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GEOCHEMISTRY OF CASSITERITE AND ITS INCLUSIONS AND EXSOLUTION PRODUCTS FROM TIN AND TUNGSTEN DEPOSITS IN PORTUGAL

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ABSTRACT

Euhedral cassiterite from Sn-bearing granitic pegmatites and stanniferous quartz veins in Portugal shows sequences of alternating parallel darker and lighter zones. The darker zones are strongly pleochroic, oscillatorily zoned, and have more Nb, Ta and Fe than the lighter zones, which are nearly pure SnO_2. Darker zones mainly show exsolved columbite–tantalite and ixiolite, rarely ferrotapiolite, rutile and, locally, ilmenite, which are less abundant in lighter zones. Columbite–tantalite inclusions were infrequently found; they generally have combined Ti, Sn and W contents lower than those of exsolved columbite–tantalite. Compositional features differentiate the columbite–tantalite minerals and varieties of ixiolite. Cassiterite from W–Sn-bearing quartz veins is generally zoned; darker zones are commonly homogeneous and slightly pleochroic, but chemically similar to lighter zones. This cassiterite has mainly inclusions of rutile and locally of ilmenite. Exsolved rutile has similar or higher combined Nb, Ta, Sn, W, Fe, Mn contents than included rutile. Euhedral to subhedral grains of massive cassiterite from a volcanogenic deposit are slightly pleochroic, and their color deepens from yellow to dark brown with increasing Fe content; such cassiterite is devoid of inclusions and products of exsolution.

Keywords: cassiterite, columbite–tantalite minerals, tapiolite, ixiolite, rutile, inclusions, exsolution, Portugal.

SOMMAIRE

Des cristaux de cassitérite idiomorphes provenant de massifs de pegmatite granitique et de veines de quartz stannifères au Portugal montrent une alternance de zones de croissance parallèles claires et plus sombres. Les zones sombres sont fortement pléochroïques, zonées de façon oscillatoire, et contiennent plus de Nb, Ta et Fe que les zones claires, qui ont une composition voisine du pôle SnO_2. Les zones sombres contiennent des produits d'exsolution, surtout columbite–tantalite et ixiolite, rarement ferrotapiolite et rutile, et, localement seulement, ilménite, qui sont moins abondants dans les zones claires. Les inclusions de columbite–tantalite ne sont pas courantes; en général, elles contiennent des teneurs en Ti + Sn + W plus faibles que dans les domaines de columbite–tantalite exsolvée. Des critères géochimiques différencient les minéraux du groupe columbite–tantalite des variétés d'ixiolite. Les cristaux de cassitérite provenant de veines de quartz minéralisées en W et en Sn sont en général zonés. Les zones plus sombres sont homogènes et légèrement pléochroïques, mais leur composition ressemble à celle des zones claires. Ce type de cassitérite contient surtout des inclusions de rutile et, localement, d'ilménite. Le rutile exsolvé contient des niveaux comparables ou plus élevés de Nb + Ta + Sn + W + Fe + Mn que le rutile en inclusion. La cassitérite massive, en cristaux idiomorphes à sub-idiomorphes et provenant d'un gisement volcanogénique, est légèrement pléochroïque; sa couleur passe du jaune au brun foncé avec une augmentation de sa teneur en fer. Ce type de cassitérite ne contient aucune inclusion ou lamelle d'exsolution.

(Traduit par la Rédaction)

Mots-clés: cassitérite, minéraux du groupe de la columbite–tantalite, tapiolite, ixiolite, rutile, inclusions, exsolution, Portugal.

INTRODUCTION

There are many occurrences of cassiterite and wolframite in northern and central Portugal, and most of them have been exploited. Cassiterite occurs in veins of granitic pegmatite, and wolframite, in veins of quartz. These veins are related to Hercynian S-type granites (Neiva 1983, 1984, 1987), except for the W–Sn-bearing quartz veins (W > Sn) from Carris (Gerez), which are related to an I-type granite (Neiva 1993). The veins of granitic pegmatite cut granites and surrounding country-rocks, which consist of pre-Ordovician, Ordovician and Silurian metapelites. The quartz veins cut these country rocks at a distance away from the granites, and rarely cut the granites themselves (Cotelo Neiva 1944). Cassiterite also occurs in the massive volcanogenic sulfide deposit at Neves–Corvo, in southern Portugal, which is related to older Hercynian felsic rocks.

Compositional studies of cassiterite are rather numerous (*e.g.*, Grice *et al.* 1972, Moore & Howie 1979, Foord 1982, Černý & Ercit 1989, Černý *et al.* 1985, Izoret *et al.* 1985, Giuliani 1987, Gonzalez & Revuelta 1989, Ogunbajo 1993, Gomes 1994). However, papers dealing with inclusions and products of exsolution in cassiterite are scarce (Murciego *et al.* 1987, Spilde & Shearer 1992, Fuente & Izard 1994, Suwinonprecha *et al.* 1995), as are those on coexisting columbite–tantalite and cassiterite (Černý & Ercit 1985, Černý *et al.* 1986a, b, Suwinonprecha *et al.* 1995).

This paper concerns the phase composition and geochemistry of Portuguese cassiterite on a broad regional and paragenetic basis. The compositions of columbite–tantalite, rutile, ilmenite inclusions and products of exsolution (including ixiolite) also are presented. The element partitioning among Nb- and Ta-bearing phases also is discussed. Twenty-one Sn and W deposits were selected for this study (Fig, 1).

PARAGENETIC RELATIONSHIPS OF PORTUGUESE CASSITERITE

In Sn-bearing veins of granitic pegmatite of the Hercynian belt in Portugal, euhedral cassiterite occurs mainly interstitially in association with albite – muscovite – quartz, or replaces mainly quartz and muscovite (Fig. 2a). The crystals, generally between 2 and 10 mm across, rarely host microscopic (≤60 × 40 µm) inclusions of quartz, muscovite and columbite–tantalite. On the other hand, they commonly show exsolved Nb- and Ta-bearing oxide minerals (≤350 × 150 µm), exsolved rutile (≤100 × 40 µm) is rarer, and only occasionally are exsolved ferrotapiolite (≤3 × 2 µm) and ilmenite (≤4 × 2 µm) found. Rutile inclusions (≤20 × 20 µm) were found only in the cassiterite from Bessa, which does not show any products of exsolution.

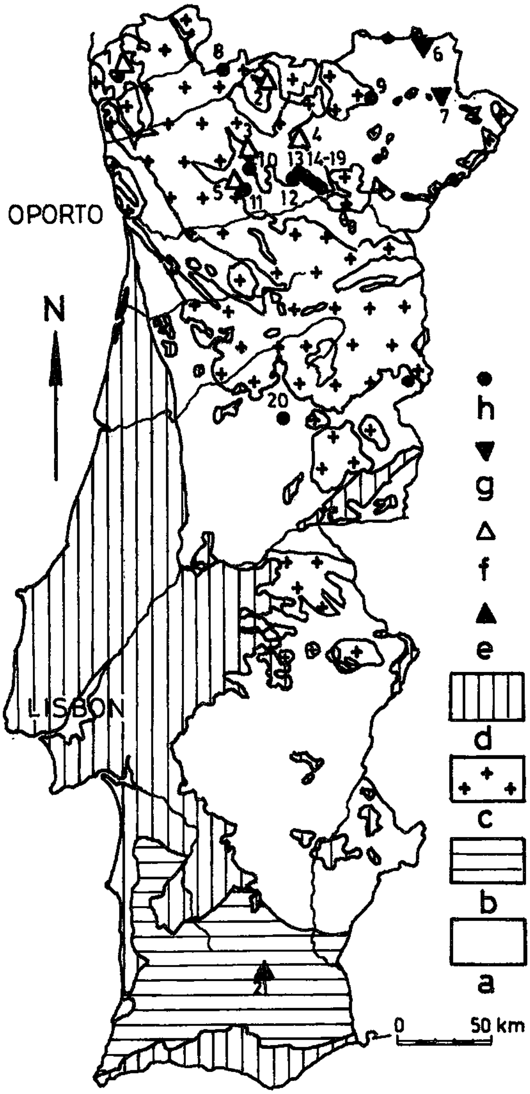

FIG. 1. Location of the twenty-one Sn and W deposits chosen for study. a: Pre-Ordovician metamorphic complexes, Paleozoic, some igneous and ultrabasic rocks and igneous complexes from Alentejo; b: Marine Carboniferous metasedimentary and metavolcanic rocks; c: Hercynian granitic rocks; d: Mesozoic and Cenozoic sedimentary rocks. Ore deposits: e: volcanogenic sulfides and Sn deposits [21: Neves Corvo (Sta. Bárbara dos Padrões, Castro Verde)]; f: Sn-bearing granitic pegmatitic veins [1: Cabração (Cabração, Ponte do Lima); 2: Bessa (Morgade, Montalegre), 3: Fental (Sto. Aleixo do Tâmega, Ribeira de Pena), 4: Revel (Três Minas, Vila Pouca de Aguiar), 5: Vieiros (Rebordelo, Amarante)]; g: stanniferous quartz veins [6: Montezinho (França, Bragança), 7: Argozelo (Argozelo, Vimioso)]; h: W–Sn-bearing quartz veins [8: Carris (Cabril, Montalegre), 9: Lombo de Boi (Lamalonga, Macedo de Cavaleiros, 10: Linhares (Ermelo, Mondim de Basto), 11: Fonte Figueira (Aboadela, Amarante),12: Vale das Gatas (S. Lourenço de Ribapinhão e Souto Maior, Sabrosa), 13: Muralha (Vilar de Maçada, Alijó), 14: Carvalhal (Cheires, Alijó), 15: Soutelinho (Favaios, Alijó), 16: Filharoso (Presandães, Alijó), 17: S. Domingos (Alijó, Alijó), 18: Folgar (S. Mamede de Ribatua, Alijó), 19: Bouço (S. Mamede de Ribatua, Alijó), 20: Panasqueira (Aldeia de S. Francisco e S. Jorge da Beira, Covilhã e Fundão)]. Parish and borough are given for the locality information.

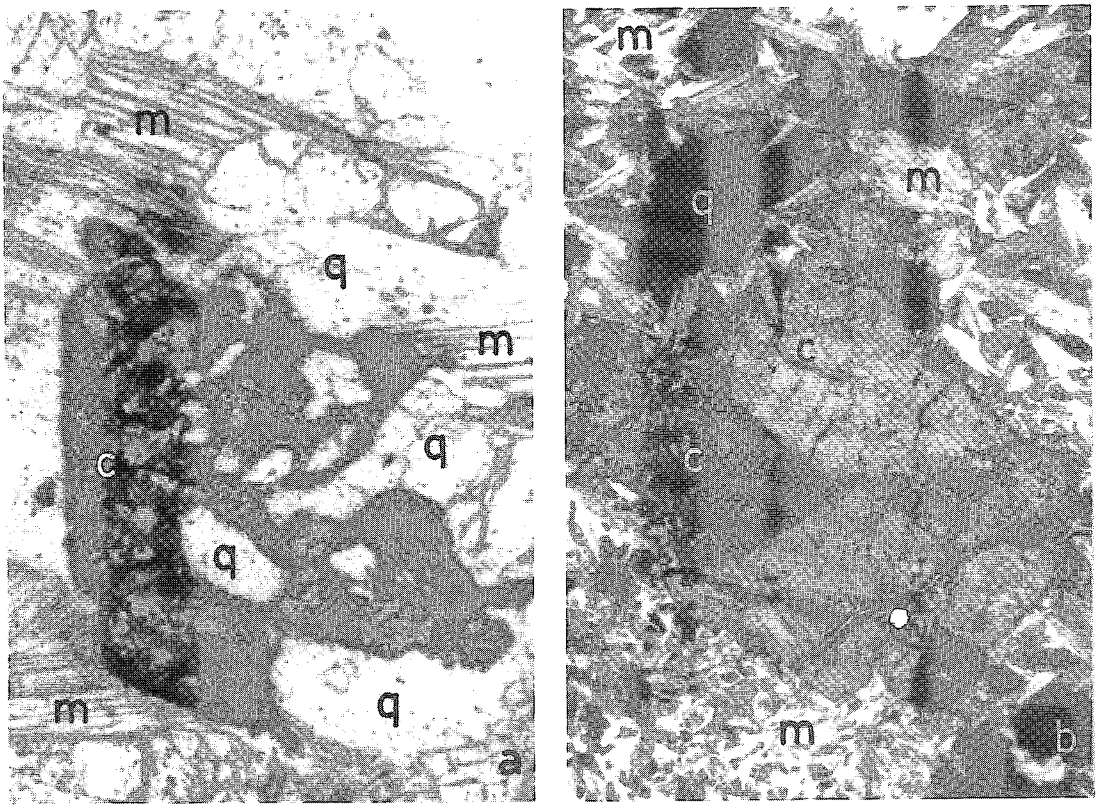

FIG. 2. a. Cassiterite (c) from the Vieiros pegmatite replacing quartz (q) and muscovite (m) (×55); b. euhedral grain of cassiterite (c) from the quartz veins from Argozelo, associated with a muscovite-rich selvage (m) and quartz (q) (×27).

In quartz veins, euhedral cassiterite occurs among quartz crystals, mainly along the vein–schist contact, associated with a muscovite-rich selvage (Fig. 2b). Cassiterite crystals from the stanniferous quartz veins from Argozelo are generally more than 1 cm across and locally cut by fracture-filling veinlets of quartz, arsenopyrite and sphalerite. Crystals of cassiterite from stanniferous quartz veins generally show exsolved Nb- and Ta-bearing oxide minerals ($\leq 80 \times 50$ μm), whereas those from W–Sn-bearing quartz veins commonly host inclusions of rutile ($\leq 70 \times 50$ μm) and rare inclusions of ilmenite ($\leq 8 \times 3$ μm). However, exsolved Nb- and Ta-bearing oxide minerals and rutile, or rutile alone ($\leq 30 \times 20$ μm), were locally found.

In the volcanogenic deposit from Neves–Corvo, meter-thick massive lenses of euhedral to subhedral cassiterite with interstitial quartz, carbonates and sulfides locally overlie the massive copper ore (Gaspar 1991). This cassiterite is intergrown with or cut by veinlets of chalcopyrite, pyrite and carbonates. Neither inclusions nor products of exsolution were found.

SAMPLES, ANALYTICAL METHODS AND TREATMENT OF DATA

A total of 1738 compositions were obtained by electron microprobe, 1100 on cassiterite in 63 selected crystals, 203 on their inclusions (82 of columbite–tantalite, 108 of rutile, and 13 of ilmenite) and 435 of their products of exsolution (293 of columbite–tantalite, 72 of ixiolite, 15 of ferrotapiolite, 43 of rutile, and 12 of ilmenite).

The oxide minerals were analyzed for major and minor elements on a Cameca Camebax electron microprobe at Instituto Geológico e Mineiro, S. Mamede de Infesta, Portugal. Analyses were conducted at an accelerating voltage of 15 kV and a beam current of 20 nA. Standards used include SnO_2 (Sn*L*α), Fe_2O_3 (Fe*K*α), $MnTiO_3$ (Mn*K*α and Ti*K*α), pure Ta (*L*α), Nb (*L*α) and W (*L*α) metals. Each element was counted for 20 seconds. ZAF corrections were applied.

Included and exsolved Nb- and Ta-bearing oxide

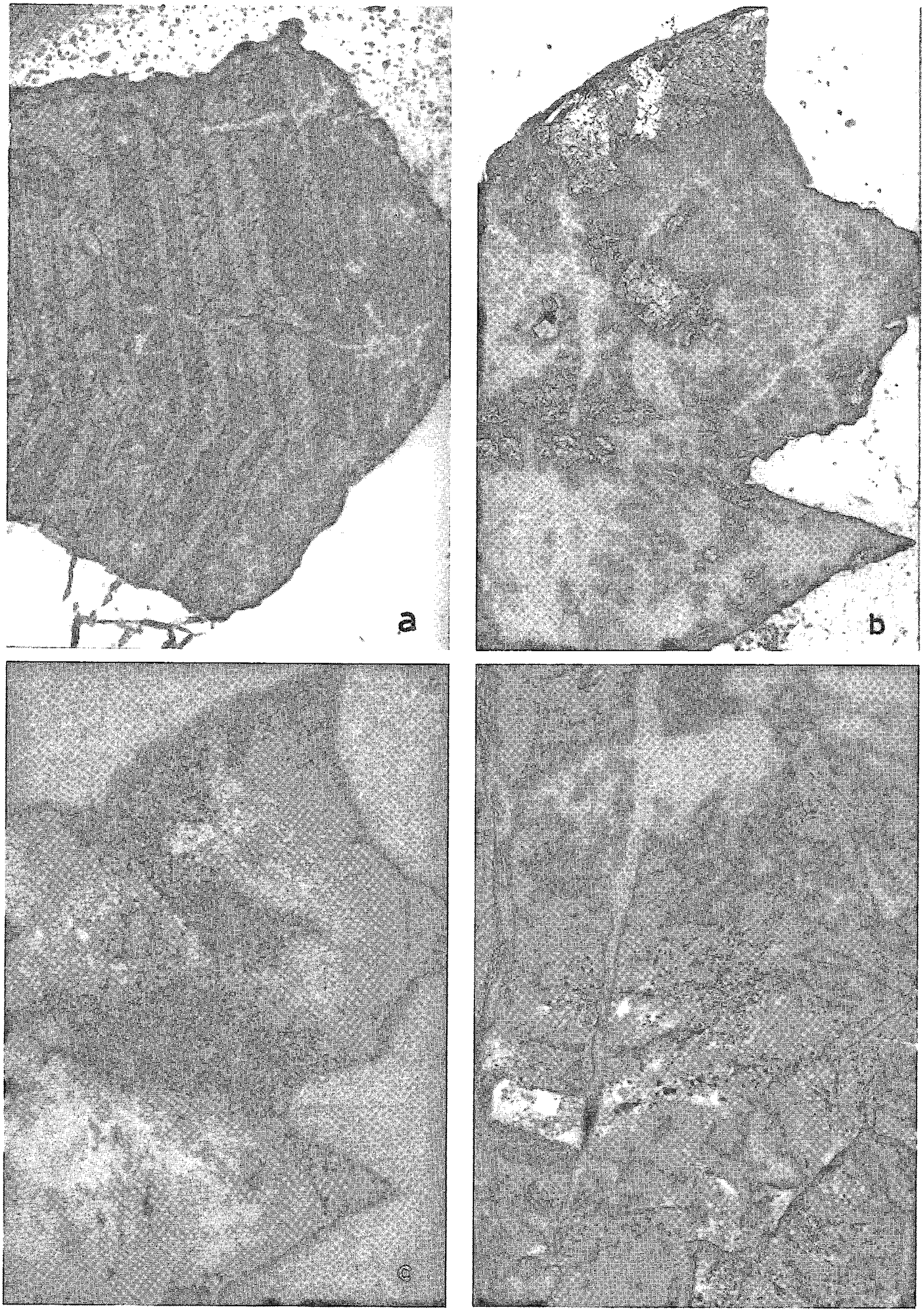
a
b
c

FIG. 3. a. Part of a crystal of cassiterite from the Revel pegmatite (×53); b. cassiterite from the Vieiros pegmatite (×214); c. distribution of Ta in b; d. cassiterite from the volcanogenic Sn deposit from Neves Corvo (×211).

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minerals in cassiterite show a variety of compositions. Owing to their small size, it was impossible to get information on their structural state and, consequently, in some cases, to identify them completely. Chemical criteria were therefore used to distinguish the relatively pure minerals of the columbite–tantalite group (whatever their structural state) from minerals of the ixiolite–wodginite series, arbitrarily called here ixiolite. Both columbite–tantalite and ixiolite phases were compared on a uniform basis of six atoms of oxygen, despite the differences in unit-cell contents. The review of niobium and tantalum minerals by Černý & Ercit (1989) provided the terminology used in this paper.

CASSITERITE ZONING, INCLUSIONS AND PRODUCTS OF EXSOLUTION

The cassiterite from most of the granitic pegmatites and quartz veins exhibits narrow parallel alternating lighter and darker growth-zones (Fig. 3a). The lighter zones are translucent, colorless to tan, whereas the darker zones are pleochroic. The darker zones generally exhibit strong pleochroism (ε red or deep red and even black, ω translucent and colorless). Some crystals of cassiterite from the pegmatite bodies at Vieiros are zoned in this way, whereas others are unzoned (Fig. 3b) and strongly pleochroic. In the darker zones of some crystals from the Sn-bearing pegmatite bodies at Fental and Revel, the pleochroism is less intense: ε reddish brown, ω beige. In crystals of cassiterite from the pegmatite bodies at Bessa, some crystals from the stanniferous quartz veins from Argozelo, and most crystals from W–Sn-bearing quartz veins, the darker zones are only slightly pleochroic: ε brown to ω light brown. However, in other crystals from W–Sn-bearing quartz veins from Carvalhal, the pleochroism of the darker zones is strong: ε red, ω translucent colorless.

Crystals of cassiterite from pegmatite bodies and stanniferous quartz veins commonly show products of exsolution, whereas accidental inclusions are common in crystals of cassiterite from the W–Sn-bearing quartz veins (Table 1). Products of exsolution were commonly found in the strongly pleochroic darker zones of cassiterite, but they were also found in lighter zones, mainly in contact with darker zones. Inclusions occur in both lighter and darker zones of the crystals. The distinction between accidental inclusions and products of exsolution was based on textural

TABLE 1. INCLUSIONS AND PRODUCTS OF EXSOLUTION IN CASSITERITE FROM GRANITIC PEGMATITES AND QUARTZ VEINS FROM NORTHERN AND CENTRAL PORTUGAL

	GRANITIC PEGMATITES						
	Inclusions		Products of Exsolution				
	Rutile	Columbite-tantalite	Columbite-tantalite	Ferrotapiolite	Ixiolite	Rutile	Ilmenite
Localities	Bessa	Vieiros	Vieiros	Vieiros	Vieiros	-	-
			Cabração	Cabração	-	-	-
			Fental	Fental	Fental	Fental	Fental
			Revel	-	Revel	Revel	-

	STANNIFEROUS QUARTZ VEINS		W-Sn-BEARING QUARTZ VEINS			
	Products of exsolution		Inclusions		Products of exsolution	
	Columbite-tantalite	Ixiolite	Rutile	Ilmenite	Ixiolite	Rutile
Localities	Montezinho	Montezinho	Carris	Carris	Muralha	Muralha
	Argozelo	Argozelo	Lombo de Boi			
			Linhares			
			Fonte Figueira			
			Vale das Gatas			
			Carvalhal			
			Soutelinho			
			Filharoso			
			S. Domingos			
			Folgar			
			Bouço			
			Panasqueira			

observations and on electron-microprobe traverses of the host cassiterite near the inclusions and products of exsolution. Inclusions occur within the crystals of cassiterite, whereas products of exsolution occur throughout the cassiterite. Chemical composition is necessary to distinguish between accidental inclusions and products of exsolution. In the case of accidental inclusions, the composition of the darker zone of the host cassiterite is homogeneous, whereas appropriate compositional gradients in the host phase are found in the case of products of exsolution.

Subhedral to euhedral cassiterite from the Neves–Corvo volcanogenic deposit (Fig. 3d) exhibits yellow, brown and deep brown components, which are only slightly pleochroic, do not define zonal sequences, are devoid of inclusions and exsolution products, and are extensively fractured.

TABLE 3. SELECTED ELECTRON MICROPROBE DATA ON CASSITERITE FROM STANNIFEROUS QUARTZ VEINS FROM NORTHERN PORTUGAL

	8				9					
	a	bl	b2	b3	a	bm	bn	bp	br	bs
Nb_2O_5	0.33	1.13	1.22	0.87	0.01	1.06	1.12	0.85	0.06	0.16
Ta_2O_5	0.04	0.29	1.75	3.19	0.04	1.71	2.37	2.87	1.66	2.04
$Ti O_2$	0.09	0.29	0.23	0.24	0.13	0.13	0.23	0.25	0.24	0.31
SnO_2	99.54	98.33	96.15	94.42	99.58	96.65	95.50	95.33	97.76	96.92
WO_3	0.05	-	-	-	-	-	-	-	0.01	-
MnO	0.01	-	0.03	0.11	-	-	0.08	0.01	-	0.05
FeO	0.13	0.52	0.71	0.87	0.03	0.79	0.89	0.98	0.35	0.48
Total	100.19	100.56	100.09	99.70	99.79	100.34	100.19	100.29	100.08	99.96
Nb	0.004	0.013	0.014	0.010	-	0.012	0.013	0.010	0.001	0.002
Ta	-	0.002	0.012	0.022	-	0.012	0.016	0.019	0.011	0.014
Ti	0.002	0.005	0.004	0.005	0.002	0.002	0.004	0.005	0.005	0.006
Sn	0.991	0.971	0.956	0.946	0.997	0.960	0.950	0.949	0.977	0.969
W	-	-	-	-	-	-	-	-	-	-
Mn	-	-	0.001	0.002	-	-	0.002	-	-	0.002
Fe	0.003	0.011	0.015	0.018	0.001	0.016	0.019	0.020	0.007	0.010
Total	1.000	1.002	1.002	1.003	1.000	1.002	1.004	1.003	1.001	1.003

8: Montezinho (a: lighter zone, bl: red zone, b2: deep red zone, b3: very deep red zone); 9: Argozelo (a: lighter zone, bm, bn, bp, br, bs: reddish brown zone with increasing distance from columbite-tantalite (bm, bn, bp) and titanian ixiolite with subordinate W ≥ Sn (br, bs) exsolution products). Oxides in wt.%; - not detected. Cation formula based on two atoms of oxygen. Analyst: A. Neiva.

GEOCHEMISTRY OF CASSITERITE

In the zoned crystals from Sn-enriched bodies of granitic pegmatite from Cabração, Fental and Revel (Table 2) and stanniferous quartz veins from Montezinho and Argozelo (Table 3), the chemical compositions of the lighter zones and darker zones are well distinguished. The lighter zones are nearly pure SnO_2, whereas the darker zones have generally higher Nb, Ta and Fe contents (Table 2, anal. 1, 3, and Table 3, anal. 8, 9). The red zones become progressively deeper red with increasing Ta and Fe contents (Table 3, anal. 8b1, b2, b3). The darker zones are heterogeneous, and their Ta/(Ta + Nb) values vary with increasing distance from exsolved Nb- and Ta-bearing oxide minerals (Fig. 4a); the zoning in each darker zone is oscillatory. The Ta and Fe contents of the darker zones decrease near exsolved columbite–

TABLE 2. SELECTED ELECTRON MICROPROBE DATA ON CASSITERITE FROM TIN-ENRICHED GRANITIC PEGMATITES FROM NORTHERN PORTUGAL

	1		2	3		4		5		6				7					
	a	b	a,b	a	b	a	b	a	b	a	bh	bk	bl	bl	b2	b3	b4	b5	b6
Nb_2O_5	0.04	1.19	0.13	0.14	1.84	0.15	0.43	0.03	0.82	0.01	0.17	0.14	0.14	-	0.25	0.60	0.62	1.29	1.48
Ta_2O_5	0.04	1.66	0.09	0.06	1.60	0.04	0.36	0.04	0.14	-	0.33	0.25	0.39	0.53	2.06	4.93	6.28	8.66	11.89
TiO_2	0.07	0.17	0.56	0.01	0.05	0.53	0.81	0.29	0.84	0.39	0.44	0.67	0.97	0.08	0.01	0.13	0.19	0.16	0.30
SnO_2	99.77	95.96	99.39	99.13	95.40	98.65	97.91	99.07	97.70	98.58	98.92	99.51	98.00	99.26	97.68	93.49	91.34	87.57	83.54
WO_3	0.03	0.17	0.09	0.08	0.08	-	-	0.03	-	0.15	0.25	-	-	-	-	-	-	-	-
MnO	0.01	0.03	0.02	-	0.04	-	-	0.01	0.01	0.01	0.03	-	-	-	-	-	0.07	0.06	0.09
FeO	0.04	0.61	0.06	0.17	0.61	0.04	0.19	0.03	0.26	0.08	-	0.11	0.33	0.11	0.43	0.87	1.52	2.08	2.58
Total	100.00	99.79	100.34	99.59	99.62	99.41	99.70	99.50	99.77	99.22	100.14	100.68	99.83	99.98	100.43	100.02	100.02	99.82	99.88
Nb	-	0.013	0.001	0.002	0.021	0.002	0.005	-	0.009	-	0.002	0.002	0.002	-	0.003	0.007	0.007	0.015	0.017
Ta	-	0.011	0.001	-	0.011	-	0.002	-	0.001	-	0.002	0.002	0.003	0.004	0.014	0.034	0.043	0.059	0.082
Ti	0.001	0.003	0.010	-	0.001	0.010	0.015	0.005	0.016	0.007	0.008	0.012	0.018	0.002	-	0.002	0.004	0.003	0.006
Sn	0.997	0.957	0.985	0.994	0.952	0.987	0.974	0.993	0.969	0.990	0.983	0.982	0.973	0.993	0.974	0.938	0.917	0.882	0.843
W	-	0.001	0.001	0.001	0.001	-	-	-	-	0.001	0.002	-	-	-	-	-	-	-	-
Mn	-	0.001	-	-	0.001	-	-	-	-	-	0.001	-	-	-	-	-	0.001	0.001	0.002
Fe	0.001	0.013	0.001	0.004	0.013	0.001	0.004	0.001	0.005	0.002	-	0.002	0.007	0.002	0.009	0.018	0.032	0.044	0.055
Total	0.999	0.999	0.999	1.001	1.000	1.000	1.000	0.999	1.000	1.000	0.998	1.000	1.003	1.001	1.000	0.999	1.004	1.004	1.005

1: Cabração, 2: Bessa, 3 and 4: Fental, 5 and 6: Revel, 7: Vieiros. a: lighter zone, b: darker zone; a,b: average of zones a and b; 6 (bh, bk, bl-red zone with increasing distance from rutile inclusion); 7 (bl-light red zone, b2 and b3-red zone, b4, b5 and b6 deep red zone). Oxides in wt.%. - not detected. Cation formula based on two atoms of oxygen. Analyst: A. Neiva.

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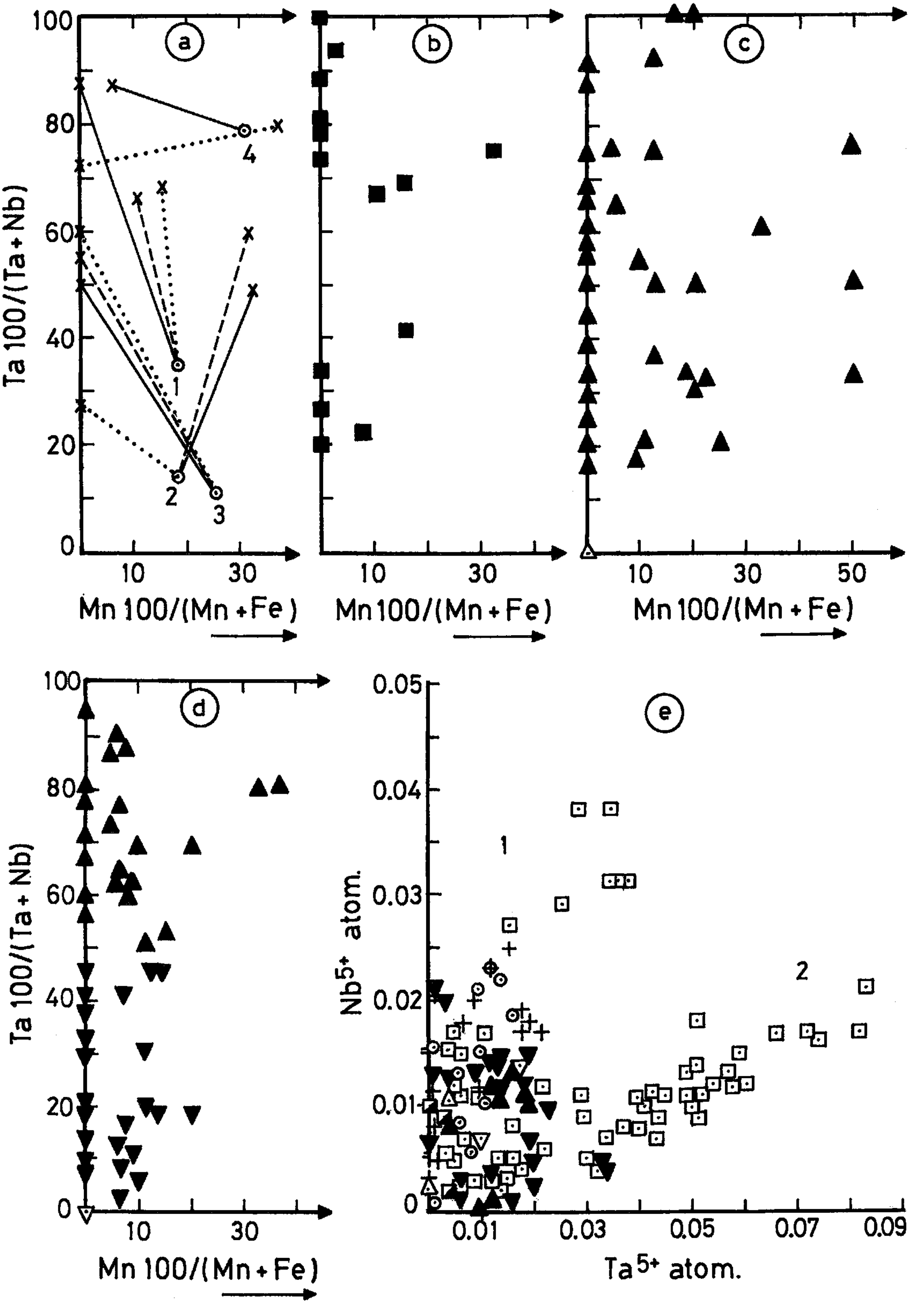
FIG. 4. a. Variation in composition of the host dark zone of cassiterite at progressively increasing distances from different grains of exsolved Nb- and Ta-bearing oxide minerals. ⊙: exsolution products of: 1, 2: ferrocolumbite, 3: titanian ixiolite with subordinate W > Sn, 4: stannian ixiolite; ×: host dark zone of cassiterite at — 10 µm; ---- 20 µm, ···· 30 µm from the rim of the exsolution product. b, c, d. Variations in chemical composition of dark zones of a single crystal of cassiterite determined at 10 µm from the rim of the exsolution product, consisting of: b: columbite–tantalite (■), c: titanian ixiolite with subordinate W > Sn (▲), d: columbite–tantalite (▼) and Sn-rich titanian ixiolite (▲); b. Vieiros; c. Argozelo; d. Montezinho; e. Correlation between Ta and Nb of cassiterite from Sn-enriched pegmatites (⊙ Cabração, + Fental, ◪ Revel, ⊡ Vieiros) and stanniferous quartz veins (▼ Montezinho, ▲ Argozelo), 1: cassiterite with Nb ≥ Ta, and 2: cassiterite with Ta > Nb.


a
b
c
d
e
Ta 100/(Ta + Nb)
Mn 100/(Mn + Fe)
0
20
40
60
80
100
10
30
50
1
2
3
4
0.05
0.04
0.03
0.02
0.01
0
Nb5+ atom.
Ta5+ atom.
0.01
0.03
0.05
0.07
0.09

tantalite (Table 3, anal. 9bm, bn, bp) and exsolved ixiolite (Table 3, anal. 9br, bs) and increase with distance from these exsolved domains. There is no significant chemical distinction among closely spaced dark zones. However, in the same crystal, significant differences in the Ta/(Ta + Nb) values can exist in dark zones that are far apart (Figs. 4b, c), although these show the same product of exsolution (either columbite–tantalite or ixiolite). For example, in a single crystal from Montezinho, deep to very deep red zones containing Ta ≥ Nb and showing mainly exsolved Sn-rich titanian ixiolite generally have higher Ta/(Ta + Nb) values (Fig. 4d) and Ta, Fe contents (Table 3, anal. 8b2, b3) than red zones characterized by Nb > Ta and showing columbite–tantalite exsolution products (Table 3, anal. 8b1).

In the pegmatite bodies at Fental and Revel, there also are crystals whose darker zones show less intense pleochroism and have more Nb, Ta, Ti and Fe than in the lighter zones (Table 2, anal. 4a, b and 5a, b), but the chemical difference between darker and lighter zones here is more subtle, because the lighter zones are less pure than usual. These crystals show generally exsolved titanian ixiolite with subordinate W > Sn, rutile ± ilmenite mainly, but not exclusively in the darker zones. The Ti content of the darker zones next to domains of exsolved rutile increases with increasing distance away from the exsolved blebs (Table 2, anal. 6h, k, l).

Cassiterite from the pegmatite bodies at Vieiros is mainly unzoned and strongly pleochroic. The red and deep red cassiterite has higher contents of Ta and Fe than the pale red cassiterite (Table 2, anal. 7b1–b6). It is heterogeneous, exhibiting a wide range of compositions (Fig. 3c); it contains inclusions of quartz and muscovite, and many small (≤2 × 1 μm) grains of exsolved columbite–tantalite and stannian ixiolite.

Cassiterite from the pegmatite bodies at Bessa and from W–Sn-bearing quartz veins from Carris, Lombo de Boi, Linhares, Fonte Figueira, Vale das Gatas, Muralha, Carvalhal, Soutelinho, Filharoso, S. Domingos, Folgar, Bouço and Panasqueira (Fig. 1) are zoned. However, in general, no significant chemical distinction was found between the darker, slightly pleochroic zones and the lighter zones, and average compositions are given in Table 2 (anal. 2) and Table 4 (anal. 10, 11, 12, 13, 14, 15, 16, 18). The samples of cassiterite from the quartz veins from Carvalhal, Soutelinho, Filharoso, S. Domingos, Folgar and Bouço, all occurring close to each other (Fig. 1) and related to the same S-type granite, have a similar chemical composition (represented collectively by anal. 16 in Table 4). However, some crystals of cassiterite from Carvalhal have strongly pleochroic darker zones, with Ti content higher than in the lighter zones (Table 4, anal. 17a, b1, b2).

In crystals that host accidental rutile or ilmenite inclusions, but lack any products of exsolution, the cassiterite is fairly homogeneous near the inclusions, which seem to be uniformly distributed in the lighter and darker zones. Furthermore, there is no chemical distinction in successive darker zones in each crystal. However, in crystals of cassiterite from Muralha, which contain exsolved rutile and ixiolite, there is a progressive increase in the Ti content of dark zones with increasing distance from these blebs (Table 4, anal. 15bh, bk, bl and br, bs, bt respectively). The chemical composition of successive closely spaced red zones generally does not change significantly, except if there is an increase in intensity of color that is accompanied by an increase in Ti content (Table 4, anal. 17bl, b2).

The brown components of cassiterite from the Neves–Corvo volcanogenic deposit have higher Fe

TABLE 4. SELECTED ELECTRON MICROPROBE DATA ON CASSITERITE FROM W ≥ Sn -BEARING QUARTZ VEINS FROM NORTHERN AND CENTRAL PORTUGAL AND A VOLCANOGENIC DEPOSIT FROM SOUTHERN PORTUGAL

	10	11	12	13	14	15							16	17			18	19		
	a,b	a,b	a,b	a,b	a,b	a,b	bh	bk	bl	br	bs	bt	a,b	a	b1	b2	a,b	d	e1	e2
Nb_2O_5	0.03	0.09	0.01	0.08	0.01	0.17	0.15	0.19	0.17	0.10	0.24	0.11	0.24	0.01	0.20	0.36	0.01	-	0.03	-
Ta_2O_5	0.07	0.01	0.08	0.12	0.05	0.22	0.39	0.29	0.39	0.28	0.37	0.34	0.19	0.02	0.29	0.12	0.06	0.11	0.05	0.40
TiO_2	0.42	0.76	0.72	0.60	0.87	0.47	0.55	0.72	0.86	0.28	0.42	0.52	0.52	0.35	0.67	0.92	0.58	0.04	-	-
SnO_2	99.13	98.75	99.26	98.85	99.00	99.05	98.73	98.78	98.20	98.96	98.68	98.58	99.07	99.68	98.59	98.43	99.32	99.85	98.17	97.72
WO_3	0.10	0.06	0.04	0.04	0.07	0.08	-	-	0.12	-	-	0.11	0.05	0.04	0.01	0.23	0.14	0.06	0.95	-
MnO	0.01	0.02	0.02	0.01	0.02	0.01	0.02	0.01	0.01	-	0.03	0.01	0.02	0.03	-	0.01	0.02	0.02	0.01	-
FeO	0.13	0.05	0.04	0.05	0.06	0.06	0.16	0.07	0.19	0.10	0.13	0.09	0.09	0.02	0.06	0.09	0.03	0.18	0.90	1.93
Total	99.89	99.74	100.17	99.75	100.08	100.06	100.00	100.06	99.94	99.72	99.87	99.76	100.18	100.15	99.82	100.16	100.16	100.26	100.11	100.05
Nb	-	0.001	-	0.001	-	0.002	0.002	0.002	0.002	0.001	0.003	0.001	0.003	-	0.002	0.004	-	-	-	-
Ta	-	-	-	0.001	-	0.001	0.003	0.002	0.003	0.002	0.003	0.002	0.001	-	0.002	0.001	-	0.001	-	0.003
Ti	0.008	0.014	0.013	0.011	0.016	0.009	0.010	0.013	0.016	0.005	0.008	0.010	0.010	0.007	0.013	0.017	0.011	0.001	-	-
Sn	0.988	0.983	0.985	0.985	0.981	0.985	0.982	0.981	0.975	0.990	0.984	0.983	0.983	0.992	0.981	0.973	0.986	0.995	0.977	0.976
W	0.001	-	-	-	-	-	-	-	0.001	-	-	0.001	-	-	-	0.001	0.001	-	0.006	-
Mn	-	-	-	-	-	-	-	-	-	-	0.001	-	-	0.001	-	-	-	-	-	-
Fe	0.003	0.001	0.001	0.001	0.001	0.001	0.003	0.001	0.004	0.002	0.003	0.002	0.002	-	0.001	0.002	0.001	0.004	0.019	0.040
Total	1.000	0.999	0.999	0.999	0.998	0.998	1.000	0.999	1.001	1.000	1.002	0.999	0.999	1.000	0.999	0.998	0.999	1.001	1.002	1.019

10: Carris; 11: Lombo de Boi; 12: Linhares; 13: Fonte Figueira; 14: Vale das Gatas; 15: Muralha (bh, bk, bl: with increasing distance from exsolved rutile and br, bs, bt: from exsolved titanian ixiolite with subordinate W ≥ Sn); 16: Carvalhal, Soutelinho, Filharoso, S. Domingos, Folgar, Bouço; 17: Carvalhal (bl: red zone, b2: deep red zone); a: lighter zone, b: darker zone; a, b: average of zones a and b; 18: Panasqueira; 19: Neves Corvo (d: yellow, el: brown, e2: deep brown). Oxides in wt.%. - not detected. Cation formula based on two atoms of oxygen. Analyst: A. Neiva.

content than the yellow components (Table 4, anal. 19d, e1, e2). The brown components become deep brown with increasing Fe content.

GEOCHEMISTRY OF CASSITERITE: A SUMMARY

Most of the cassiterite crystals analyzed tend to be richer in Fe than Mn. Dark zones of crystals from granitic pegmatites and stanniferous quartz veins generally contain more Nb than Ta, but some deep red zones and also deep red unzoned crystals contain significantly more Ta than Nb. As a result, two distinct trends with different slopes were defined in the diagram showing Ta *versus* Nb for dark cassiterite (Fig. 4e). In general, these crystals contain exsolved columbite–tantalite or ixiolite (or both), preferentially in the dark zones. Note that the cassiterite from

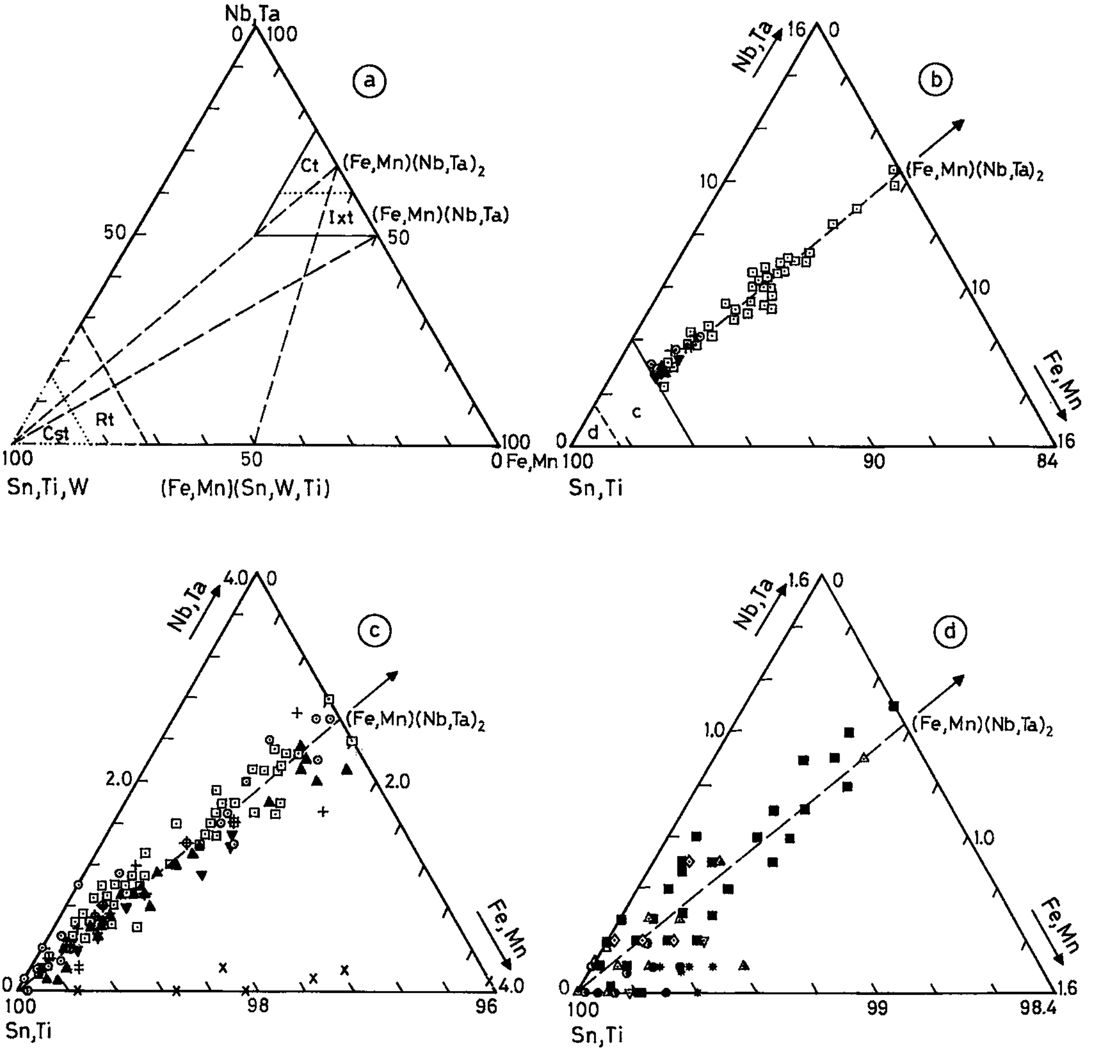


FIG. 5. a. A (Nb,Ta) – (Fe,Mn) – (Sn,Ti,W) diagram showing the location of triangular plots for Portuguese cassiterite (Cst), rutile (Rt), columbite–tantalite (Ct), ixiolite (Ixt). b. Compositions of the cassiterite richest in Nb + Ta of Portuguese Sn-enriched pegmatites and stanniferous quartz veins, plus the locations of cassiterite diagrams (c) and (d), expanded in the following figures. c. Compositions of cassiterite from Portuguese Sn-enriched pegmatites and stanniferous quartz veins. d. Compositions of cassiterite from Portuguese W > Sn-bearing quartz veins. Symbols: Sn-enriched pegmatites (⊙ Cabração, ⦶ Bessa, + Fental, ◪ Revel, ⊡ Vieiros); stanniferous quartz veins (▼ Montezinho, ▲ Argozelo); W > Sn-bearing quartz veins (✱ Carris, ▽ Lombo de Boi, ◑ Linhares, ◈ Fonte Figueira, ● Vale das Gatas, △ Muralha, ■ Carvalhal, Soutelinho, Filharoso, S. Domingos, Folgar, Bouço, ◭ Panasqueira); volcanogenic deposit (× Neves–Corvo).

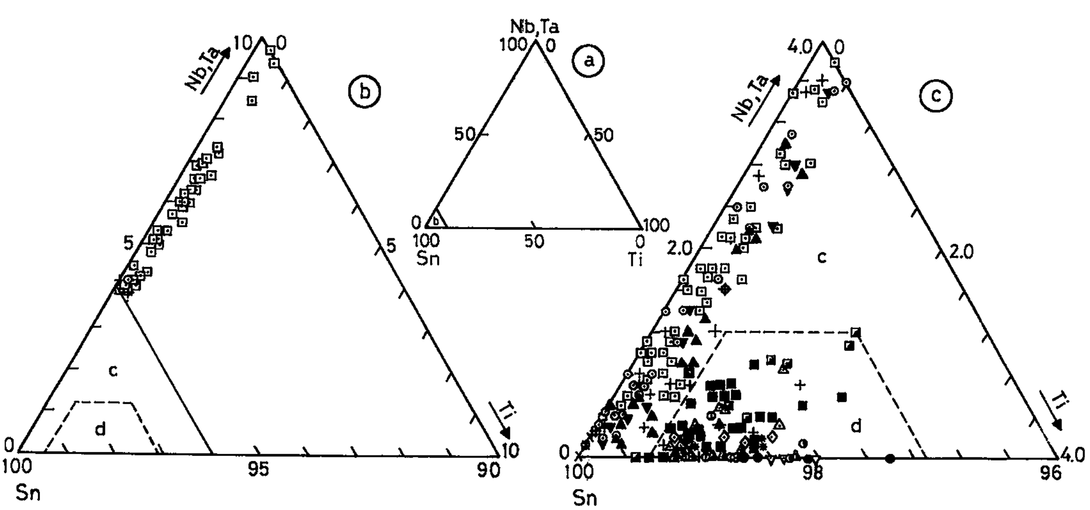


FIG. 6. a. A (Nb,Ta) – Ti – Sn diagram showing the location of diagram (b). b. Composition of the cassiterite richest in Nb + Ta from bodies of Sn-enriched pegmatite mainly from Vieiros, but also from Cabração and Fental and showing the location of cassiterite diagram (c) and of its area (d), which are expanded in the following figure to avoid data superposition. c. Compositions of cassiterite from Portuguese Sn-enriched pegmatites, stanniferous quartz veins and W–Sn-bearing quartz veins. Cassiterite hosting rutile ± ilmenite inclusions or rutile ± ilmenite ± ixiolite ± columbite–tantalite exsolution products fall in area (d). Symbols as in Fig. 5.

pegmatite bodies and stanniferous quartz veins is generally richer in Nb, Ta and Fe, particularly concentrated in dark zones, than cassiterite from W–Sn-bearing quartz veins.

The crystals of cassiterite analyzed contain up to 2.42 wt.% Nb_2O_5 (from pegmatite bodies at Cabração), 2.84 wt.% Ta_2O_5 and 0.98 wt.% FeO (both from pegmatite bodies at Fental). However, higher values are found in cassiterite from pegmatite bodies at Vieiros (up to 3.26 wt.% Nb_2O_5, 11.89 wt.% Ta_2O_5 and 2.58 wt.% FeO). Niobium, Ta and Fe may be incorporated in submicroscopic inclusions and products of exsolution indistinguishable with the electron microprobe. Furthermore, the (Ta + Nb)/(Fe + Mn) values are less than 2, ranging between 1.5 and 1.7 for cassiterite containing from 6.28 to 11.89 wt.% Ta_2O_5, indicating than the Ta + Nb content in cassiterite is not exclusively controlled by included particles and exsolved blebs of columbite–tantalite (Möller *et al.* 1988).

The concentration of Ti does not exceed 0.40 wt.% TiO_2 in the dark zones of cassiterite from pegmatite bodies and stanniferous quartz veins, where free of exsolved or included rutile. However, in dark zones in the cassiterite from pegmatite bodies at Revel, which contains exsolved rutile, it reaches 0.97 wt.% TiO_2 away from these blebs (Table 2, anal. 5 and 6). The Ti content of cassiterite from W–Sn-bearing quartz veins attains 1.82 wt.% TiO_2 (Vale das Gatas), but uniformly distributed in both lighter and darker zones.

The data on Portuguese cassiterite (Tables 2, 3, 4) suggest that the pleochroism of cassiterite can be related to the presence of Ta and Nb, which agrees with findings of Hall & Ribbe (1971), but it can also be attributed either to Ti or to Fe.

TABLE 5. REPRESENTATIVE COMPOSITIONS OF INCLUDED AND EXSOLVED COLUMBITE-TANTALITE AND EXSOLVED TAPIOLITE IN CASSITERITE FROM THE GRANITIC PEGMATITES FROM VIEIROS, NORTHERN PORTUGAL

	Inclusions				Exsolution Products				
	1	2	3	4	5	6	7	8	9t
Nb_2O_5	39.52	39.57	26.54	21.77	41.31	41.05	36.97	30.62	5.71
Ta_2O_5	42.22	41.58	55.87	61.30	37.96	37.03	41.60	46.90	77.59
TiO_2	0.52	0.56	0.63	0.38	1.97	2.71	2.27	2.19	0.76
SnO_2	0.37	0.73	0.17	0.33	1.23	1.56	1.62	3.48	1.00
WO_3	n.d.	n.d.	n.d.	n.d.	0.20	0.19	0.04	0.11	0.41
MnO	4.53	12.37	4.06	14.75	1.36	4.59	1.13	2.98	1.03
FeO	12.74	5.12	12.30	1.96	16.10	12.56	15.65	13.40	13.75
Total	99.90	99.93	99.57	100.49	100.13	99.69	99.28	99.68	100.25
Nb	1.205	1.204	0.870	0.727	1.228	1.217	1.129	0.961	0.209
Ta	0.775	0.761	1.101	1.231	0.679	0.660	0.764	0.886	1.712
Ti	0.026	0.028	0.034	0.021	0.097	0.134	0.115	0.114	0.046
Sn	0.010	0.020	0.005	0.010	0.032	0.041	0.044	0.096	0.032
W	-	-	-	-	0.003	0.003	0.001	0.002	0.009
Mn	0.259	0.705	0.249	0.923	0.076	0.255	0.065	0.175	0.071
Fe	0.719	0.288	0.746	0.121	0.885	0.689	0.884	0.778	0.933
Total	2.994	3.006	3.005	3.033	3.000	2.999	3.002	3.012	3.012
$\frac{100Mn}{Mn+Fe}$	26	71	25	88	8	27	7	18	7
$\frac{100Ta}{Ta+Nb}$	39	39	56	63	36	35	40	48	89

1: ferrocolumbite, 2: manganocolumbite, 3: niobian ferrotantalite, 4: manganotantalite inclusions; 5, 6: ferrocolumbite, 7: tantalian ferrocolumbite, 8: tantalian ferrocolumbite grading to ixiolite, 9: ferrotapiolite exsolution products. Oxides in wt.%. n.d. - not detected. Cation formula based on 6 atoms of oxygen. Analyst: A. Neiva.

TABLE 6. REPRESENTATIVE COMPOSITIONS OF EXSOLVED COLUMBITE-TANTALITE AND TAPIOLITE (t) FROM CASSITERITE FROM GRANITIC PEGMATITES AND STANNIFEROUS QUARTZ VEINS FROM NORTHERN PORTUGAL

	10	11	12t	13	14	15	16	17t	18	19	20	21	22	23	24
Nb_2O_5	50.23	27.88	10.18	42.56	37.07	60.80	26.69	5.65	62.23	69.80	36.65	26.75	22.84	52.37	63.91
Ta_2O_5	29.91	55.62	73.64	37.11	42.53	19.47	55.28	77.28	12.80	6.48	42.88	52.92	56.02	26.06	10.22
TiO_2	0.41	0.23	0.21	1.28	1.53	0.33	0.47	0.57	3.06	1.63	1.81	2.10	2.80	1.46	2.69
SnO_2	0.38	0.18	1.01	0.59	0.48	0.20	0.34	1.04	1.07	0.62	0.76	0.89	1.52	0.77	0.91
WO_3	0.23	0.04	0.33	0.28	0.15	0.20	0.13	0.26	1.02	0.56	0.26	0.35	0.26	0.42	3.00
MnO	4.02	3.41	0.42	3.67	0.97	13.46	4.22	0.69	3.26	1.28	2.39	3.12	10.52	3.40	11.42
FeO	14.50	13.08	14.37	14.21	16.61	5.17	12.56	14.09	15.99	19.35	15.03	13.47	5.49	14.98	7.45
Total	99.68	100.44	100.16	99.70	99.34	99.63	99.69	99.58	99.43	99.72	99.78	99.60	99.45	99.46	99.60
Nb	1.453	0.904	0.366	1.268	1.138	1.674	0.873	0.209	1.660	1.819	1.120	0.860	0.746	1.487	1.697
Ta	0.520	1.085	1.593	0.665	0.785	0.322	1.088	1.721	0.205	0.102	0.788	1.024	1.100	0.445	0.163
Ti	0.020	0.012	0.013	0.063	0.078	0.015	0.026	0.035	0.136	0.071	0.092	0.112	0.152	0.069	0.119
Sn	0.010	0.005	0.032	0.016	0.013	0.005	0.010	0.034	0.025	0.014	0.020	0.025	0.044	0.019	0.021
W	0.004	-	0.007	0.005	0.003	0.003	0.002	0.006	0.016	0.008	0.005	0.006	0.005	0.007	0.046
Mn	0.218	0.207	0.028	0.205	0.056	0.694	0.259	0.048	0.163	0.062	0.137	0.188	0.643	0.181	0.568
Fe	0.776	0.785	0.956	0.783	0.943	0.263	0.760	0.965	0.789	0.933	0.850	0.801	0.332	0.787	0.366
Total	3.001	2.998	2.995	3.005	3.016	2.976	3.018	3.018	2.994	3.009	3.012	3.016	3.022	2.995	2.980
$\frac{100\,Mn}{Mn+Fe}$	22	21	3	21	6	73	25	5	17	6	14	19	66	19	61
$\frac{100\,Ta}{Ta+Nb}$	26	55	81	34	41	16	55	89	11	5	41	54	60	23	9

10: ferrocolumbite, 11: niobian ferrotantalite, 12: ferrotapiolite from Cabração; 13: ferrocolumbite, 14: tantalian ferrocolumbite, 15: manganocolumbite, 16: niobian ferrotantalite, 17: ferrotapiolite from Fental; 18: ferrocolumbite from Revel; 19: ferrocolumbite, 20: tantalian ferrocolumbite, 21: niobian ferrotantalite, 22: niobian manganotantalite grading to ixiolite from Montezinho; 23: ferrocolumbite, 24: manganocolumbite from Argozelo. Oxides in wt.%. Cation formula based on 6 atoms of oxygen. Analyst: A. Neiva.

The composition of the Sn, Nb, Ta oxide minerals was plotted in terms of (Nb,Ta) – (Fe,Mn) – (Sn,Ti,W) diagram (Fig. 5a), in which triangular areas for cassiterite (Cst), rutile (Rt) and columbite–tantalite and ixiolite (Ct–Ixt) are shown. All the compositions of the cassiterite from these bodies of pegmatite and quartz veins plot close to the trend defined by the ideal substitution $(Fe,Mn)^{2+} + 2(Nb,Ta)^{5+} \rightleftharpoons 3(Sn,Ti)^{4+}$ (Černý *et al.* 1985) or close to the (Sn,Ti) corner of the (Sn,Ti) – (Ta,Nb) – (Fe,Mn) diagram (Figs. 5b, c, d), as found by Spilde & Shearer (1992). To avoid superposition, compositions of cassiterite from the pegmatite occurrences and stanniferous quartz veins are plotted in Figures 5b and c. Cassiterite from W–Sn-bearing quartz veins shows a more restricted substitution (Fig. 5d).

The dominant mechanism of incorporation of Nb, Ta, Fe, Mn and Ti in cassiterite from Sn-enriched grainitic pegmatite, stanniferous quartz veins and W–Sn-bearing quartz veins clearly is $2(Nb,Ta)^{5+} + (Fe,Mn)^{2+} \rightleftharpoons 3(Sn,Ti)^{4+}$. The (Nb,Ta) – (Fe,Mn) – (Sn,Ti) diagram (Figs. 5b, c, d) does not suggest a significant role for any other substitution.

Cassiterite from the volcanogenic deposit at Neves–Corvo is poor in Nb + Ta, but rich in Fe, and plots close to the (Sn,Ti) – (Fe,Mn) join (Fig. 5c).

The cassiterite compositions were plotted in the triangular diagram (Nb,Ta) – Sn – Ti (Fig. 6). Cassiterite hosting inclusions of rutile or ilmenite and cassiterite with exsolved rutile, ilmenite and ixiolite plots in the area d of Figures 6b and 6c. This category of cassiterite is richer in Ti than that which has exsolved columbite–tantalite and ixiolite only and that contains local inclusions of columbite–tantalite, and which plots outside area d.

Geochemistry of the Columbite–Tantalite Inclusions and Products of Exsolution

Representative compositions of columbite–tantalite inclusions and products of exsolution, as well as of exsolved ferrotapiolite, are given in Tables 5 and 6. The accidental inclusions, recognized in crystals of cassiterite from Sn-enriched pegmatite bodies at Vieiros, have compositions ranging from ferrocolumbite to manganocolumbite, occasionally extending into the manganotantalite and ferrotantalite quadrants (Fig. 7a) (Černý *et al.* 1989b). The Ta/(Ta + Nb) values tend to increase with increasing Mn/(Mn + Fe) from ferrocolumbite to manganotantalite.

Both oscillatory and smoothly progressive zoning have been reported in columbite–tantalite (Barsanov *et al.* 1971, Sahama 1980, von Knorring & Condliffe

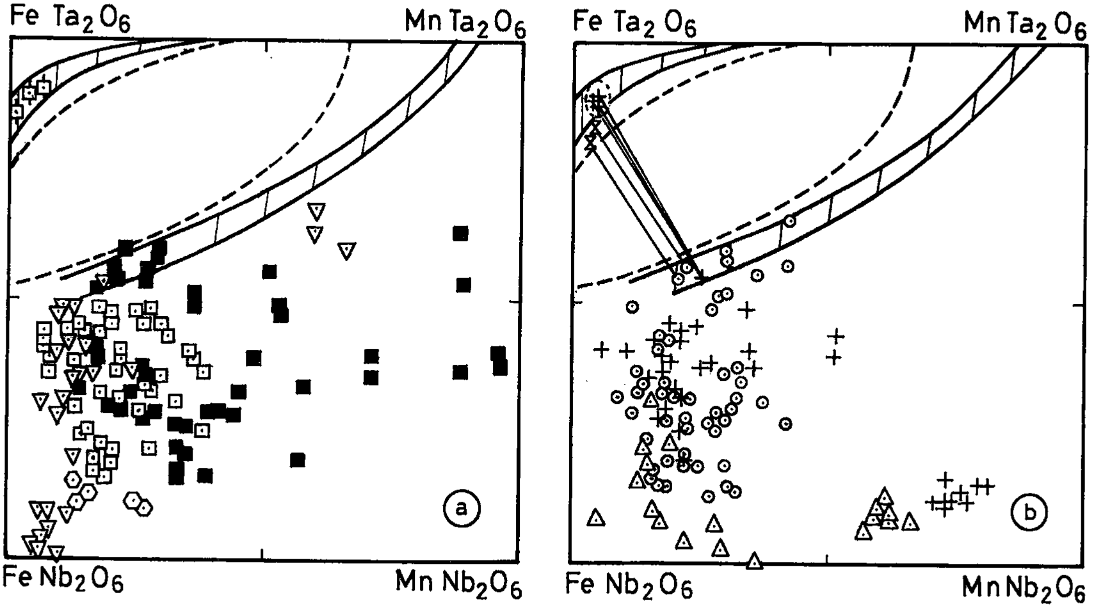


FIG. 7. Compositions of included and exsolved Portuguese columbite–tantalite and ferrotapiolite in the columbite quadrilateral: a. from Sn-enriched pegmatites from Vieiros and Revel and stanniferous quartz veins from Montezinho; b. from Sn-enriched pegmatites from Cabração and Fental, and stanniferous quartz veins from Argozelo. Bands of coexisting or associated ferrotapiolite and tantalite compositions and the gap (dashed) between individual compositions in ferrotapiolite and ferrotantalite are taken from Černý *et al.* (1992a). Symbols: columbite–tantalite inclusions (■ Vieiros); columbite–tantalite products of exsolution (⊡ Vieiros, (⬡ Revel, ∇ Montezinho, ⊙ Cabração, + Fental, △ Argozelo); exsolved ferrotapiolite (⊞ Vieiros, ⊠ Cabração, ⊕ Fental).

1984, Lahti 1987, Spilde & Shearer 1992, Černý *et al.* 1992b). Oscillatory zoning is mainly controlled by the growth dynamics of the crystals and the concentration and diffusion of the main elements, particularly Nb and Ta (Lahti 1987). In primary columbite–tantalite crystals, the oscillatory zoning represents a state of high free energy even at the late-magmatic stage of their crystallization (Černý *et al.* 1992b). Oscillatory zoning was observed in single inclusions of manganocolumbite within cassiterite from a pegmatite at Vieiros, showing more restricted range in Ta/(Ta + Nb) than in Mn/(Mn + Fe) (Table 7, A), and is attributed to a state of high free energy. A decrease in Nb, Mn, Mn/(Mn + Fe) and an increase in Ta, Fe, Ta/(Ta + Nb) from core to rim was found in single inclusions of ferrocolumbite in cassiterite from the same pegmatite (Table 7, B).

Most of the exsolved orthorhombic phases have compositions of ferrocolumbite (Figs. 7a, b). However, rare niobian ferrotantalite was exsolved from cassiterite from pegmatite occurrences at Cabração and Fental and from stanniferous quartz veins of Montezinho. Very rarely, cassiterite from these quartz veins also contains exsolved manganotantalite. Cassiterite from Fental and stanniferous quartz veins at Argozelo also exsolved manganocolumbite. A clear trend of increasing Mn/(Mn + Fe) and Ta/(Ta + Nb) values from ferrocolumbite to manganocolumbite is defined for products of exsolution in the cassiterite from Montezinho.

Some of the individual blebs of exsolved columbite–tantalite are homogeneous (Fig. 8a), but in general they display several types of zoning. Oscillatory zoning is the most common, and probably is the result of the concentration and diffusion of Nb and Ta, and also of the growth dynamics of the crystals. Some single blebs of ferrocolumbite show an increase in Nb and Mn, and a decrease in Ta and Fe, from core to rim (Table 8), but Ta and Mn decrease and Nb and Fe increase from core to rim in other blebs of ferrocolumbite (Figs. 8b, c).

Compositional data also were obtained on exsolved ferrotapiolite and niobian ferrotantalite from the same crystals of cassiterite found in the pegmatite bodies from Cabração and Fental (Table 6), but the products of exsolution are not in mutual contact. The tie-lines linking these coexisting minerals run across the length of a two phase-region (Fig. 7b) and are slightly convergent, suggesting equilibrium. The compositions fall within the boundaries defined by Černý *et al.* (1992a), as is characteristic of coexisting ferrotapiolite + tantalite. Crystals of cassiterite from the Vieiros pegmatite bodies commonly exsolved ferrocolumbite, but very rarely exsolved ferrotapiolite (Table 5, Fig. 7a), found only in cassiterite crystals that do not show any other product of exsolution. The ferrocolumbite and ferrotapiolite exsolved from the Vieiros cassiterite carry more Ti, Sn and W than the columbite–tantalite inclusions hosted by this cassiterite (Table 5), which agrees with the findings of Suwinonprecha *et al.* (1995).

GEOCHEMISTRY OF EXSOLVED IXIOLITE

The chemical compositions of exsolved ixiolite from cassiterite from bodies of granitic pegmatite and quartz veins are presented in Table 9. The ixiolite is not in contact with the exsolved columbite–tantalite in a given crystal of cassiterite.

The findings of several authors were used here to define two parallel boundaries in the diagram of Ta^{5+} *versus* Nb^{5+} (Figs. 9a, b) to distinguish chemically between minerals of the columbite–tantalite group and those of the ixiolite–wodginite family. The columbite–tantalite compositions plot between the boundaries. Compositions grading to ixiolite fall on the lower boundary, ixiolite and wodginite plot below that boundary, but wodginite with 0.35 wt.% Li_2O falls on the upper boundary, and lithiowodginite lies above this boundary (Fig. 9a). Columbite containing 7–18 wt.% WO_3, ≤1.90 wt.% Sc_2O_3 and ≤4.7 wt.% TiO_2 (Beddoe-Stephens & Fortey 1981) (Fig. 9b) and 9.8–11.3 wt.% WO_3 (Suwinonprecha *et al.* 1995) (Fig. 9a) plots below the lower boundary and is probably ixiolite.

The proportion of Nb and Ta of the included columbite–tantalite and exsolved columbite–tantalite, ferrotapiolite and ixiolite in the cassiterite studied here is plotted in Figures 10a and b. Most of the compositions fall within the columbite–tantalite field, but those containing substantial contents of combined Ti, W and Sn or of Sn alone fall below the lower boundary and are arbitrarily considered to be ixiolite. Those from the pegmatite bodies at Vieiros and some from the stanniferous quartz veins from Montezinho are stannian ixiolite $(Ta,Sn,Nb,Fe{\gtrless}Mn,Ti)_4O_8$, and others from Montezinho are Sn-rich titanian ixiolite $(Ta,Nb,Ti{>}Sn,Mn{>}Fe)_4O_8$. However, others from the pegmatite bodies at Fental and Revel, stanniferous quartz veins from Argozelo and the W–Sn-bearing quartz veins from Muralha are titanian ixiolite with subordinate W ≥ Sn $(Nb,Ta,Ti,Fe{\gtrless}Mn,W,Sn)_4O_8$ (Table 9). Sn-rich titanian ixiolite and stannian ixiolite have Ta > Nb, whereas titanian ixiolite with subordinate W ≥ Sn has Ta < Nb.

The data of several authors plotted in Figure 9 also were plotted in the (Sn,Ti,W) – (Nb,Ta) – (Fe,Mn) diagram (Figs. 11a, b, an enlargement of the triangular area Ct–Ixt shown in Fig. 5a). It is possible to distinguish between columbite–tantalite (field Ct) and ixiolite (field Ixt) in Figure 11, because the data on these minerals fall within the respective fields (except for lithiowodginite, which was not plotted here).

The data on columbite–tantalite (included and exsolved) in Portuguese cassiterite studied here plot in the corresponding field in Figures 12a, b, c. Columbite–tantalite has higher levels of Nb + Ta than ixiolite and lower Sn + Ti + W than stannian

TABLE 7. ELECTRON MICROPROBE DATA ON ZONED COLUMBITE INCLUSIONS IN CASSITERITE FROM GRANITIC PEGMATITES FROM VIEIROS

	A					B				
	Core	→	→	→	Rim	Core	→	→	→	Rim
	1	2	3	4	6	1	2	3	4	5
Nb_2O_5	42.64	33.08	40.83	27.09	40.47	50.72	48.90	48.08	45.71	44.24
Ta_2O_5	39.92	49.45	40.56	55.86	41.45	29.61	30.97	32.51	35.43	36.99
TiO_2	0.39	0.27	0.35	0.20	0.36	0.77	0.79	0.81	0.52	0.71
SnO_2	0.26	0.16	0.20	0.25	0.28	0.17	0.23	0.21	0.11	0.18
MnO	15.63	8.92	16.80	8.16	16.52	6.12	5.43	4.07	4.27	2.43
FeO	1.86	8.03	0.64	7.93	0.64	12.82	13.42	14.26	14.04	15.28
Total	100.70	99.91	99.38	99.49	99.72	100.21	99.74	99.94	100.08	99.83
Nb	1.272	1.046	1.242	0.889	1.230	1.453	1.418	1.399	1.348	1.316
Ta	0.716	0.940	0.742	1.103	0.758	0.510	0.540	0.569	0.629	0.662
Ti	0.019	0.014	0.018	0.011	0.018	0.037	0.038	0.039	0.026	0.035
Sn	0.007	0.004	0.005	0.007	0.008	0.004	0.006	0.005	0.003	0.005
Mn	0.874	0.528	0.957	0.502	0.941	0.329	0.295	0.222	0.236	0.135
Fe	0.103	0.470	0.036	0.482	0.036	0.680	0.720	0.768	0.766	0.841
Total	2.991	3.002	3.000	2.994	2.991	3.013	3.017	3.002	3.008	2.994
$\frac{100\,Mn}{Fe+Mn}$	89	53	96	51	96	33	29	22	24	14
$\frac{100\,Ta}{Ta+Nb}$	36	47	37	55	38	26	28	29	32	33

A: complex oscillatory zoned manganocolumbite; B: regularly zoned ferrocolumbite. Oxides in wt.%. Cation formula based on 6 atoms of oxygen. Analyst: A. Neiva.

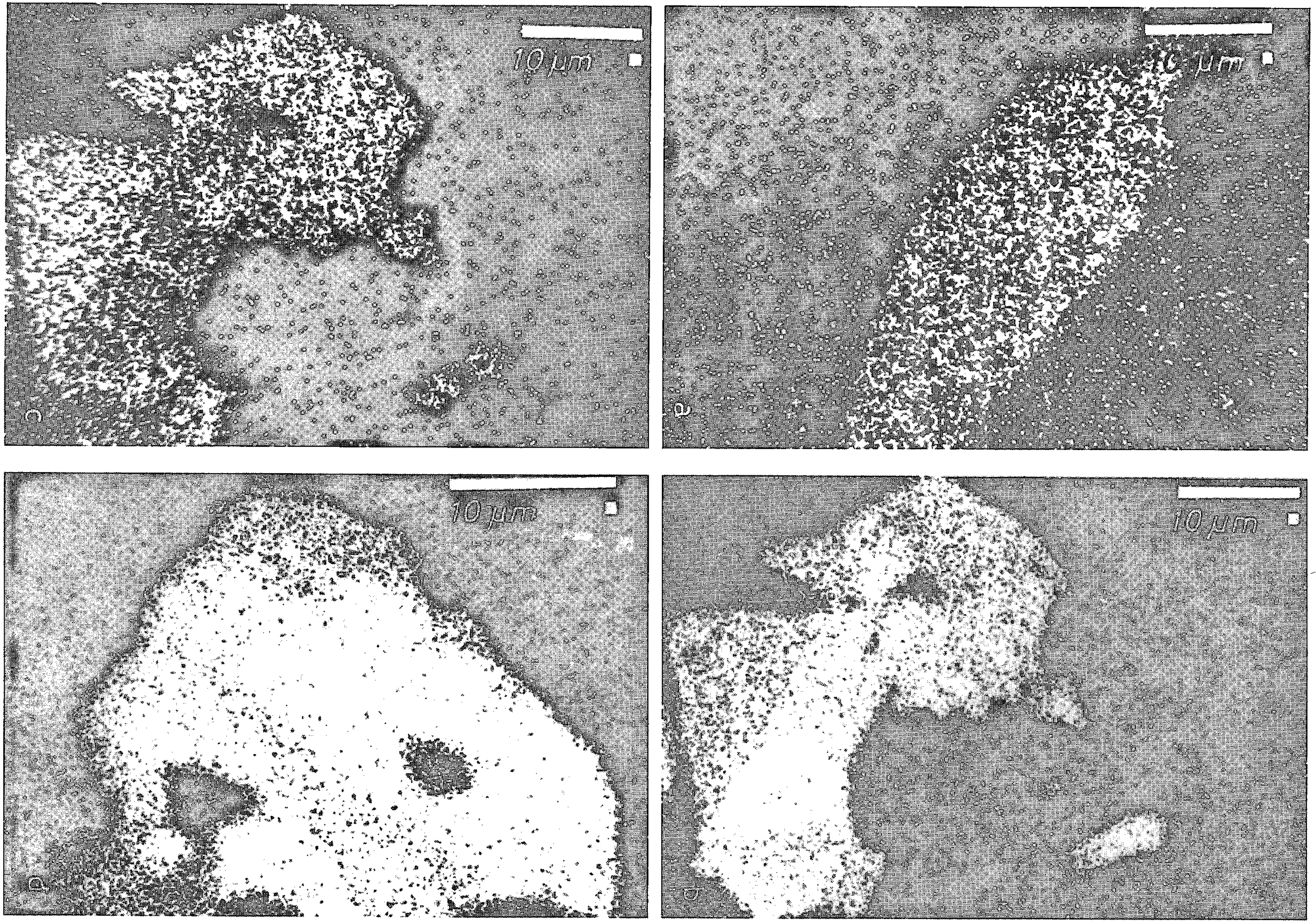

10 μm
c
10 μm
a
10 μm
d
10 μm
b

FIG. 8. Distribution of elements in products of exsolution from cassiterite. a. Homogeneous distribution of Ta in ferrocolumbite from Argozelo. b. Decrease in Ta from core to rim of ferrocolumbite from Montezinho. c. Increase in Fe from core to rim of the same grain of ferrocolumbite. d. Distribution of Ta in rutile from Muralha, but this grain has two small inclusions of cassiterite.

←

TABLE 8. ELECTRON MICROPROBE DATA ON EXSOLVED ZONED FERROCOLUMBITE FROM CASSITERITE FROM STANNIFEROUS QUARTZ VEINS FROM ARGOZELO

	Core		Rim	
	1	2	3	4
Nb_2O_5	44.57	46.94	65.96	68.73
Ta_2O_5	35.09	32.37	11.95	9.61
TiO_2	0.61	1.06	1.11	0.61
SnO_2	0.57	0.66	0.83	0.42
WO_3	0.22	0.07	1.08	0.30
MnO	2.66	2.31	3.13	3.27
FeO	15.05	15.10	16.14	16.21
Total	98.77	98.51	100.20	99.15
Nb	1.333	1.386	1.754	1.826
Ta	0.632	0.575	0.191	0.154
Ti	0.030	0.052	0.049	0.027
Sn	0.015	0.017	0.019	0.010
W	0.004	0.001	0.017	0.005
Mn	0.149	0.128	0.156	0.163
Fe	0.833	0.825	0.794	0.797
Total	2.996	2.984	2.980	2.982
$\frac{100\,Mn}{Fe+Mn}$	15	13	16	17
$\frac{100\,Ta}{Ta+Nb}$	32	29	10	8

1, 2, 3 and 4-ferrocolumbite. Oxides in wt.%. Cation formula based on 6 atoms oxygen. Analyst: A. Neiva

ixiolite and Sn-rich titanian ixiolite. The exsolved columbite–tantalite in the Vieiros cassiterite generally has higher Sn + Ti + W contents and, consequently, lower Nb + Ta contents than the columbite–tantalite inclusions in cassiterite from the same deposit (Fig. 12a). Tapiolite falls in the field Ct (Figs. 12a, c).

Stannian ixiolite has higher levels of Ta, Sn and lower levels of Nb, Ti than Sn-rich titanian ixiolite (Table 9). Both have higher levels of Ta, Sn and lower levels of Nb, W than titanian ixiolite with subordinate W ≥ Sn. Stannian ixiolite and Sn-rich titanian ixiolite fall within the ixiolite field of Černý & Ercit (1989) and have greater Ta/(Ta + Nb) values than titanian ixiolite with subordinate W ≥ Sn, which falls outside that field (Fig. 13a).

The stannian ixiolite and Sn-rich titanian ixiolite have more Sn, Ta, a greater Ta/(Ta + Nb), and less Nb than the columbite–tantalite. The Sn-rich titanian ixiolite also has more Ti than columbite–tantalite and stannian ixiolite. These ixiolite compositions have a greater Ta/(Ta + Nb) value than the columbite–tantalite of corresponding Mn/(Mn + Fe) ratio, which agrees with the findings of Černý & Ercit (1985, 1989) and Černý *et al.* (1986b).

On an atomic basis, the titanian ixiolite with subordinate W > Sn from Fental, Revel, Argozelo and Muralha has Ti > W, whereas that from the Lake District of England (Beddoe-Stephens & Fortey 1981) has W ≷ Ti, but generally W > Ti, and the phase probably corresponds to "wolframo-ixiolite". Both

TABLE 9. COMPOSITIONS OF EXSOLVED IXIOLITE FROM CASSITERITE FROM GRANITIC PEGMATITIC VEINS AND QUARTZ VEINS FROM NORTHERN PORTUGAL

	Stannian ixiolite					Titanian ixiolite																
	1				2	3				4				5	6				7			
	Mean	s	Minimum	Maximum	Mean	Mean	s	Minimum	Maximum	Mean	s	Minimum	Maximum	Mean	Mean	s	Minimum	Maximum	Mean	s	Minimum	Maximum
Nb_2O_5	7.12	1.84	4.13	9.51	9.24	11.83	0.58	11.09	13.03	55.38	10.65	40.16	67.75	60.18	59.90	7.93	46.43	72.43	48.67	4.74	41.83	55.76
Ta_2O_5	64.20	3.11	61.08	69.58	63.17	61.04	1.61	58.54	63.69	18.39	11.45	4.62	35.14	12.31	9.17	8.04	0.26	26.72	23.72	4.11	16.09	31.25
TiO_2	0.28	0.27	0	0.76	3.37	6.23	0.76	4.45	7.19	3.77	0.64	2.82	4.71	4.18	3.29	0.99	1.79	5.98	4.16	0.76	2.97	5.19
SnO_2	14.94	1.30	13.21	16.15	11.46	7.08	1.55	4.87	10.23	0.95	0.33	0.55	0.43	1.33	0.95	0.52	0.27	1.95	1.10	0.29	0.74	1.60
WO_3	0.22	0.15	0	0.43	0.24	0.34	0.25	0	0.81	2.23	0.63	1.36	3.23	2.23	6.64	2.53	3.11	13.09	3.60	1.38	2.29	6.57
MnO	8.72	1.25	7.43	10.76	4.01	6.90	0.22	6.51	7.38	4.98	1.84	2.06	6.32	3.11	6.70	2.54	1.41	11.87	11.29	2.20	7.41	14.09
FeO	4.01	1.32	2.14	5.25	8.26	6.31	0.24	5.94	6.84	14.24	0.87	13.35	15.15	16.14	12.80	2.97	7.46	18.10	6.67	2.56	3.38	10.88
Total	99.49				99.75	99.73				99.94				99.48	99.45				99.21			
n	8				3	17				6				3	23				12			
Nb	0.343	0.084	0.204	0.454	0.428	0.526	0.025	0.494	0.575	2.015	0.300	1.559	2.325	2.142	2.141	0.215	1.772	2.464	1.829	0.144	1.609	2.016
Ta	1.863	0.118	1.750	2.064	1.758	1.632	0.043	1.554	1.703	0.402	0.274	0.096	0.820	0.264	0.198	0.183	0.005	0.614	0.536	0.101	0.351	0.713
Ti	0.022	0.021	-	0.060	0.259	0.460	0.055	0.331	0.531	0.228	0.049	0.161	0.304	0.247	0.196	0.060	0.104	0.340	0.260	0.049	0.185	0.328
Sn	0.635	0.049	0.572	0.683	0.468	0.278	0.061	0.191	0.404	0.030	0.013	0.016	0.049	0.042	0.030	0.017	0.008	0.062	0.036	0.010	0.024	0.053
W	0.006	0.004	-	0.012	0.006	0.009	0.006	-	0.021	0.046	0.012	0.031	0.064	0.045	0.136	0.053	0.065	0.277	0.077	0.030	0.048	0.136
Mn	0.788	0.125	0.663	0.987	0.348	0.575	0.018	0.546	0.614	0.340	0.114	0.149	0.420	0.207	0.449	0.173	0.093	0.786	0.795	0.156	0.503	0.969
Fe	0.358	0.113	0.194	0.463	0.707	0.519	0.020	0.489	0.566	0.959	0.092	0.876	1.077	1.063	0.846	0.193	0.488	1.214	0.464	0.173	0.238	0.728
Total	4.015				3.374	3.999				4.020				4.010	3.996				3.997			

1, 2: stannian ixiolite; 3: Sn-rich titanian ixiolite; 4, 5, 6, 7: titanian ixiolite with subordinate W ≥ Sn; 1: Vieiros; 2, 3: Montezinho; 4: Fental; 5: Revel; 6:Argozelo; 7: Muralha. Oxides in wt.%. s-standard deviation. n- number of analyses. Cation formula based on 8 atoms of oxygen. Analyst: A. Neiva.

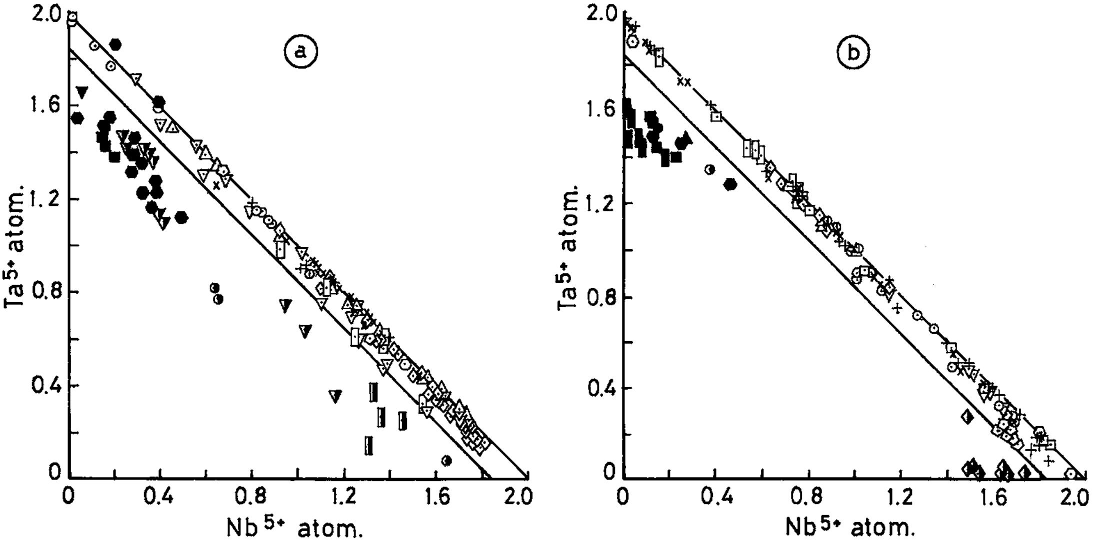


FIG. 9. Diagram of Nb^{5+} *versus* Ta^{5+} of columbite–tantalite minerals located between the two parallel boundaries; minerals of the ixiolite–wodginite family plot below the lower boundary, except lithio-wodginite. Columbite–tantalite, Ct (open symbol); ixiolite, Ixt (half-closed symbol); wodginite, Wdg (closed symbol). Symbols: a. Cotelo Neiva (1954) (⦶ Ct); von Knorring *et al.* (1969a) (◑ Ixt); von Knorring & Condliffe (1984) (× Ct); Wise & Černý (1984) (⊡ Ct, ■ Wdg); Černý *et al.* [(1986b) (▽ Ct, ⧨ Ixt, ▼ Wdg); (1992a) (⊙ Ct); (1992b (+ Ct)]; Černý & Lenton (1995) (⬠ Ct); Lahti (1987) (⟐Ct); Wenger *et al.* (1991) (⬡Ct); Ercit *et al.* (1992a, b, c) (⬢ Wdg); Spilde & Shearer (1992) (△ Ct); Suwinonprecha *et al.* (1995) (▯ Ct, ◧ Ixt). b. Nickel *et al.* (1963) (◑ Ixt); von Knorring *et al.* (1969b) (▲ Wdg); Grice *et al.* (1972) (▯ Ct, ▮ Wdg); Zelt (1975) (+ Ct); Ferguson *et al.* (1976) (● Wdg); Sahama (1980) (× Ct); Beddoe-Stephens & Fortey (1981) (⬖ probably Ixt); Černý *et al.* [(1985) (⊡ Ct, ■ Wdg); (1989a) (⦶ Ct); (1989b) (⬠ Ct); (1989c) (△ Ct)]; Foord (1982) (⬡ Ct, ⬢ Wdg); Gomes (1991) (⊙ Ct); Wenger & Ambruster (1991) (▽ Ct).

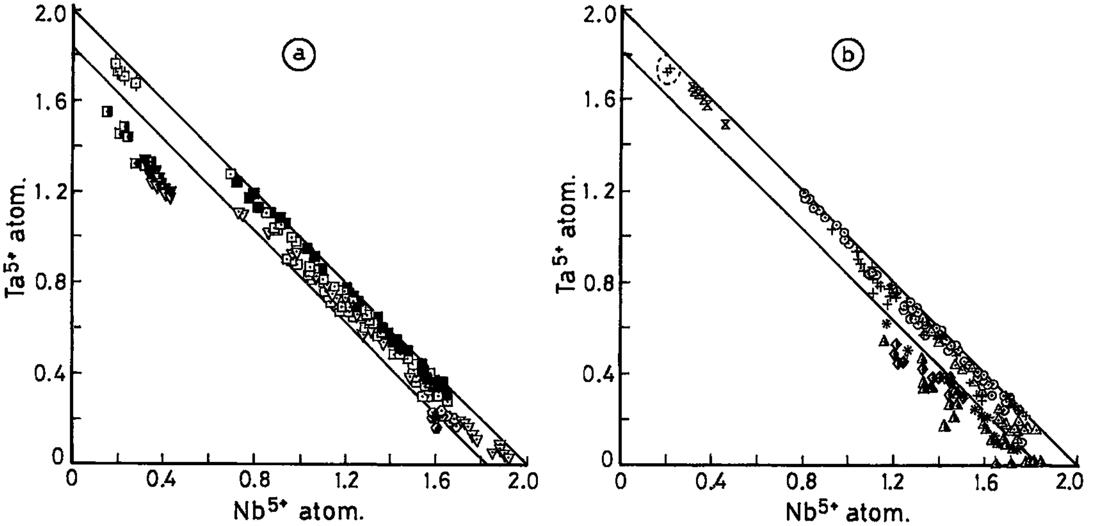


FIG. 10. Diagram of Nb^{5+} *versus* Ta^{5+} of Portuguese columbite–tantalite and ixiolite minerals. a. Included and exsolved columbite–tantalite and ferrotapiolite from Vieiros, Revel and Montezinho (symbols as in Fig. 7), exsolved stannian ixiolite (◧ Vieiros, ⧨ Montezinho), Sn-rich titanian ixiolite (▼ Montezinho) and titanian ixiolite with subordinate W > Sn (◕ Revel). b. Exsolved columbite–tantalite and ferrotapiolite from Cabração, Fental and Argozelo (symbols as in Fig. 7) and exsolved titanian ixiolite with subordinate W ≥ Sn (✳ Fental, ▲ Argozelo, ⬖ Muralha).

have Ta < Nb, but the ratio Ta100/(Ta + Nb) ranges between 0 and 34 in this Portuguese ixiolite and between 2 and 4 in the English ixiolite. Furthermore, the ranges of Mn100/(Mn + Fe) are 7–80 and 61–72 in the former and latter, respectively, both falling outside the ixiolite field in Figure 13a. This Portuguese titanian ixiolite has a heterogeneous composition, whereas that from the Lake District is homogeneous. The highest values of Ti and W in ixiolite were found in the stanniferous quartz veins from Argozelo (Table 9).

The small blebs of exsolved ixiolite generally show oscillatory zoning, which is probably due to the concentration and diffusion of Ta and Nb and the growth dynamics of the crystals. Progressive zoning also occurs, as documented in Table 10. An increase in Nb, Sn and a decrease in Ta, Ta/(Ta + Nb), and Ti from core to rim of single crystals of Sn-rich titanian ixiolite (Table 10, A) were found. In single crystals of titanian ixiolite with subordinate W > Sn, an increase in Nb and a decrease in Ta, Ta/(Ta + Nb), Ti, and W from core to rim also were observed (Table 10, B).

In the Sn-rich titanian ixiolite and stannian ixiolite, the substitution $(Fe,Mn)^{2+} + 2(Nb,Ta)^{5+} \rightleftharpoons 3(Sn,Ti)^{4+}$ dominates, as suggested by their alignment along the (Sn,Ti) – $(Fe,Mn)(Nb,Ta)_2$ join (Fig. 12d), extending from columbite–tantalite data (Černý *et al.* 1986b). These compositions may contain some Fe^{3+}, because some of them deviate slightly from that join in the direction (Sn,Ti) – (Fe,Mn) (Nb,Ta) (Figs. 12a, b, d). However, their Fe^{3+} content is probably low, as their cation totals normalized to 8 atoms of oxygen do not generally exceed 4.00, except in some grains of stannian ixiolite.

Titanian ixiolite with subordinate W > Sn plots between the (Sn,Ti) – $(Fe,Mn)(Nb,Ta)_2$ and $(Fe,Mn)(Nb,Ta)_2$ – (Fe,Mn) (Sn,W,Ti) joins (Figs. 12b, c, d) and below the data for columbite–tantalite. The higher the W content, the more pronounced is the shift to the latter join (Fig. 12d), probably drifting toward a $(Fe,Mn)WO_4$ composition, which agrees with findings of Suwinonprecha *et al.* (1995), although wolframite was not found as an exsolution product of cassiterite.

GEOCHEMISTRY OF INCLUDED AND EXSOLVED RUTILE

Rutile inclusions were mainly found in cassiterite from W–Sn-bearing quartz veins and also from the pegmatite bodies at Bessa (Table 11). Rutile included in cassiterite from quartz veins from Carvalhal, Soutelinho, Filharoso, S. Domingos, Folgar and Bouço has a similar composition. These systems of veins all are related to the same S-type granite (Fig. 1). Thus, an average composition for the rutile in these veins is given in Table 11 (anal. 7). However, rutile from Bouço contains up to 11.37 wt.% Nb_2O_5, 5.78 wt.% Ta_2O_5 and 4.15 wt.% FeO. The rutile richest in W (4.95 wt.% WO_3) is included in cassiterite from the W–Sn-bearing quartz veins from Panasqueira.

Rutile was interpreted as a product of exsolution in the cassiterite from pegmatite bodies at Fental and Revel and the W–Sn-bearing quartz veins from Muralha. Some of these crystals of cassiterite also show the presence of exsolved columbite–tantalite, titanian ixiolite with subordinate W > Sn and, locally,

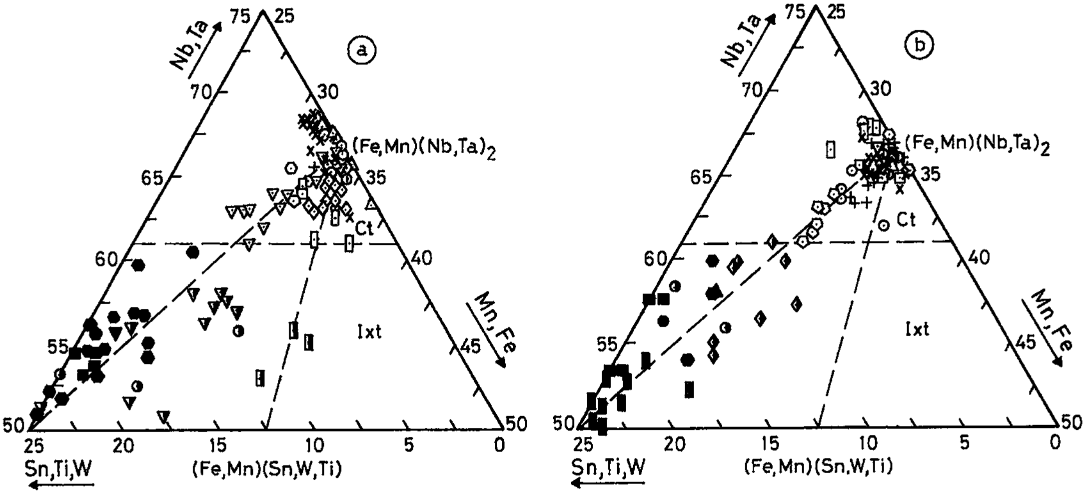


FIG. 11. Compositions of columbite–tantalite minerals and ixiolite–wodginite minerals in the (Sn,Ti,W) – (Nb,Ta) – (Fe,Mn) diagram. a. and b. The compositions plotted in the Figures 9a, b respectively. Enlargements of the triangular area Ct–Ixt shown in Figure 5a.

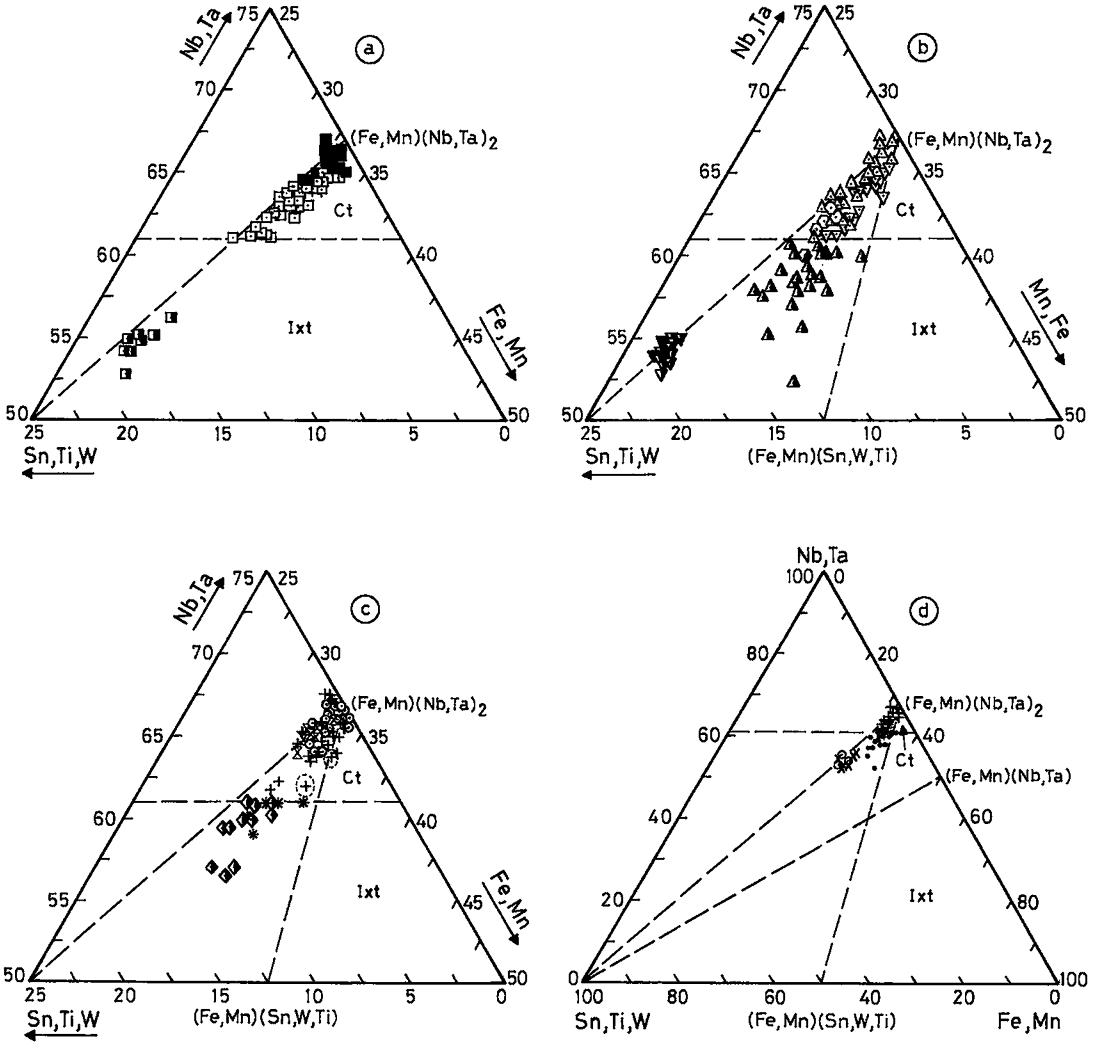


FIG. 12. Compositions of included and exsolved Portuguese columbite–tantalite; exsolved ferrotapiolite, stannian ixiolite, Sn-rich titanian ixiolite and titanian ixiolite with subordinate W ≥ Sn in the (Sn,Ti,W) – (Nb,Ta) – (Fe,Mn) diagram. a. Vieiros; b. Revel, Argozelo, Montezinho; c. Cabração, Fental, Muralha; a, b, c. Enlargements of the triangular area Ct–Ixt shown in Figure 5a. Symbols as in Figures 7 and 10. d. Selected representative data of a, b, c on the whole diagram; + columbite–tantalite, × stannian ixiolite, ⊙ Sn-rich titanian ixiolite, ● titanian ixiolite with subordinate W ≥ Sn.

ilmenite, but these phases are never in mutual contact. The rutile richest in Sn, Nb and Fe (4.24 wt.% SnO_2, 21.39 wt.% Nb_2O_5, 7.22 wt.% FeO) was exsolved from cassiterite at Revel, whereas the rutile richest in Ta (20.90 wt.% Ta_2O_5) was exsolved from cassiterite at Muralha. In the exsolved rutile, Σ(Nb + Ta + Sn + W + Fe + Mn) is similar to or exceeds that in the included rutile.

In general, the cation totals normalized to two atoms of oxygen exceed the ideal value of 1.00, except in the rutile poorest in Nb and Ta. Most of the crystals of rutile, therefore, probably contain Fe^{3+}, which is also supported by the cluster of rutile compositions between the (Sn,Ti,W) – (Fe,Mn) $(Nb,Ta)_2$ and (Sn,Ti,W) – (Fe,Mn) (Nb,Ta) joins (Fig. 13b).

In rutile, Nb usually predominates over Ta (Table 11), and the crystals are heterogeneous (irregularly zoned), but homogeneous crystals were found. Only rutile exsolved from cassiterite from the W–Sn-bearing quartz veins from Muralha shows a general tendency for Ta > Nb; most but not all of these crystals seem homogeneous (Fig. 8d). In rutile, Sn

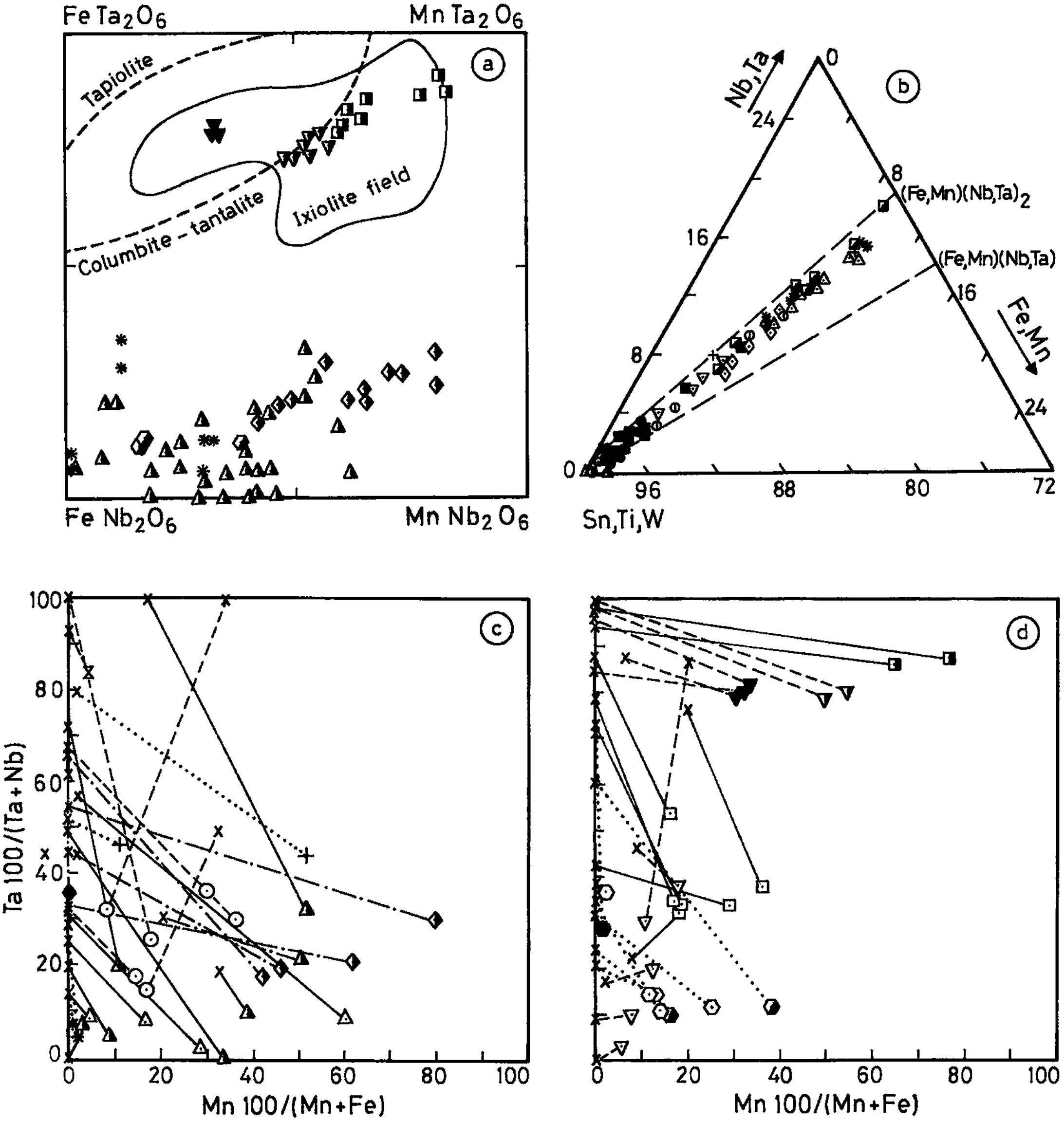


FIG. 13. a. Portuguese stannian ixiolite, Sn-rich titanian ixiolite and titanian ixiolite with subordinate W ≥ Sn in the columbite quadrilateral. Symbols as in Figure 10. Compositional gap separating columbite–tantalite from tapiolite and the ixiolite field from Černý & Ercit (1989). b. Compositions of included and exsolved rutile in the (Sn,Ti,W) – (Nb,Ta) – (Fe–Mn) diagram. Symbols: ⦶ Bessa, ✳ Carris, ▽ Lombo de Boi, ◑ Linhares, ◇ Fonte Figueira, ● Vale das Gatas, ■ Carvalhal, Soutelinho, Filharoso, S. Domingos, Folgar, Bouço, ▲ Panasqueira inclusions; + Fental, ◪ Revel, △ Muralha exsolution products. c, d. Selected examples of dark zones of cassiterite host and their exsolution products. Symbols: as in Figures 7 and 10, rutile from ⬢ Revel, ✳ Fental, ◆ Muralha, × dark zone of cassiterite host at 10 µm from the rim of exsolved mineral; c. ---- Cabração, ···· Fental, —— Argozelo, -·-·- Muralha; d. —— Vieiros, ···· Revel, ---- Montezinho.

normally predominates over W, but locally, at Vale das Gatas and Panasqueira (Table 11), rutile inclusions with W ≥ Sn were found. However, W concentrations can vary significantly in a single crystal, with between 0 up to 3.70 wt.% WO_3.

The ratio Fe/(Fe + Mn) is extremely high, generally 1 or close to it. The ratio (Fe + Mn)/(Nb + Ta) generally varies from 0.5 to 1.1, but higher values were found in the rutile richest in W, included in cassiterite from the W–Sn-bearing quartz veins from Vale das

TABLE 10. ELECTRON MICROPROBE DATA ON EXSOLVED ZONED IXIOLITE FROM CASSITERITE FROM STANNIFEROUS QUARTZ VEINS

	A					B			
	Core	→			Rim	Core	→		Rim
	1	2	3	4	5	1	2	3	4
Nb_2O_5	11.11	11.20	11.85	12.17	13.03	51.49	60.88	62.27	66.17
Ta_2O_5	63.69	62.22	60.72	59.14	58.54	9.43	5.96	5.52	4.61
TiO_2	7.02	7.09	6.94	5.11	5.63	3.33	2.82	2.69	2.75
SnO_2	4.87	5.69	6.22	8.89	8.83	1.27	0.61	0.73	0.75
WO_3	0.09	0.45	0.48	0.81	0.61	13.09	8.49	7.66	5.78
MnO	6.79	6.65	7.26	6.84	7.10	4.35	8.13	6.87	5.63
FeO	6.25	6.32	6.27	6.68	6.28	16.06	11.90	13.14	14.08
Total	99.82	99.62	99.74	99.64	100.02	99.02	98.79	98.88	99.77
Nb	0.494	0.497	0.525	0.544	0.575	1.902	2.180	2.219	2.308
Ta	1.703	1.660	1.618	1.589	1.554	0.209	0.128	0.118	0.096
Ti	0.519	0.523	0.496	0.380	0.413	0.205	0.168	0.160	0.159
Sn	0.191	0.223	0.243	0.350	0.344	0.041	0.019	0.023	0.023
W	0.002	0.011	0.012	0.021	0.015	0.277	0.174	0.156	0.115
Mn	0.565	0.553	0.602	0.573	0.587	0.301	0.545	0.458	0.368
Fe	0.514	0.519	0.514	0.552	0.513	1.097	0.788	0.866	0.909
Total	3.988	3.986	4.010	4.009	4.001	4.032	4.002	4.000	3.978
$\frac{100\,Mn}{Fe+Mn}$	52	52	54	51	53	22	41	35	29
$\frac{100\,Ta}{Ta+Nb}$	78	77	76	74	73	10	6	5	4

A: Sn-rich titanian ixiolite from Montezinho, B: titanian ixiolite with subordinate W > Sn from Argozelo. Oxides in wt.%. Cation formula based on 8 atoms of oxygen. Analyst: A. Neiva.

Gatas and Panasqueira (3.2–9.0 and 2.6–12, respectively). Such rutile has a low Fe + Mn content and is among the most deficient in Ta + Nb. These W-enriched rutile crystals do not fit the expected correlations between (Nb + Ta) and Fe^{2+}, nor between (Ta + Nb) and Ti. The ratio Ta/(Ta + Nb) varies between 0 and 0.69, but Ti/(R^{2+} + R^{5+}) varies widely, between 3.1 and 994.

The exchange $2(Nb,Ta)^{5+} + (Fe,Mn)^{2+} \rightleftharpoons 3Ti^{4+}$ may well be a mechanism of incorporation of Nb, Ta, Fe^{2+}, and Mn in rutile, whereas $W^{6+} Fe^{2+} \rightleftharpoons 2Ti^{4+}$ may explain the rutile enriched in W that is very deficient in Nb and Ta. The substitution $Sn^{4+} \rightleftharpoons Ti^{4+}$ explains the incorporation of Sn in rutile.

GEOCHEMISTRY OF INCLUDED AND EXSOLVED ILMENITE

Accidentally included and exsolved ilmenite are scarce and without contact with other inclusions or products of exsolution. Chemical compositions, given in Table 11, show Nb > Ta. The exsolved ilmenite has higher contents of Nb, Ta and Sn than the included ilmenite, which is richer in Mn. Exsolved ilmenite contains up to 0.70 wt.% SnO_2, 0.66 wt.% Nb_2O_5 and 0.06 wt.% Ta_2O_5, and included ilmenite contains up to 4.70 wt.% MnO. The contents of Nb and Ta are too low to indicate any specific mechanism of substitution. However, a mechanism such as $(Nb,Ta)^{5+} + Fe^{3+} \rightleftharpoons 2Ti^{4+}$ is suggested by the progressive decrease in Ti with increasing (Fe + Mn + Nb + Ta).

ELEMENT PARTITIONING AMONG Nb- AND Ta-BEARING PHASES

In veins of granitic pegmatite, a single crystal of cassiterite may show isolated exsolved grains of different compositions, *e.g.*, some of columbite–tantalite, others of ixiolite and rutile, and none of them in mutual contact. Grains of the same species may have various compositions, which suggest that they are not

TABLE 11. AVERAGE COMPOSITIONS OF INCLUDED AND EXSOLVED RUTILE AND ILMENITE (i) IN CASSITERITE FROM GRANITIC PEGMATITES AND QUARTZ VEINS FROM NORTHERN AND CENTRAL PORTUGAL

	Inclusions									Exsolution products			
	1	2	3	4	5	6	7	8	9i	10	11	12	13i
TiO_2	88.61	77.55	89.14	95.98	78.55	91.25	92.11	94.98	53.52	80.92	69.08	68.28	51.58
SnO_2	2.06	1.71	2.75	2.34	1.93	1.78	1.43	1.14	0.04	1.84	2.30	1.65	0.60
Nb_2O_5	5.07	8.64	5.39	0.83	10.10	2.54	3.09	0.30	0.32	12.26	14.33	7.74	0.45
Ta_2O_5	2.07	7.65	0.05	0.10	4.81	0.08	1.63	0.04	n.d.	1.11	8.44	16.38	0.04
WO_3	0.21	0.08	0.67	0.13	0.25	2.71	0.18	2.34	0.01	0.16	0.10	0.14	0.02
FeO	2.30	4.01	1.77	0.30	4.30	1.15	1.42	0.79	42.84	4.04	5.91	5.78	45.36
MnO	0.01	0.03	0.01	0.01	0.01	0.08	0.01	n.d.	3.63	0.01	0.03	0.04	1.67
Total	100.33	99.67	99.78	99.69	99.95	99.59	99.87	99.59	100.36	100.34	100.19	100.01	99.72
n	8	6	10	13	9	10	41	11	2	8	17	18	3
Ti	0.924	0.855	0.927	0.978	0.855	0.944	0.951	0.970	2.016	0.861	0.783	0.797	1.973
Nb	0.032	0.057	0.034	0.005	0.066	0.016	0.019	0.002	0.007	0.078	0.098	0.054	0.010
Ta	0.008	0.030	-	-	0.019	-	0.006	-	-	0.004	0.035	0.069	0.001
Sn	0.011	0.010	0.015	0.013	0.011	0.010	0.008	0.006	0.001	0.010	0.014	0.010	0.012
W	0.001	-	0.002	-	0.001	0.010	0.001	0.008	-	0.001	-	0.001	-
Fe	0.027	0.049	0.020	0.003	0.052	0.013	0.016	0.009	1.794	0.048	0.074	0.075	1.929
Mn	-	-	-	-	-	0.001	-	-	0.154	-	-	0.001	0.072
Total	1.003	1.001	0.998	0.999	1.004	0.994	1.001	0.995	3.972	1.002	1.004	1.007	3.997

1: Bessa, 2: Carris, 3: Lombo de Boi, 4: Linhares, 5: Fonte Figueira, 6: Vale das Gatas, 7: Carvalhal, Soutelinho, Filharoso, S. Domingos, Folgar, Bouço, 8: Panasqueira, 9: Carris, 10: Fental, 11: Revel, 12: Muralha, 13: Fental. Oxides in wt.%. n.d. - not detected. n-number of analyses of rutile and number of analyzed grains of ilmenite. Cation formula of rutile and ilmenite based on 2 and 6 atoms of oxygen respectively. Analyst: A. Neiva.

in equilibrium. However, both ferrotapiolite and ferrotantalite are homogeneous, and probably in equilibrium (Fig. 7b). The former is enriched in Ta and Fe in comparison with the latter.

Exsolved Sn-rich titanian ixiolite and stannian ixiolite are enriched in Ta and Mn compared to coexisting columbite and tantalite. Exsolved titanian ixiolite with subordinate W > Sn, however, may have greater or smaller values of Ta/(Ta + Nb) and Mn/(Mn + Fe) than coexisting columbite–tantalite. Exsolved rutile is normally enriched in Ta and Fe relative to coexisting columbite–tantalite and titanian ixiolite with subordinate W > Sn. This is in agreement with the data of Černý *et al.* (1981, 1986b) and Černý & Ercit (1989); however, at Fental, the rutile phase shows preference for Nb and Fe. Exsolved ilmenite occurs too infrequently to be compared with others.

As the composition of the dark zones of the host cassiterite varies with the distance from the products of exsolution (Fig. 4a), the composition of the cassiterite 10 μm from exsolved particles was arbitrarily taken for purposes of comparison. The composition of selected pairs (host cassiterite – exsolution product) are shown in Figures 13c, d. In general, all the products of exsolution are enriched in Nb and Mn in comparison with the host cassiterite, in agreement with data of Wise & Černý (1984), Černý *et al.* (1985, 1986b) and Suwinonprecha *et al.* (1995). Equilibrium is suggested between cassiterite and some of its products of exsolution, as shown by parallel tielines.

Columbite–tantalite inclusions have greater or smaller Ta/(Ta + Nb) and Mn/(Mn + Fe) values than the host cassiterite. Rutile inclusions and host cassiterite usually have Mn/(Mn + Fe) = 0, but Ta/(Ta + Nb) is either greater or smaller in the inclusion.

CONCLUSIONS

(1) Euhedral cassiterite from bodies of Sn-bearing granitic pegmatite and stanniferous quartz veins, related to Hercynian S-type granites, generally has Fe > Mn and Nb > Ta and is zoned, with alternating parallel darker pleochroic zones richer in Fe, Ta and Nb than the lighter zones, which are nearly pure SnO_2. Some deep red, strongly pleochroic cassiterite has Ta > Nb. The darker zones are oscillatorily zoned and show exsolution blebs of columbite–tantalite or ixiolite or both, but where these zones also contain exsolved rutile ± ilmenite, they are richer in Ti than the lighter zones. Successive very closely spaced, red zones have a similar composition, but in any single crystal, a large range of Ta/(Ta+Nb) values can be found throughout the red zones. Occasionally, columbite–tantalite inclusions were found in both lighter and darker zones.

(2) Euhedral cassiterite from W–Sn-bearing quartz veins, related mainly to Hercynian S-type granites and rarely to a Hercynian I-type granite, has Fe > Mn and Nb > Ta and is usually zoned. The darker zones are generally slightly pleochroic and chemically indistinct from the alternating parallel lighter zones. Both types of zone may contain rutile ± ilmenite inclusions. If the darker zones are strongly pleochroic, they host exsolved rutile ± titanian ixiolite with subordinate W > Sn, and have more Ti than the lighter zones.

(3) The darker zones of cassiterite from pegmatites and stanniferous quartz veins have a much larger range of Nb + Ta and Fe than cassiterite from W–Sn-bearing quartz veins, which is normally the richest in Ti. The main mechanism responsible for Nb, Ta, Fe, Mn and Ti incorporation in cassiterite is probably $2(Nb,Ta)^{5+} + (Fe,Mn)^{2+} \rightleftharpoons 3(Sn,Ti)^{4+}$.

(4) Euhedral to subhedral cassiterite crystals of Sn-ore overlying cupriferous ores from a volcanogenic deposit are related to older Hercynian felsic rocks. This cassiterite is only very slightly pleochroic, with brown to deep brown components richer in Fe than yellow components. It is Fe-enriched and devoid of inclusions and products of exsolution.

(5) The exsolved columbite–tantalite is mostly composed of ferrocolumbite. Cassiterite from the pegmatites at Vieiros hosts accidental inclusions ranging from ferrocolumbite to manganocolumbite. These inclusions generally carry less Ti + Sn + W than exsolved columbite–tantalite. Exsolved ferrotapiolite is rare in cassiterite from pegmatite occurrences and is probably in equilibrium with coexisting ferrotantalite.

(6) The diagram Ta^{5+} *versus* Nb^{5+} and the triangular diagram (Nb,Ta) – (Sn,Ti,W) – (Fe,Mn) distinguish between minerals of the columbite–tantalite group (whatever their structural state) and minerals of the ixiolite–wodginite family, in this work arbitrarily called ixiolite. Furthermore, these diagrams differentiate stannian ixiolite and Sn-rich titanian ixiolite from titanian ixiolite with subordinate W ≥ Sn. The main mechanism of incorporation of elements in these compositional varieties of ixiolite is probably the same as that found in cassiterite.

(7) Complex oscillatory zoning in common in the included and exsolved columbite–tantalite and ixiolite, but smoothly progressive zoning also was found, as well as occasional homogeneous crystals.

(8) Inclusions of rutile are common in cassiterite from the W–Sn-bearing quartz veins, whereas exsolved rutile is scarce in cassiterite from these veins and from pegmatites. Both the inclusions and exsolution products are generally heterogeneous; the former have less Nb + Ta + Sn + W + Fe + Mn than the latter. Rutile usually has Nb > Ta and Sn > W, but included rutile with W ≥ Sn and exsolved rutile with Ta > Nb were found. The mechanism responsible for incorporation of Nb, Ta, Fe^{2+} and Mn in rutile is probably $2(Nb,Ta)^{5+} + (Fe,Mn)^{2+} \rightleftharpoons 3Ti^{4+}$; $W^{6+}Fe^{2+} \rightleftharpoons 2Ti^{4+}$ is the mechanism responsible for incorporation of W and Fe in rutile deficient in Nb and Ta, and

$Sn^{4+} \rightleftharpoons Ti^{4+}$ explains the incorporation of Sn in rutile.

(9) Ilmenite inclusions were rarely found in cassiterite from W–Sn-bearing quartz veins, containing in addition, inclusions of rutile. Ilmenite exsolved from cassiterite was only found in a granitic pegmatite. It has low Nb > Ta contents. The inclusions have less Nb, Ta and Sn and more Mn than the products of exsolution. There is a regular decrease in Ti as Fe + Mn + Nb + Ta increases, suggesting that the mechanism $(Nb,Ta)^{5+} + Fe^{3+} \rightleftharpoons 2Ti^{4+}$ might have operated.

(10) The host cassiterite shows preference for Ta and Fe relative to Nb and Mn with respect to all the products of exsolution, but no distinct preference was found with respect to its columbite–tantalite inclusions.

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