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Nb–Ta-Minerals from the Cap de Creus pegmatite field, eastern Pyrenees: distribution and geochemical trends

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With 6 Figures

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Summary

Internal structure and mineralogy facilitate distinction of four main pegmatite types at the eastern end of the Pyrenees. Three main trends in compositional variations in Nb–Ta–Sn–REE–Ti minerals have been established: a regional trend, with Ta/(Ta + Nb) ratio increasing towards the more evolved pegmatites, Mn/(Mn + Fe) being relatively low and increasing only slightly; a single-body trend, with similar enrichment toward the late pegmatite units; a single-crystal trend, with zoning related to both Ta/(Ta + Nb) and Mn/(Mn + Fe) ratios and a tendency toward Ta-enrichment in the late growth stages. The regional geochemical enrichment trends in the Mn/(Mn + Fe) ratios and Ta/(Ta + Nb) are those expected for a beryl-columbite pegmatite type. In a single pegmatite, the evolution depends on the simultaneous growth of other mineral species. Three factors seem to control the development of zoning in columbite-tantalite crystals: availability of Mn, Ta, Fe, Nb, significant differences in solubility between mineral group end members and re-equilibria with late pegmatite fluids.

Zusammenfassung

Nb–Ta-Minerale aus dem Pegmatit-Feld vom Cap de Creus, östliche Pyrenäen: Verteilung und geochemische Trends

Am Ostrand der Pyrenäen können anhand des inneren Aufbaus und der Mineralogie vier Haupttypen von Pegmatiten unterschieden werden. Die Zusammensetzungen von Nb–Ta–Sn–SEE–Ti-Mineralen folgen drei Haupttrends: einem regionalen Trend, bei dem das Verhältnis Ta/(Ta + Nb) zu den höher entwickelten Pegmatiten hin zunimmt, während Mn/(Mn + Fe) relativ niedrig ist und nur leicht zunimmt; einem lokalen (auf das jeweilige Vorkommen beschränkten) Trend mit einer ähnlichen Anreicherung zu den spätpegmatitischen Einheiten hin; einem auf Einzelkristalle bezogenen Trend mit Zonierung in bezug auf die Verhältnisse Ta/(Ta + Nb) und Mn/(Mn + Fe) und einer Tendenz zur Ta-Anreicherung in den späten Wachstumsphasen. Die regionalen geochemischen Anreicherungstrends in den Mn/(Mn + Fe)- und Ta/(Ta + Nb)-Verhältnissen entsprechen jenen, wie sie für den Beryll-Columbit-Pegmatit-Typ erwartet werden. In einem einzelnen Pegmatit hängt die Entwicklung vom gleichzeitigen Wachstum anderer Mineral-Spezies ab. Drei Faktoren scheinen die Ausbildung einer Zonierung in Columbit-Tantalit-Kristallen zu kontrollieren: das Angebot an Mn, Ta, Fe und Nb, deutliche Unterschiede in der Löslichkeit der Endglieder von Mineralgruppen und die Reequilibrierung mit spätpegmatitischen Lösungen.

Introduction

Abundant recent literature is devoted to columbite-tantalite and its compositional variation (e.g. *Grice* et al., 1972; *Lahti*, 1981; *Foord*, 1982; *Uher*, 1991), and some works are focussing on their distribution throughout the different types of zoned pegmatite fields (*Černý* and *Ercit*, 1989; *Černý* et al., 1985, 1986; *Černý*, 1990), throughout the different zones of a single pegmatite body (*Černý* et al., 1985; *Wise*, 1987; *Spilde* and *Shearer*, 1992), or throughout a single crystal (*von Knorring* and *Condliffe*, 1984; *Lahti*, 1987; *Černý* et al., 1992a). The aim of this paper is to compare on all these scales the compositional variation of Nb–Ta bearing minerals from the Cap de Creus pegmatite field: at the scale of pegmatite field, at the scale of single pegmatite body for each subtype and at the scale of a single crystal.

Although in the Cap de Creus only 2 pegmatite dikes were mined for micas or ceramic minerals, the field is well exposed, with a nearly complete representation of pegmatite types as defined by *Černý* (1982, 1991) for a zoned rare-element field. Systematic sampling was carried out by pegmatite types and, within a pegmatite type, by the internal units.

Experimental methods

In order to examine the chemical variations inside single crystals of Nb–Ta bearing minerals, backscattered electron images were obtained with SEM-EDS at the Serveis Científico Tècnics de la Universitat de Barcelona. Using these images for guidance, microprobe analyses were performed at the Museum Nationale d'Histoire Naturelle, Paris. Electron microprobe analyses were carried out on a Camebax instrument, with beam diameter of 2 μm, an accelerating potential of 15 kV and a sample current of 10 nA. Time of counting were 10 s. Standards used were: $Li_2Nb_2O_6$ (Nb$L\alpha$), $Li_2Ta_2O_6$ (Ta$L\alpha$), Fe_2O_3 (Fe$K\alpha$), rhodonite (Mn$K\alpha$), TiO_2 (Ti$K\alpha$), UO_2 (U$K\alpha$), SnO_2 (Sn$L\alpha$), pure W (W$L\alpha$).

Altogether, more than 100 single crystals from more than 30 representative pegmatites were analyzed. Crystal size permitting (only possible on some columbite-tantalite minerals and rutile) X-ray powder diffraction was used to obtain unit cell dimensions and an approximation to the bulk composition of a single crystal. Data from very small size crystals were obtained using an INEL CPF 120 diffractometer (with a multichannel detector of 120° 2θ) with acquisition time comprised between

30 min and 3 h, using quartz-monochromatized Cu$K\alpha_1$ radiation at 40 kV and 30 mA. NBS silicon (batch 640b, a = 5.430940 Å) was used as external standard to calibrate the channel positions of the INEL detector. Data from other crystals were obtained with a Siemens D500 automated powder diffractometer at 0.50° 2θ/min, with graphite monochromatized Cu$K\bar{\alpha}$ radiation at 40 kV and 30 mA. In all the cases, refinements were done using the AFFMA least squares program (Bordeaux University, pers. com.), as modified in PC version by *Rodriguez-Carvajal* (pers. comm.).

Mineral identification of most of the oxide minerals from the Cap de Creus pegmatite field (ixiolite, wodginite, tanteuxenite, microlite, rynersonite) is based on chemical composition, due to the small size of all these minerals.

Geology of the Cap de Creus region

The Cap de Creus peninsula, located in the northeast of Spain, is the easternmost outcrop of the Hercynian basement of the Pyrenees. The stratigraphy of this peninsula is restricted to two mainly detrital series, correlated with the Canavelles and Jujols units as defined by *Cavet* (1957) in the eastern Pyrenees. The ensemble, classically attributed to the Cambrian-Ordovician, was affected by regional metamorphism, ranging from the chlorite-muscovite zone in the south to the cordierite-andalusite, sillimanite and migmatitic zones in the north, with isograds trending NW-SE. Two main episodes of Hercynian deformation have been distinguished. The first generated a dominant foliation; the second folded the previous foliation during several deformation phases terminated by the development of NW–SE trending shears (*Carreras* and *Casas*, 1987). The two episodes were separated in time by the metamorphic peak.

The intrusive rocks of the area are pre-Hercynian porphyritic granites and Hercynian pegmatites and granitoids. Two types of Hercynian granitoids have been found: in the northern area, in the migmatitic zone, small intrusions of quartz gabbros, quartz diorites, tonalites, granodiorites and leucogranites (*Druguet*, 1992); in the south and southwest, two stocks of granodiorites and quartz diorites (Roses and Roda intrusions, *Carreras* et al., 1975). The latter has developed a small contact aureole.

Classification of pegmatites

About 400 pegmatite bodies were located in the northern part of the Cap de Creus peninsula, all of them within rocks of medium to high metamorphic grade. Four main types of pegmatites were recognized according to their dominant mineralogy and internal structure (*Corbella* and *Melgarejo*, 1990a). The distribution of the different pegmatite types in the field is shown in Fig. 1.

Type I pegmatites are the most abundant (more than 200 outcropping bodies) and their internal structure is simple (Fig. 2a). A border zone, one to several tens of cm wide, and a wall zone are always present. Muscovite crystals perpendicular to the contact are characteristic of the border zone. The aplitic wall zone consists mainly of quartz, microcline, albite-oligoclase and muscovite, with layering generally marked by the alignment of accessory minerals (garnet, biotite, cordierite, schorl and sillimanite). The wall zone grades to a coarse-grained zone of the same mineral-

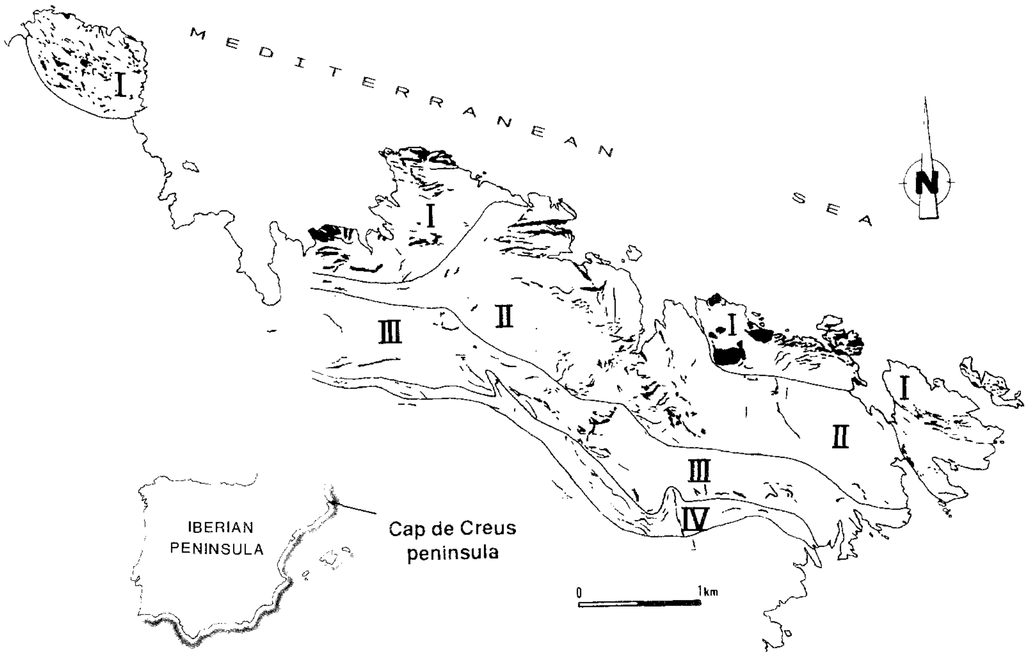

Fig. 1. Pegmatite distribution in the Cap de Creus Peninsula: I) area with barren, type I microcline pegmatites; II) area with type II transitional pegmatites, with Fe–Mn–Ca–Mg phosphates, Be and sparse Ti–Nb–Ta–W–U minerals; III): area with type III microcline-albite pegmatites, with Li–Na–Fe–Mn–Be phosphates, Be and common Nb–Ta–(Sn) minerals; IV) area with type IV albite pegmatites, with Al–Li–Be–Na–Fe phosphates, Be and Ta–Nb–Sn–REE minerals

ogy (first intermediate zone). In the largest pegmatites (more than 50 m thick) this last zone grades to a blocky zone (second intermediate zone) with microcline, branching biotite or muscovite, and quartz-feldspar graphic intergrowths. Schorl or quartz veins crosscut the bodies. Tourmalinization is widespread in the exocontacts. Oxide minerals are very rare: magnetite, ilmenite, scarce niobian rutile, columbite and ixiolite. Zircon is ubiquitous in all the zones.

Type II pegmatites (Fig. 2b) show similar border, aplitic and intermediate zones as in type I pegmatites. Moreover, quartz cores, some tens of centimeters in size, and incipient replacement phenomena occur in these pegmatites. Accessory minerals are common and varied: andalusite (locally replaced by sillimanite), schorl, beryl or chrysoberyl, gahnite, an association of primary Fe–Mn–Mg–Ca phosphates (magniotriplite, sarcopside, graftonite) and their metasomatic plus supergenic derivatives, and an assemblage of Nb–Ta–U–W minerals (ixiolite, columbite, wolframite, uraninite). Interestingly, all the Al-bearing silicates are partly replaced by the primary Ca–Fe–Mg phosphates (*Corbella* and *Melgarejo*, 1990b).

Type III pegmatites exhibit a more complex internal structure (Fig. 2c). They have a well developed quartz core and late replacement events (albitization and veining) are more widespread than in type II. Therefore, albite is a more abundant phase here than in the above types. Veins are composed of either fine-grained cleavelandite or a late generation of quartz-muscovite intergrowths. Aluminous minerals such as garnet, cordierite and the Al_2SiO_5 polymorphs are absent. Schorl

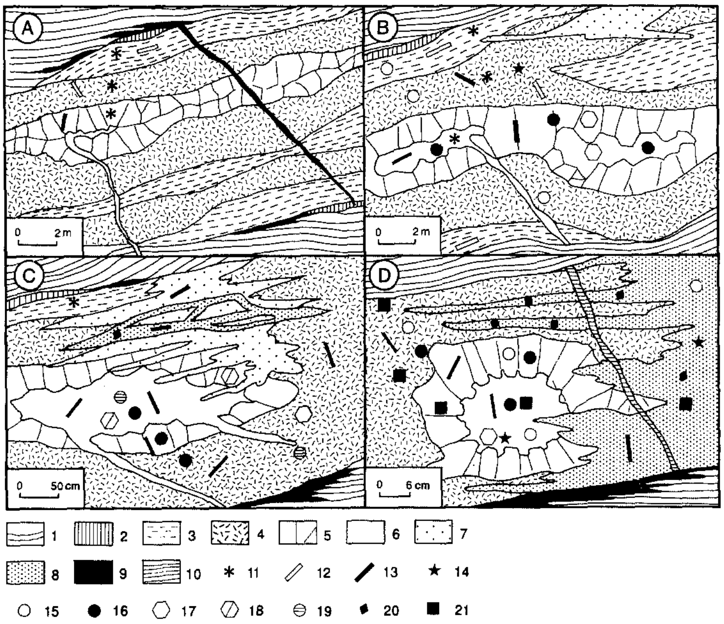

Fig. 2. Idealized models on internal structure and mineral distribution in pegmatite types from the Cap de Creus pegmatite field: **A** Type I pegmatites; **B** Type II pegmatites; **C** Type III pegmatites; **D** Type IV pegmatites. 1) country rock; 2) border zone; 3) wall zone; 4) 1st intermediate zone; 5) 2nd intermediate zone; 6) quartz core; 7) albitic replacements; 8) quartz-muscovite veins; 9) schorl veins and tourmalinization; 10) Al–Li–Be phosphates within late veins; 11) peraluminous silicate minerals; 12) rutile and other Ti-rich oxides; 13) columbite-tantalite minerals; 14) chrysoberyl; 15) lazulite; 16) Ca–Fe–Mn–Mg phosphates; 17) beryl; 18) Be phosphates pseudomorphic after beryl; 19) Li–Fe–Mn phosphates; 20) cassiterite; 21) REE bearing oxides

is very rare although exocontact tourmalinization is common. The association of accessory minerals is also more evolved, with a typical assemblage of primary Li–Fe–Mn phosphates, Ta–Nb–Sn–U oxide minerals and beryl. Primary phosphates are triphylite (completely altered to ferrisicklerite and heterosite), montebrasite, sarcopside and graftonite. The first locally forms skeletal crystals associated with coarse albite crystals in the blocky zone; the two minerals are often found as centimeter-size nodular crystals in the quartz core. Metasomatic alkali phosphates (alluaudite, fillowite, arrojadite) replacing the primary phosphates, and the replacement of beryl by Be-phosphates (hurlbutite, herderite, beryllonite) at the quartz core are characteristic features. Graphite spherulites are very common in both the late albite and quartz-muscovite veins. Finally, an association of gold, native bismuth and bismuthinite enclosed in arsenopyrite crystals is present. Arsenopyrite is disseminated in all pegmatite zones, or it occurs in veinlets that transect the pegmatite body. This pegmatitic gold is possibly generated by assimilation of the Cambrian-Ordovician metasediments which host As–Au–Bi ore bodies in the region (*Ayora* and *Casas*, 1986).

Type IV pegmatites represent the most evolved bodies in the area; only 10 of them belong to this category. They are rather thin, vein-like bodies (from 10 cm to 1 m thick). As in the other types, the presence of aplitic wall zones, intermediate zones and quartz cores are observed; however, albite is the only feldspar present. The zonal ensemble is cross-cut by quartz-muscovite veinlets (Fig. 2d) that contain cassiterite and graphite spherulites. Late veins crosscutting pegmatite bodies carry a hydrothermal Al-Li-Be-Na phosphate association: berlinite, trolleite, montebrasite, lazulite and wyllieite. The aluminous chemistry of the phosphates is in marked contrast with the absence of peraluminous silicates. Nb–Ta–REE minerals are very common in these pegmatites. Tourmalinization, phosphatization (apatite) and graphitization are also developed in the exocontacts.

Finally, quartz veins (up to 1 m thick) are found surrounding the pegmatite field. They are not mineralized, although they contain Nb, Ta-poor rutile and disseminated graphite.

On the basis of their geological setting, internal structure and mineralogy, pegmatites of the Cap de Creus field belong to the rare-element class, which is represented specifically here by barren, beryl-columbite-phosphate and albite categories of *Černý* (1991).

Oxide minerals in type I pegmatites

Type I pegmatites contain only a simple assemblage of oxide minerals, in minor quantities. Selected representative compositions of Nb–Ta minerals from these pegmatites are given in Tables 1 and 2, and all data are shown in Fig. 3a.

Niobian rutile ("ilmenorutile") is dominant in the aplitic wall zone, although columbite also occurs as sparse rounded crystals (up to 50 microns) associated with

Table 1. *Chemical analyses of columbite-tantalite*

Type zone	Sample	WO_3	Nb_2O_5	Ta_2O_5	TiO_2	SnO_2	UO_2	FeO	MnO	Total
		W^{6+}	Nb^{5+}	Ta^{5+}	Ti^{4+}	Sn^{4+}	U^{4+}	Fe^{2+}	Mn^{2+}	
I.W	1 *	2.97	67.96	6.23	3.37	-	-	16.84	2.51	99.88
	**	0.044	1.760	0.097	0.145	-	-	0.808	0.122	2.970
II.FI	2 *	0.62	49.52	29.27	0.24	0.26	0.42	12.90	6.65	99.88
	**	0.010	1.436	0.511	0.012	0.007	0.006	0.692	0.361	3.035
SI	3 *	1.05	65.42	10.38	1.49	0.06	0.06	13.94	6.13	98.53
	**	0.018	1.756	0.168	0.067	0.001	-	0.692	0.308	3.010
C	4 *	0.88	45.60	34.42	1.27	0.06	-	9.16	8.58	99.97
	**	0.015	1.337	0.607	0.062	0.002	-	0.497	0.471	2.991
								13.57	6.52	100.02
III.FI	5 *	-	63.09	16.29	0.31	-	-	0.682	0.332	3.012
	**	-	1.714	0.266	0.014	-	-			
C	6 *	-	61.82	17.67	0.54	0.04	0.22	13.89	6.21	100.53
	**	-	1.681	0.289	0.024	0.001	0.003	0.699	0.316	3.015
	7 *	0.08	52.59	27.22	0.96	0.16	0.36	13.64	5.89	100.67
	**	0.001	1.485	0.462	0.045	0.004	0.005	0.713	0.312	3.025
AB	8 *	0.35	22.92	57.30	1.95	0.86	0.13	12.58	4.03	99.99
	**	0.007	0.752	1.131	0.106	0.025	0.002	0.763	0.248	3.032
	9 *	-	53.95	26.62	0.32	-	0.21	13.25	5.61	99.96
	**	-	1.531	0.455	0.015	-	0.007	0.698	0.298	3.002
IV.W	10 *	0.18	43.83	35.77	0.25	0.37	-	12.08	6.51	98.97
	**	0.003	1.317	0.646	0.012	0.010	-	0.671	0.366	3.027
	11 *	0.64	56.96	20.55	0.61	0.47	-	13.56	7.32	100.11
	**	0.010	1.582	0.343	0.028	0.012	-	0.697	0.381	3.052
SI	12 *	0.67	63.31	12.32	1.33	0.33	0.18	15.47	4.94	98.36
	**	0.012	1.718	0.201	0.060	0.008	0.002	0.776	0.251	3.028
C	13 *	-	33.63	48.72	0.04	-	-	11.97	5.01	99.41

W wall zone, *FI* first intermediate zone, *SI* second intermediate zone, *C* quartz core, *AB* albite veins, *QM* quartz-muscovite veins. * weight %, ** atomic content p.f.u. on the basis of 6 oxygens

Table 2. *Chemical analyses of rutile (ir), ixiolite (ix), tapiolite (t), cassiterite (cst) and wodginite (wg)*

Type zone	Sample	WO_3	Nb_2O_5	Ta_2O_5	TiO_2	SnO_2	UO_2	Fe_2O_3■	FeO	MnO	Total
		W^{6+}	Nb^{5+}	Ta^{5+}	Ti^{4+}	Sn^{4+}	U^{+4}	Fe^{3+}	Fe^{2+}	Mn^{2+}	
I.FI	1ix *	3.55	57.46	13.02	6.54	0.05	0.05	-	15.43	3.57	99.67
	**	0.072	2.030	0.277	0.384	0.002	0.001	-	1.008	0.236	4.010
	2ir *	1.06	23.68	12.51	51.87	0.16	-	-	10.96	0.05	100.29
	**	0.008	0.346	0.110	1.264	0.002	-	-	0.298	0.002	2.030
II.FI	3ir *	0.95	12.36	10.11	68.13	1.39	-	-	7.46	0.06	100.46
	**	0.008	0.170	0.084	1.560	0.016	-	-	0.190	0.002	2.030
	4ir *	-	2.26	0.68	95.06	0.11	0.03	-	1.55	0.15	99.84
	**	-	0.028	0.006	1.938	0.002	0.001	-	0.036	0.004	2.015
SI	5ix *	-	8.47	59.33	13.34	0.33	-	-	18.59	0.62	100.68
	**	-	0.355	1.496	0.930	0.012	-	-	1.441	0.049	4.285
III.SI	6t *	-	3.86	80.90	0.21	0.48	-	-	13.72	0.66	99.83
	**	-	0.290	3.662	0.026	0.032	-	-	1.910	0.094	6.14
AB	7ix *	-	21.53	60.36	1.66	0.04	-	-	9.17	6.48	99.24
	**	-	0.961	1.620	0.123	0.002	-	-	0.757	0.542	4.005
	8wg *	-	6.63	64.90	0.53	11.82	-	1.92	6.29	5.25	97.34
	**	-	1.301	7.662	0.173	2.046	-	0.627	2.284	1.93	16.023
IV.QM	9cst*	-	-	2.49	-	96.48	-	-	0.54	-	99.51
	**	-	-	0.034	-	1.946	-	-	0.022	-	2.002
	10cst*	-	0.01	0.92	-	96.88	-	-	0.35	-	99.16
	**	-	0.024	0.012	-	1.948	-	-	0.014	-	1.998

FI, first intermediate zone, *SI* second intermediate zone, *AB* albitic units, *QM* quartz-muscovite veins. * weight %, ** atomic content per unit cell. *ix* ixiolite (on the basis of 8 oxygens), *ir* ilmenorutile (on the basis of 4 oxygens), *t* tapiolite (on the basis of 12 oxygens), *wg* wodginite (on the basis of 32 oxygens), *cst* cassiterite (on the basis of 4 oxygens). Fe_2O_3 calculated from charge balance and stoichiometry

late quartz. Both phases locally display compositional zoning in Ta–Nb, whereas Mn/(Mn + Fe) remains constant and low ($\leq$.15).

Oxide minerals of the intermediate zones include ilmenite, rutile, magnetite, columbite-tantalite and ixiolite. Ilmenite forms prismatic crystals a few microns in size, associated with biotite, and is probably related to a late hydrothermal alteration of this mineral. Niobian rutile is found locally in this association instead of ilmenite. Magnetite rarely occurs as cm-scale crystals in the first intermediate zones of some pegmatites.

Most of the columbite-tantalite found in this pegmatite type is concentrated in the intermediate zones (Table 1, Fig. 3a). It is not very common, forming thin plates $\leq$100 microns in length. Two generations are present: the first (Ta/(Ta + Nb) ~ 0.14) is associated with early equigranular microcline-quartz-albite assemblage; the second (Ta/(Ta + Nb) ~ 0.30–0.40) is associated with schorl and late microcline. This columbite is always somewhat enriched in Ti and W (up to 4% oxides combined). Crystals are always zoned, commonly patchy. Zoning reflects always in the Ta/(Ta + Nb) ratio, whereas Mn/(Mn + Fe) is about constant; zoning is locally inverse, with Ta contents lower in the sub-surface rims.

Radial aggregates of thin tabular cystals of ixiolite ($\leq$500 μm long) are very rare. These crystals locally resemble exsolutions from niobian rutile (Fig. 4a). Both are enclosed in quartz. Ixiolite is always Nb-rich, with noticeable amounts of WO_3 ($\leq$6.53 wt%, Table 2) and minor Sc content, or with high Ti content. The chemistry of ixiolite is complex, and analyses of a single grain reveal strong internal variations. Grains of niobian rutile have irregular shape and patchy zoning related to variations in Nb_2O_5. The Nb_2O_5 content can attain over 20 wt%, but the Ta_2O_5 content rarely exceeds 10 wt%. As in columbite, the MnO content is very low (less than 4 wt%).

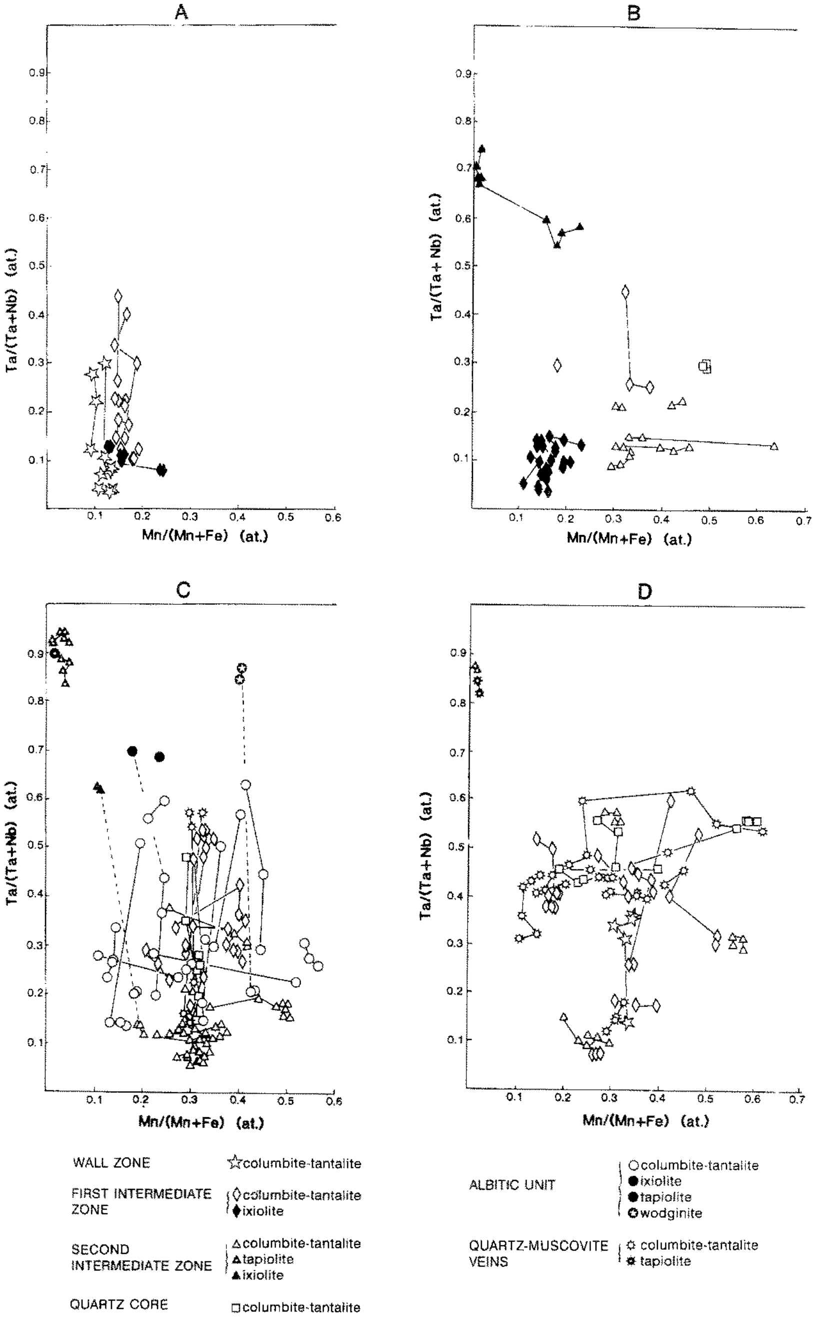

Fig. 3. Compositional ranges of columbite-tantalite and tapiolite minerals in the columbite quadrilateral (atomic proportions): **A** type I pegmatites **B** type II pegmatites; **C** type III pegmatites; **D** type IV pegmatites. Solid lines connect compositions within a single crystal; dashed lines connect mineral associations

Oxide minerals in type II pegmatites

Type II pegmatites contain a broader spectrum of oxide mineral species than type I, but these minerals are again sparse and normally ≤ 1 mm long. Tables 1 and 2, and Fig. 3b illustrate the compositions of these phases.

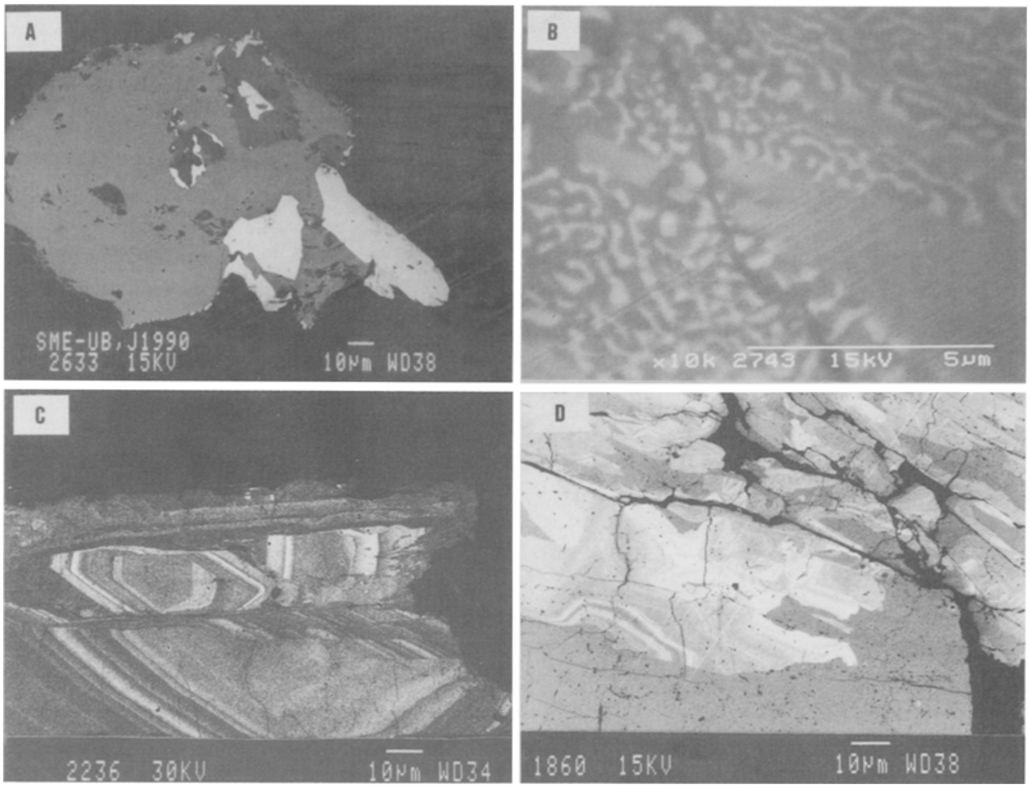

Fig. 4. Backscattered images of the Nb,Ta oxide minerals. **A** Rutile crystals with exsolved W-rich ixiolite (brightest minor grains), on a columbite crystal. Tone differences in rutile mark differences in the Nb content. Intermediate zone, type I pegmatites. **B** Ilmenite-columbite myrmekites replacing Nb-bearing rutile crystals. Wall zone, type II pegmatites. **C** Oscillatory Nb–Ta zoning in columbite-tantalite crystals. Note some contacts between zones that can be related to progressive Ta enrichment (brighter). Note syntectonic crystal growth during contemporaneous shearing. First intermediate zone, type III pegmatite. **D** Convolute zoning in columbite-tantalite crystals (type III pegmatites, second intermediate zone, albitized). The bright areas are enriched in Ta

Niobian rutile is the dominant phase in the aplitic wall zone. Irregular grains of this mineral locally enclose small but abundant irregular exsolutions of Nb-rich ixiolite (Ta/(Ta + Nb) ~ 0.05), especially near the margins. Also, myrmekitic ilmenite-columbite intergrowths replace rutile crystals along grain borders or fractures (Fig. 4b). Beside niobian rutile, columbite also is found as irregular crystals with patchy zoning: Ta-rich compositions replace Nb-enriched cores.

Well formed platy crystals of columbite occur in the intermediate zones, with compositions similar to those from type I pegmatites. Nb-dominant ixiolite associated with niobian rutile also is found in the first intermediate zones as irregular grains enclosed in chrysoberyl or Ti-rich magniotriplite. Their Ta/(Ta + Nb) ratio is again strongly and irregularly variable within each oscillatorilly zoned crystal.

In quartz cores, columbite can reach several cm in size. Whereas columbite-tantalite minerals from the intermediate zones are Mn-poor, columbite from the quartz cores is enriched in Mn. Moreover, the oscillatory zoning of individual crystals reflects changes in Mn/(Mn + Fe). Although the MnO content can reach 9.28 wt%, all compositions plot in the ferrocolumbite field.

A significant Ta enrichment is observed in columbite-tantalite from albitic units, in which it is locally widespread, and attains several mm in size. Columbite-tantalite crystals are always zoned, in an oscillatory and/or convolute manner. Some of these crystals are partly replaced by small cystalls of tapiolite and/or veinlets of uraninite.

Oxide minerals in type III pegmatites

Compositions of the Nb–Ta bearing phases are shown in Tables 1 and 2, and in Fig. 3c.

So far, no opaque minerals have been found in the aplitic wall zone.

Columbite-tantalite minerals are characteristic and common in the intermediate zones, particularly in the blocky zone, associated with Ca–Fe–Mn–(Li) phosphate

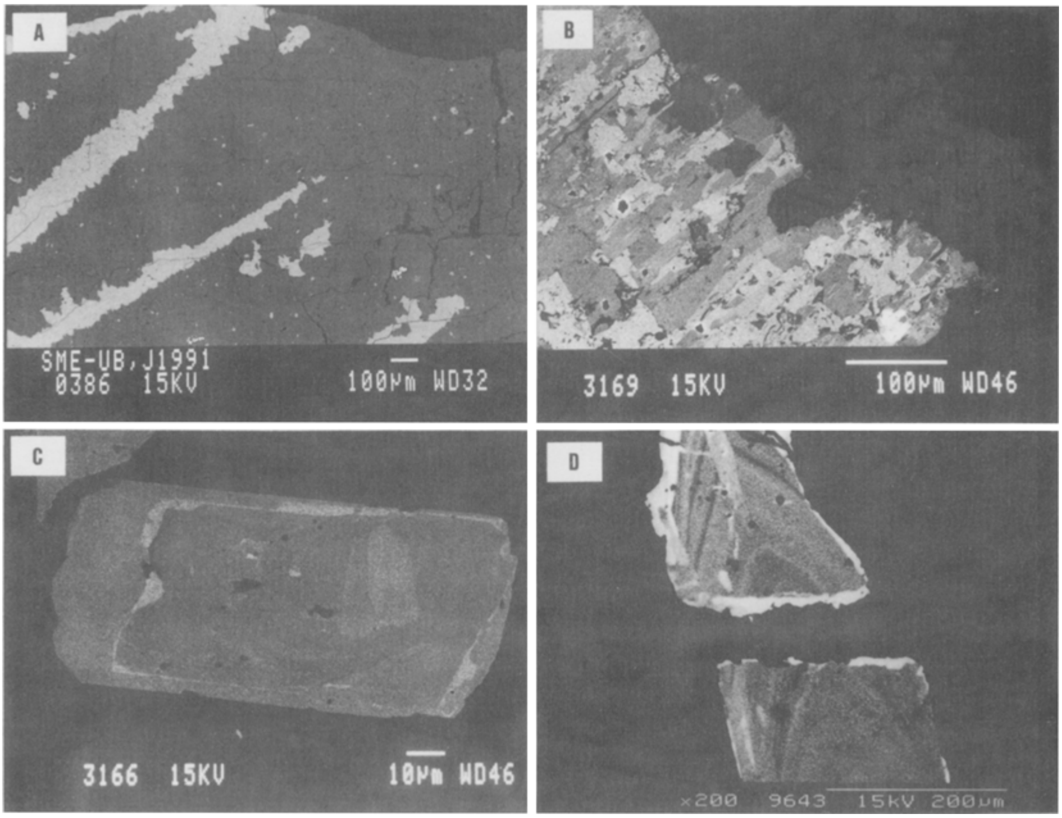

Fig. 5. Backscattered images of the Nb,Ta oxide minerals. **A** Skeletal intergrowths of ixiolite (bright) and columbite (dark grey). Note the poor zoning in columbite, generated by variations in Mn/(Mn + Fe). **B** Patchy zoning of columbite in type IV pegmatites (first intermediate zone), related to Ta/(Ta + Nb) variations. **C** Oscillatory zoning in columbite-tantalite crystal. Brighter areas are Ta-rich, darker areas are Ta-poor. Type IV pegmatites, quartz-muscovite veins. **D** Complex internal structure in columbite-tantalite from quartz + muscovite veins (type IV pegmatites): oscillatory zoning formed before deformation, followed by fracturing and the growth of a Ta-rich zone (brightest rim)

minerals. They always develop euhedral to subhedral platy crystals, up to 30 cm in size in the second intermediate zone. Their Mn and Ta content is similar to those from quartz cores of type II pegmatites (Table 1). Crystals always show oscillatory zoning related to variations of both Ta/(Ta + Nb) and Mn/(Mn + Fe) ratios. The composition of each zone is either homogeneous or progressive in its Ta content (Fig. 4c). Resorption phenomena are widespread, suggesting disequilibrium between these crystals and residual fluids. Furthermore, convoluted zoning can be present, particularly in albitized units, possibly also suggesting a lack of equilibrium during growth. Crystals with this texture exhibit very complex zoning, and the data indicate replacement of relatively Nb-rich phases by Ta-enriched compositions (Fig. 4d).

Ta-rich, Ti-,W-poor ixiolite occurs as skeletal crystals cogenetic with Ta-poor columbite-tantalite (Fig. 5a). The Mn/(Mn + Fe) ratio of both minerals is similar, suggesting a common origin with Ta partitioning into ixiolite and Nb into columbite.

In the quartz cores, some columbite-tantalite crystals reach several tens of centimeters in length, but are rare in this zone: only a few crystals close to the contact with the second intermediate zone were found, and their compositions are richer in Ta/(Ta + Nb) than those from intermediate zones. However, their composition remains similar to those from intermediate zones in terms of Mn/(Mn + Fe).

The most Ta-, Mn-enriched columbite-tantalite minerals are found closely related to late albitic units, commonly intimately associated with fine-grained saccharoidal albite +/− quartz +/− muscovite. Columbite-tantalite is very fine-grained here (platelets ≤ 1 mm long) but very common. Ta-rich ixiolite and wodginite crystals are closely associated with them, and their Mn/(Mn + Fe) ratio is similar to that of the coexisting columbite-tantalite. Thus, partitioning of Ta into ixiolite and wodginite, and Nb into columbite-tantalite is again observed. The above minerals are locally replaced by uraninite, tapiolite, cassiterite and fergusonite. The late minerals constitute fine-grained irregular aggregates along the margins of columbite-tantalite or cross-cutting veinlets.

Oxide minerals in type IV pegmatites

Type IV pegmatites are the best Sn–Nb–Ta–REE mineralized bodies of the field. The Nb–Ta mineralogy is also complex. Columbite-tantalite from all zones shows the lowest contents of minor elements (such as Ti, Sn, Y) relative to its occurrences in other pegmatite types. Tables 1 and 2, and Fig. 3d show the compositions of the Nb–Ta bearing phases from this type of pegmatites.

In aplitic zones near the pegmatite contact with the host rock, the dominant Nb–Ta bearing phases are tantalian rutile ("strüverite"), euxenite and yttrian-aeschynite. These minerals, very commonly, form small elongated crystals disseminated among muscovite flakes or in thin quartz veins. Columbite occurs as small rounded crystals (≤ 100 μm long).

Columbite-tantalite is predominant in the intermediate zones. Crystals longer than 2 mm have rarely been found. They are always zoned in terms of the Ta/(Ta + Nb) ratio, and an oscillatory or patchy style (Fig. 5b). A Ta-enrichment in columbite-tantalite is observed from the border zone toward the intermediate zones, where tantalite is the dominant phase, but there is no substantial difference between the columbite from the blocky zones and quartz cores. Columbite-tantalite minerals are locally totally replaced by a complex mineral association: the alteration progresses especially along the crystal borders, cleavages and fractures. Rynersonite and tapiolite formed early, and the ensemble is replaced by Y-rich microlite.

In the quartz cores, columbite-tantalite forms euhedral cm-sized crystals. Most of these crystals are partially replaced by the same Ta, REE-enriched assemblage identified in the intermediate zones: tapiolite, rynersonite and Y-rich microlite.

Cassiterite is the dominant oxide mineral in the quartz-muscovite veins, in cm-sized euhedral crystals. They are locally elongated and commonly twinned, growing from the vein border toward the center. Small irregular inclusions of Ta-rich members of the columbite-tantalite group are widespread in them, but in other cases cassiterite crystals develop as epitaxial overgrowths on large well-formed crystals of columbite-tantalite. Columbite-tantalite displays oscillatory zoning, mainly related to changes in the Mn/(Mn + Fe) ratio and only to slight changes in Ta/(Ta + Nb) (Fig. 5c), and they are locally replaced by rynersonite and tanteuxenite. Some crystals with oscillatory zoning were deformed or broken during the second stage of regional deformation (shear zones), and later overgrown by Ta-rich rims (Fig. 5d).

Abundant octahedral mm-sized crystals of gahnite occur in the quartz-muscovite veins. Some of these crystals are partly replaced by platy euhedral crystals of nigerite. This association is similar to that reported by *Jacobson* and *Webb* (1947). The abundance of cassiterite in these veins and the replacement of gahnite by nigerite seems to indicate a Sn-enrichment in the late S-poor pegmatite fluids, a hypothesis proposed by *Kloosterman* (1974) for the Brazilian occurrences of nigerite.

Finally, thin albite-chlorite veins locally carry allanite-Ce. This mineral appears as cm sized euhedral prismatic crystals, in radial groups. This association is related to circulation of late hydrothermal fluids.

Geochemical evolution of the Nb–Ta bearing minerals

A quick review of the mineral distribution throughout the pegmatite field allows us to establish three main trends in columbite mineral composition.

a) Regional trend. Despite the perturbances due to crystal zoning, average composition of columbite-tantalite displays a progressive increase in Ta/(Ta + Nb) ratio from type I pegmatites toward type IV pegmatites. The increase in Mn/(Mn + Fe) is especially effective between type I and II pegmatites, but the Mn/(Mn + Fe) and Ta/(Ta + Nb) ratios are in general the highest in type IV pegmatites. Despite of this relative trend, the bulk of the absolute regional composition is mainly Mn-poor and Fe-rich. The observed relationships are similar to those described from several other fields by *Černý* and *Ercit* (1985) and *Černý* et al. (1985, 1986), and are consistent with those expected for beryl-type pegmatites (*Černý*, 1989). This author attribute low Mn/(Mn + Fe) ratios to poor fractionation due to low F_2 activities; in fact, the Cap de Creus field is P-rich but F-poor, as pointed out by *Corbella* and *Melgarejo* (1990b) on the basis of mineralogical criteria.

Compositions from the most evolved pegmatites (type IV) are similar to those from the latest zones (albite replacements) from relatively less evolved pegmatites (type III). Similar relationships are observed between type III and II and type II and I. The Ta/(Ta + Nb) ratio also increases in other oxides (ixiolite, rutile) from type I to type IV (see Table 2), and minerals very rich in Ta (such as rynersonite or tapiolite) are very common in type IV pegmatites. This indicates a bulk enrichment in Ta from type I to type IV.

The amount of minor elements (Ti, Sn, W, Y, U) in columbite-tantalite decreases in the same direction, probably in consequence of the appearance of coexisting separate phases: rutile (Ti), cassiterite and wodginite (Sn), wolframite (W), uraninite (U) and fergusonite, microlite or other complex oxide minerals (REE and Y).

In addition to these regional variations in composition, the size and abundance of the crystals of Nb, Ta-oxide minerals increase generally towards the more evolved pegmatites.

The X-ray diffraction study of single crystals of columbite-tantalite from type II, III and IV pegmatites (size in type I is too small for this technique) confirms the general increase in Mn/(Mn + Fe) in columbite-tantalite from type II to type IV pegmatites. The degree of structural order, calculated according to *Ercit*'s (1986) equation (in *Černý* and *Ercit*, 1989) is very uniform in all crystals, and generally exceeds 90% (Fig. 6).

b) Single-body trend in individual pegmatites: in spite of some complications in detail, each pegmatite type displays similar variations in distribution of Nb–Ta mineral species, and similar trends in the evolution of their compositions in terms of Ta/(Ta + Nb) and Mn/(Mn + Fe) (Fig. 3).

In the early zones (wall and border), rutile is the most important Ta-Nb bearing phase, and its Ta/(Ta + Nb) ratio increases on the average from type I to type IV pegmatites. Furthermore, the restriction of rutile to the border and wall zones of all

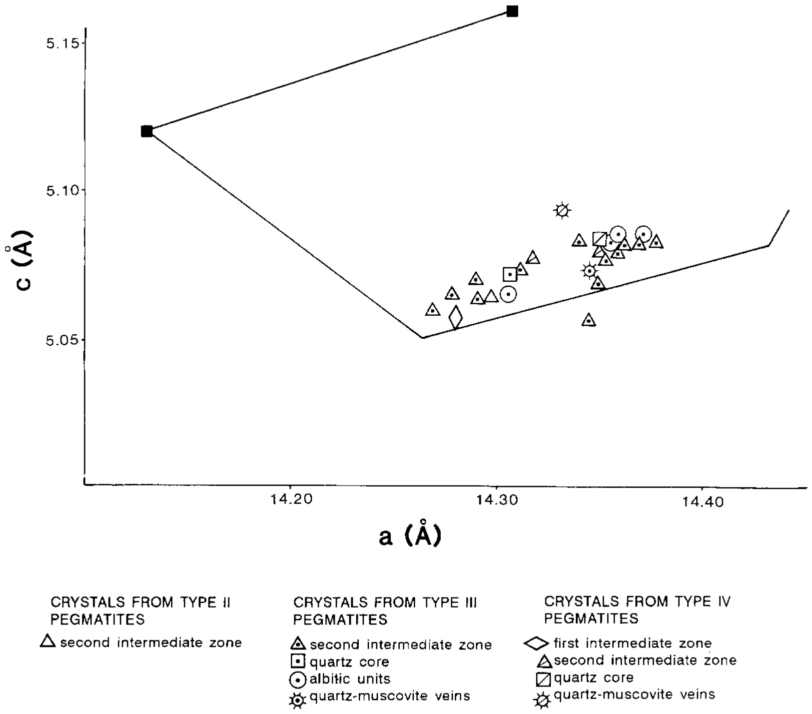

Fig. 6. Plot of columbite-tantalite crystals in the a–c diagram of *Wise* et al. (1985)

the pegmatite types suggests that most of the Ti could be a product of host-rock assimilation.

Columbite and ixiolite become the dominant phases in the intermediate zones of all pegmatites. In type I and II Fe,Nb-rich ixiolite is more common, in agreement with the abundance of Ti and Fe in other oxides (ilmenite, magnetite), silicates (cordierite, garnet, biotite, tourmaline) and phosphates (Ti-rich magniotriplite, lazulite, and other Mn-poor, Fe–Mg rich phosphates such as sarcopside or graftonite). Niobian rutile is unstable in these zones, and is replaced by ilmenite-ixiolite myrmekites. In pegmatite types III and IV, Fe–Mn bearing silicates are absent but the Mn/(Mn + Fe) ratio becomes influenced by the voluminous crystallization of primary Fe-Mn bearing phosphates. These phosphates are richer in Mn than in type I and II pegmatites, and the early columbite-tantalite crystals are Mn-poor.

The quartz core occurs only in types II, III and IV. Columbite-tantalite is always the dominant phase, and its compositional variation is again affected by the crystallization of other minerals, particularly phosphates. However, the phosphates are scarce in the cores, and local zoning in the Mn/(Mn + Fe) ratios of columbite-tantalite is observed.

The albite veins and quartz-muscovite veins are usually P-poor and free of Fe, Mn-bearing silicates; columbite-tantalite usually displays zoning in both Mn/(Mn + Fe) and Ta/(Ta + Nb) ratios.

The size and abundance of the crystals increase from the wall zone toward the core. Within the replacement units (albite and quartz-muscovite veins) the size is always very small but the number of crystals increases considerably.

c) Single-crystal trend. Zoning is a common feature in all columbite-tantalite crystals in all the pegmatite zones from all pegmatites. This zoning is related to compositional variation in one or both Ta/(Ta + Nb) and Mn/(Mn + Fe). Although patchy or convolute zoning is locally present, oscillatory zoning is by far the commonest style of chemical variation within individual crystals. The trends and limits in compositional variation within a single crystal are characteristic for each pegmatite zone in each pegmatite type, but in general Ta/(Ta + Nb) zoning evolves in the early pegmatite zones (wall and intermediate zones) of all pegmatite types, whereas zoning in Mn/(Mn + Fe) becomes prominent only in columbite-tantalite crystals from the pegmatite cores and late cross-cutting veins.

Concluding remarks

The overall trends in the Mn/(Mn + Fe) and Ta/(Ta + Nb) ratios, and in the Ta- and Mn-enrichment from type I to type III pegmatites are those expected for a beryl-columbite pegmatite population, and are similar to those from other pegmatite fields (e.g. *Wise*, 1987). Furthermore, the Ta/(Ta + Nb) and Mn/(Mn + Fe) trends suggest a common origin with type IV (albite pegmatites) which corresponds to the more evolved group in the field. However, the evolution is extremely complicated in a single pegmatite or in a single crystal and it is influenced by the simultaneous growth of other minerals (phosphates, silicates, other oxides). Our observations indicate that in the Cap de Creus field Sn, Ta and Mn became enriched in the residual pegmatite fluids, whereas Nb and Fe (and most of Ti, U, Sc, W and other minor elements) were precipitated in the early-formed crystals.

The oxide minerals crystallized in different pegmatite stages: some crystals grew during magmatic stages but others from late hydrothermal fluids. Rutile (Nb- or Ta-rich) is preserved in the early zones, but breaks down in the inner zones; this suggests that homogeneous Nb–Ta bearing rutile crystallizes only at relatively high temperatures, but exsolves or becomes replaced during cooling (*Černý* et al., 1964; *Černý* and *Ercit*, 1989).

All crystals of columbite-tantalite display oscillatory zoning in all pegmatite zones. *Putnis* et al. (1992) have experimentally demonstrated that solubilities of two end-members of a solid solution, if significantly different, determine the threshold supersaturation for nucleation from supersaturated solutions and facilitate oscillatory zoning, even in the absence of oscillations in the intensive parameters. The tendency of Ta to become enriched in the more evolved pegmatites and in more evolved zones seems to indicate a higher solubility for the Ta-rich member. However, the system in question is more complicated than a simple series with two end-members, and complexing of Nb and Ta in pegmatite melts and fluids may be a significant factor (*Černý* et al., 1985). Thus the mechanism of oscillatory zonal growth in columbite-tantalite may be more complex.

The more complicated zoning structures are largely restricted to pegmatites with well-developed hydrothermal replacements (types III and IV), and they are particularly typical of early crystals. In absence of metamorphic effects that could causate disturbances of original zoning (e.g. *Černý* et al., 1992a), these structures probably result from reequilibration of these crystals with late pegmatite fluids. In fact, the growth of some individual crystals must have been extended over long periods of time: as mentioned above, many columbite crystals with primary, pre-deformation oscillatory zoning were broken during the deformation and subsequently were overgrown by a "post-tectonic" Ta-rich rim. The crystal zoning in Nb–Ta bearing minerals could therefore be a consequence of 3 factors: availability of Mn, Fe, Ta, Nb (as influenced by the simultaneous crystallization of other pegmatite minerals), factors facilitating oscillatory zoning, and reequilibration with late fluids.

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References

Ayora C, Casas JM (1986) Strata-bound As–Au mineralization in pre-Caradocian rocks from the Vall de Ribes, Eastern Pyrenees, Spain. Mineral Deposita 21: 278–287

Carreras J, Orta JM, San Miguel A (1975) El área pegmatítica del litoral N de la Península del Cap de Creus y su contexto metamórfico y estructural. Rev Inv Geol Univ Barcelona 30: 11–34

Carreras J, Casas JM (1987) On folding and shear zone development: a mesoscale structural study on the transition between two different tectonic styles. Tectonophysics 135: 87–98

Cavet P (1957) Le Paléozoique de la zone axiale des Pyrénées Orientales françaises entre le Roussillon et l'Andorre. Bull Serv Carte Géol Fr 55, 254: 303–518

Černý P (1982) Anatomy and classification of granitic pegmatites. In: *Černý P* (ed) Granitic pegmatites in science and industry. M A C Short Course Handbook 8: 1–40

Černý P (1989) Characteristics of pegmatite deposits of tantalum. In: *Möller P, Černý P, Saupé F* (ed) Lanthanides, tantalum and niobium. Springer, Berlin Heidelberg New York Tokyo, pp 195–239

Černý P (1990) Distribution, affiliation and derivation of rare-element granitic pegmatites in the Canadian Shield. Geol Rundschau 79/2: 183–226

Černý P (1991) Rare-element granitic pegmatites, part I. Anatomy and internal evolution of pegmatite deposits. Geosc Canada 18, 2: 49–67

Černý P, Turnock AC (1971) Niobium-Tantalum minerals from granitic pegmatites at Greer Lake, Southeastern Manitoba. Can Mineral 10: 755–772

Černý P, Ercit TS (1989) Mineralogy of niobium and tantalum: crystal chemical relationships, paragenetic aspects and their economic implications. In: *Möller P, Černý P, Saupé F* (eds) Lanthanides, tantalium and niobium. Springer, Berlin Heidelberg New York Tokyo, pp 27–79

Černý P, Ercit TS (1985) Some recent advances in the mineralogy and geochemistry of Nb and Ta in rare-element granitic pegmatites. Bull Mineral 108: 499–532

Černý P, Čech F, Povondra P (1964) Review of ilmenorutile-strüverite minerals. N Jb Mineral Abh 101: 142–172

Černý P, Meintzer RE, Anderson AJ (1985) Extreme fractionation in rare-element granitic pegmatites: selected examples of data and mechanisms. Can Mineralogist 23: 381–421

Černý P, Goad BE, Hawthorne FC, Chapman R (1986) Fractionation trends of the Nb- and Ta-bearing oxide minerals in the Greer Lake pegmatitic granite and its pegmatite aureole, southeastern Manitoba. Am Mineral 71: 501–517

Černý P, Novák M, Chapman R (1992a) Effects of sillimanite-grade metamorphism and shearing on Nb–Ta oxide minerals in granitic pegmatites: Maršikov, Northern Moravia, Czechoslovakia. Can Mineral 30: 699–718

Corbella M, Melgarejo JC (1990a) Rare-element pegmatites of the Cap de Creus Peninsula, Northeast Spain: a new field of the Beryl-Phosphate subtype. In: *Taylor RP* (ed) 8th Quadrennial IAGOD Symposium Volume, Ottawa 1990. E Schweizerbart śche Verlagsbuchhandlung, Stuttgart

Corbella M, Melgarejo JC (1990b) Características y distribución de los fosfatos de las pegmatitas graníticas de la Península del Cap de Creus (Pirineo Oriental Catalán). Bol Soc Esp Min 13: 169–182

Druguet E (1992) Petrologia del complex migmatitic de l'àrea de la Punta dels Furallons (Cap de Creus). Thesis, Universitat de Barcelona, 235 p (unpublished)

Foord EE (1982) Minerals of Sn, Ti, Nb and Ta. In: *Černý P* (ed) Granitic pegmatites in science & industry. Mineral Assoc Canada, Short Course Handbook 8: 187–238

Grice JD, Černý P, Ferguson RB (1972) The Tanco pegmatite at Bernic Lake, Manitoba. II. Wodginite, tantalite, pseudo-ixiolite and related minerals. Can Mineral 11: 609–642

Jacobson R, Webb JS (1947) The occurrence of nigerite, a new tin mineral in quartz-sillimanite rocks from Nigeria. Mineral Mag 28: 118–128

Kloosterman JB (1974) Nigerite in the tin-tantalum pegmatites of Amapá, Brazil. Mineral Mag 39: 837–846

Von Knorring O, Condliffe E (1984) On the occurrence of niobium-tantalum and other rare element minerals in the Meldon aplite, Devonshire. Mineral Mag 48: 443–448

Lahti SI (1981) On the granitic pegmatites of the Eräjärvi area in Orivesi, Southern Finland. Geol Surv Finland Bull 314: 82 p

Lahti SI (1987) Zoning in columbite-tantalite crystals from the granitic pegmatites of the Eräjärvi area, Southern Finland. Geochim Cosmochim Acta 51: 509–517

Putnis A, Fernández-Díaz L, Prieto M (1992) Experimentally produced oscillatory zoning in the $(Ba,Sr)SO_4$ solid solution. Nature 358: 743–745

Spilde MN, Shearer ChK (1992) A comparison of tantalum-niobium oxide assemblages in two mineralogically distinct rare-element granitic pegmatites, Black hills, South Dakota. Can Mineral 30: 719–737

Uher H (1991) Be–Nb–Ta Granitic pegmatites- a new type of rare-element mineralization in the western Carpathians. Geol Carpathica 42, 6: 331–339

Wise M, Turnock AC, Černý P (1985) Improved unit cell dimensions for ordered columbite-tantalite end members. N Jb Mineral Mh 8: 372–378

Wise MA (1987) Geochemistry and crystal chemistry of Nb, Ta and Sn Minerals from the Yellowknife Pegmatite Field, N.W.T. Thesis, University of Manitoba, 326 p (unpublished)

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