Fe}+\text{Mn})/(\text{Nb}+\text{Ta})$  atomic ratios (Fig. 3) and correlation between these element pairs allow us to propose and discuss the different charge compensation mechanisms in which  $\text{Sn}^{4+}$  is substituted. Ratios lower than 0.5 may be interpreted by the equations:

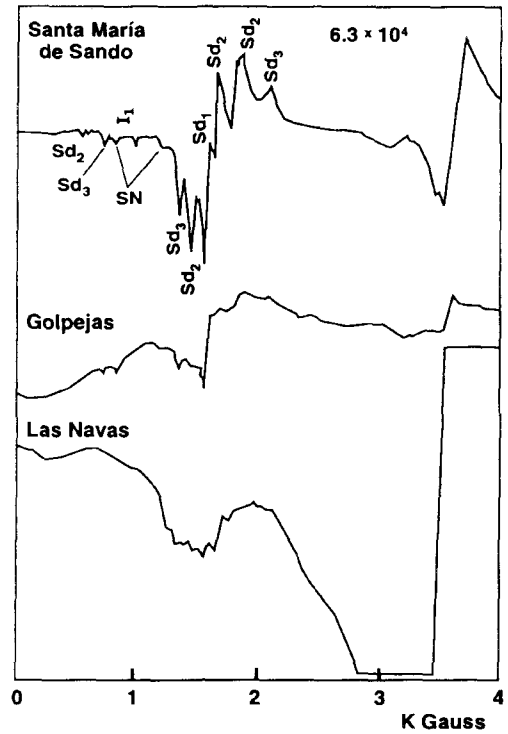


Equation (a) describes the isomorphous replacement of  $\text{Sn}_3\text{O}_6$  by  $(\text{Fe}, \text{Mn})(\text{Nb}, \text{Ta})_2\text{O}_6$ , natural solid solution (columbo-tantalite). For  $(\text{Fe} + \text{Mn})/(\text{Nb} + \text{Ta}) < 0.5$  (samples of dissemination, pegmatites and high- $T$  quartz-vein types) we propose the (a) mechanism where Fe will be coupled with part of  $(\text{Nb}, \text{Ta})$  with an atomic ratio = 0.5, the excess of  $(\text{Nb}, \text{Ta})$  could be incorporated in the cassiterite structure after equations (b) and (c). The correlation between these element pairs is coherent with the (a) mechanism; (b) and (c) are subordinate. The (b) mechanism implies the





4b

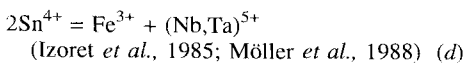


4c

FIG. 4(a-c). Fe<sup>3+</sup> EPR spectra of cassiterites from the different environments studied; quartz veins: (a and b) (El Serranito deposit); disseminations and pegmatites: (b and c).

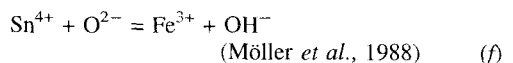
existence of cationic holes and (c) describes a homovalent substitution (simple substitution mechanism), the solid solution of (Nb,Ta)O<sub>2</sub> in SnO<sub>2</sub>. Both end-members crystallize in the same structure (rutile type). This last mechanism should be very limited due to the low probability of reducing conditions for the existence of (Ta,Nb)<sup>4+</sup>, and of Fe-poor fluids, in their genetic environments.

(Fe+Mn)/(Nb+Ta) atomic ratios range from 0.5 to 1 in some quartz-vein cassiterites. We propose, in addition to the (a) mechanism, the substitution:



representing the isomorphous replacement of Sn<sub>2</sub>O<sub>4</sub> by Fe(Ta,Nb)O<sub>4</sub>; a natural compound of this type is

known as ilmenorutile (Ti,Nb,Fe<sup>3+</sup>)O<sub>2</sub>. Ilmenorutile and columbo-tantalite inclusions were found in the samples from quartz veins. Values of (Fe + Mn)/(Nb + Ta) > 1 in some quartz-vein samples, and from the light zones of cassiterites from different genetic types reveal an 'excess' of Fe that would be incorporated as Fe<sup>3+</sup> by the following substitutions:



The lack of correlation between (Fe,Mn) and (Nb,Ta) in these samples supports this assumption and indicates that these elements are not always incorporated in the cassiterite structure by coupled

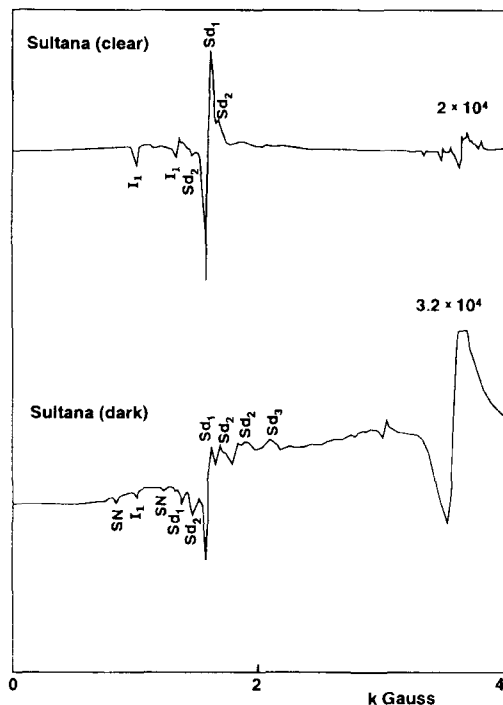
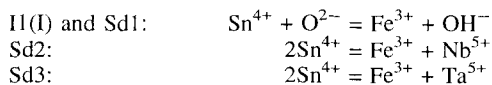


FIG. 5.  $\text{Fe}^{3+}$  EPR of dark and clear zones of cassiterite from the Sultana quartz-vein deposit.

substitution. The above proposed substitutions show that the oxidation state of Fe varies as a function of genetic environment. In high-temperature environments ( $>300^\circ\text{C}$ ) there is a deficit of (Fe,Mn) with respect to (Nb,Ta). These samples largely accommodate Fe as  $\text{Fe}^{2+}$ , whereas in low-temperature environments there is an excess of (Fe,Mn) largely hosted in the cassiterite structure as  $\text{Fe}^{3+}$ . Infrared spectra of these samples (Murciego *et al.*, 1990) show an absorption band with frequency value of  $3400\text{ cm}^{-1}$ , belonging to  $\text{OH}^-$  groups in the cassiterite lattice (Bréhat *et al.*, 1990), and supports the mechanism (f).

Five paramagnetic centres due to  $\text{Fe}^{3+}$  have been described in the cassiterite structure (Calas and Cottrant, 1982; Dusausoy *et al.*, 1988; Ruck *et al.*, 1988, 1989): SN, I(I), Sd1, Sd2 and Sd3. Different charge compensation mechanisms have been proposed:



In samples with RPE of the (a) group (Fig. 4),  $\text{Fe}^{3+}$  is mainly in Sd1 and I(I) centres and to a lesser

extent in the Sd2 centre. SN centre bands are clearly of lower intensity than those from the other centres. This is in agreement with the literature: the SN centre presents a higher degree of occupation in synthetic cassiterites than in natural ones. In the EPR spectra of cassiterites of the (b) group (Fig. 4), a new paramagnetic centre appears, Sd3, which may be related to the presence of Ta.

These spectra when compared with those from the (a) group show: (1) a decrease in the intensity of the bands Sd1 and I(I); in some spectra they are even not present; (2) an increase in the intensity of the bands belonging to the Sd2 centre; and (3) the intensity of these spectra are lower than those from the (a) group. This is clear in cassiterite from La Fregeneda and is even more clear in cassiterites from Golpejas. The spectrum from the Las Navas cassiterite cannot be compared due to the presence of Mn instead of Fe. The comparison of dark and clear zones in cassiterite from a quartz-vein deposit (Sultana), Fig. 5, shows some differences: the intensity of the Sd1 and I(I) centres decreases in the darker zones, while the Sd2 and SN intensity increases; moreover, the Sd3 centre appears as well. The intensity or width of spectra from the darker zones is lower than those from the clear zones. However, as we have stated earlier, the darker zones present higher contents of Fe, Nb and Ta, as deduced from the analytical data. Most of the Fe in the zones or patches of darker colour appears to be present as  $\text{Fe}^{2+}$ , while the ratio  $\text{Fe}^{3+}/\text{Fe}^{2+}$  is increased in the lighter zones.

If we assume that the content in Fe, Mn, Nb and Ta is due to solid inclusions of columbite-tantalite a good correlation along the line  $R = 0.5$  may be expected (Fig. 3). Nevertheless, most data plot away from this line, which means that there is an excess of (Nb,Ta) or (Fe,Mn). These observations, together with the homogeneous distribution of Fe, Nb, Ta and Mn in cassiterite samples from each single deposit, and the good correlation between geochemically coherent element pairs (Fe-Mn, Nb-Ta), support an isomorphic substitution rather than the presence of solid inclusions only.

Otherwise, (Nb,Ta)-rich samples from high- $T$  deposits (disseminations, pegmatites) accommodate mainly  $\text{Fe}^{2+}$  in substitution for tin, whereas samples from lower- $T$  deposits (quartz veins) largely host  $\text{Fe}^{3+}$  ions.

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