PARAGENESIS AND COMPOSITIONAL EVOLUTION OF HIGH TA OXIDES IN EARLIER VARISCAN PEGMATOI-DS OF NORTHERN PORTUGAL

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INTRODUCTION

In northern Portugal, strongly deformed and metamorphosed aplite-pegmatites (cataclastic to milonitic) occur in the form of veins of variable thickness (1 cm to 360 cm) intruding Silurian metavolcanic to metasedimentary formations (Fig.1). From a compositional point of view they can be considered Na rich hyper-aluminous pegmatoids with the following cardinal minerals: quartz, andalusite, white mica (paragonite, margarite and muscovite) and albite. The most common accessory phases are tourmaline (schorl> dravite), ilmenite, rutile or anatase, Nb - tantalates, cassiterite, xenotime, monazite, zircon, beryl, chrysoberyl and phosphates (mainly from the lazulite-scorzalite series). The most aluminous facies, here referred as ultra-aluminous, lack albite, have abundant silimanite, andalusite and, sometimes, corundum. Thicker ultra – aluminous veins are internally zoned showing quartz cores, comb-structured prismatic andaluzite at the intermediate zones and metassomatic to segregated fringes of tourmaline at the contact with the host metapelites.

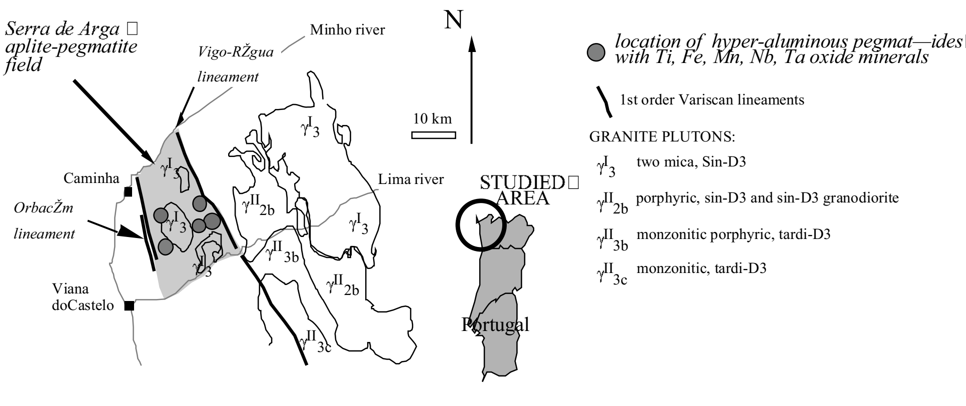

Figure 1 - Location of the studied Nb-tantalates bearing pegmatoids.

Virtually all kinds of veins hold the characteristic assemblage, andalusite, lazulite-scorzalite, and Fe – Ti - Nb - Ta (rarely Sn) in singular to composite oxide intergrowths, with the more complex textures located in the more deformed, metamorphosed and metassomatized rocks.

Hypothetically the diversity of Nb-Ta oxides is attributed to subsolvus - subsolidus transitions (metamorphic - metassomatic) and not to magmatic - hydrothermal primary crystallization and fractionation. Geometric to cinematic analysis suggests that the host veins represent the first expression of early differentiated Variscan pegmatoids, possibly generated by metamorphic segregation. Ultra-aluminous neossome is collected in dilation environments generated along structures of 2nd Variscan folding phase and its subsequent shear reactivations (Leal Gomes, 1994). The presence of xenotime and Fe-columbite and the absence of Li and Cs mineralization suggest an inclusion in the NYF pegmatite class.

Fe, Ti, Nb and Ta oxides observed in the fine-grained muscovite rich veins were studied in X-ray diffraction and its compositions were obtained by electron microprobe analyses. Textures and morphologies of composite blasts and clasts and crystal zoning were studied in reflected and transmitted light microscope and scanning electron microscope (SEM) in backscattered electrons mode (BE). Presumably, some of the observed intergrowths can be interpreted as a set of early compositional balances between Ti, Nb and Ta oxide minerals.

INTERGROWTHS AND ZONING PATTERNS

Ta is expressed in tapiolite, struverite, ilmenorutile, Ti-ixiolite, ilmenite, rutile, anatase and columbite-tantalite in variable paragenetic combinations. Intergrowths with the main silicates express some peculiar aspects such as “augen”-like textures including quartz, mica and Nb-tantalates with some “snow-ball” helicitic sets of inclusions corresponding to rotational deformation during metamorphic evolution. The absence of a preferential location of high-Ta minerals at the internal structure of the veins, contributes to sustain the existence of a diffuse redistribution of oxides in response to metamorphism or metassomatism and therefore not strictly due to pegmatitic fractionation.

Idiomorphic tapiolites are frequently hosted in cavities filled with lazulite-scorzalite. Peculiar inter-growths of zircon and columbite-tantalite/tapiolite can be seen in some veins, in which the zircon predates Nb-tantalate. An inverse succession is illustrated in fig. 2A where tapiolite inclusions are scattered inside late zircon. Deposition of Nb - tantalate occurs in various stages, some of which are attributed to unbalance imposed by shear reactivation and reactions occurring after the first stage of Nb – Ta - Ti mineralization.

Some strongly deformed veins exhibit epitaxic growths of tapiolite over columbite. In this case tapiolite is the latest mineral occurring after the most striking deformation (Fig. 2B). Frequently oscillatory zoning is obliterated or truncated by multistage growth or sector zoning, subjected to the influence of stretching and rotational deformation (Fig. 2C). Since late greisenization doesn’t seem to affect the zoning patterns, inter-growths and morphologies (Leal Gomes, 1994), it can be said that initially, Ta minerals disequilibrium is mainly related to the changes in pressure and temperature and less related to the activity of exogenic fluids. However, these may facilitate a limited chemical remobilization. Some veins show less transformed/deformed portions with internal zoning and elongated comb crystals revealing less significant cataclasis. This suggests „in situ“ primary fractionation, very similar to that typical of pegmatites. It is in these remaining compartments, testifying an earlier fractionation, that the Ti richest phases predominate possibly representing persistent crystal structures carrying the primitively cogenetic Nb-Ta-Ti metals.

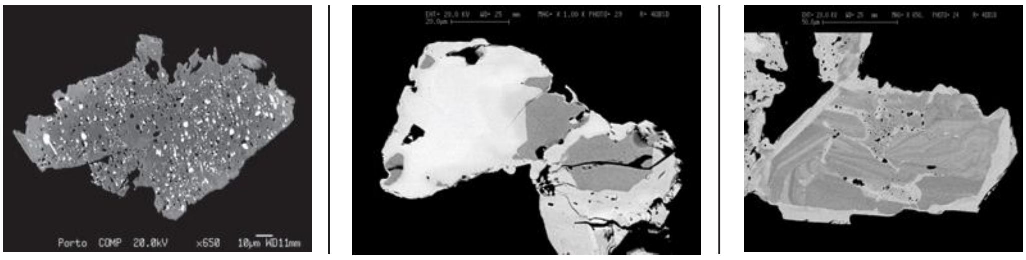

Figura 2 – SEM back-scattered electron imagery of heterogeneous Nb – tantalates. Graphic scale = 20 μm (See text for definition of A,B,and C).

COMPOSITION OF NB-TANTALATES

All studied oxides are strongly ferriferous (Mn/(Mn + Fe) <0.4 in columbite quadrilateral – Fig. 3A). Different fractionation trends converge to the tapiolite domain, regardless the compositional starting point or the original crystalline structure from where Ta was released (Fig. 3A). In the context of pegmatitic fractionation this compositional organization is rare - Mn does not increase as in the typical pegmatitic sequences (Cerny et al., 1992). It suggests that fractionation postdates the crystallization of some primitive crystalline carrier. In fig. 3B ilmenite and rutile (gray spot) projects away from the reference line (Ta^{5+}, Nb^{5+}) = 2.00, approaching the field of tapiolite. In figure 3C the positive Sc-Ta increase, accompanies the global evolutionary trend, towards tapiolite. However there are 2nd order evolutionary trends, limited to the tapiolite field indicating an oscillatory behaviour of its own evolution. The variation of Ti in relation to (Ta, Nb) expresses a boomerang-like graphic expansion (Fig. 3D). This is in accordance with exsolution/exudation/recovery phenomena, developed in "subsolidus" conditions. In the various diagrams, some gaps of the linear trends may be interpreted as compositional hiatus resulting from inertial accommodation of chemical constituents to crystal structure transitions and changing rates of crystal growth.

Table 1 – Selected compositions of Nb-tantalates and titanium oxides (electron microprobe analysis).

	Tapiol.	Tapiol.	Tapiol.	Tapiol.	Struv.	Struv.	Col.	Col.	Col.	Ilm.	Ilm.	Rutile	Anatase
Ta_2O_5	78.67	73.08	75.17	73.56	49.29	38.12	16.45	43.15	46.76	0.00	0.00	0.00	0.07
Nb_2O_5	4.32	6.81	6.66	8.33	10.46	11.34	60.97	36.50	33.00	0.10	0.12	0.10	0.20
Al_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.06	0.16	0.01	0.00
Sc_2O_3	0.60	0.60	0.63	0.12	0.00	0.28	0.11	0.38	0.18	0.00	0.00	0.00	0.02
V_2O_3	0.00	0.00	0.00	0.00	0.00	0.68	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SnO_2	0.60	2.06	1.48	1.30	1.56	2.13	0.25	0.29	0.52	0.00	0.00	0.00	0.00
TiO_2	0.32	2.08	1.55	0.80	23.19	35.12	0.57	0.58	0.73	53.01	52.82	99.23	98.90
FeO	13.61	13.84	13.82	14.49	15.90	10.94	15.45	13.34	16.58	43.81	43.01	0.71	0.00
MnO	0.40	0.40	0.50	0.16	0.38	0.00	4.10	3.86	0.43	2.07	2.99	0.00	0.00
MgO	0.13	0.09	0.05	0.00	0.00	0.26	0.00	0.00	0.00	0.19	0.21	0.10	0.00
WO_3	0.00	0.00	0.00	0.09	0.00	0.16	0.62	0.38	0.24	0.00	0.00	0.00	0.00
Total	98.63	98.94	99.88	98.92	100.77	99.03	98.53	98.48	98.44	99.24	99.31	100.14	99.30

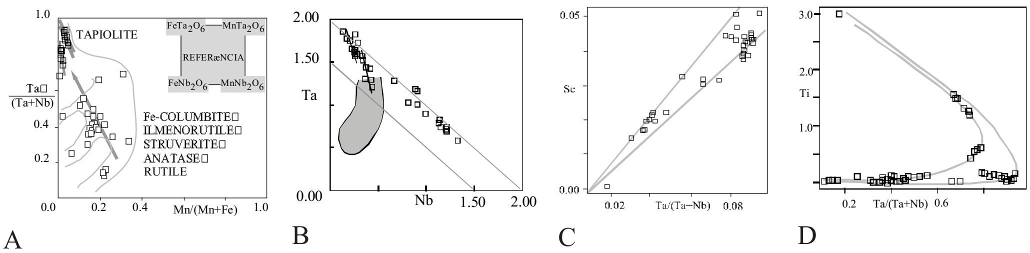

Figure 3 – Fractionation trends deduced from apfu values calculated for the compositions of the main Ta oxides and associated minerals (See text for definition of A,B,and C).

DISCUSSION AND CONCLUSIONS

At the global level of organisation rutile structure is often considered to be the main carrier for Ta and Nb. However, Nb/Ta ratio in the continental crust is not consistent with such an assumption (Barth et al., 2000) and therefore the systematic sequester in rutile is debatable, at least for Ta. Furthermore the geochemistry of aplite-pegmatite sequences suggests the much more compatible character of Nb. During the partition between magma and fluid, Nb clearly favours the magmatic fraction. In the studied hyper-aluminous pegmatoids, tri-rutile structure phases (tetragonal tapiolite) and α-PbO_2 structures (such as orthorhombic columbite) can coexist and exhibit paragenetic consanguinity between simple rutile (primitive paragenetic stages) and Nb and Ta rich phases generated by later crystal-chemical re-balances. As expected the release of Ta from Ti loci to form tapiolite predates the release of Nb (more static and compatible). Thus Ta/Nb mobilization, related with metamorphic - metassomatic transitions and ascribed to high Ta "subsolvus" to "subsolidus" crystal adjustments, includes annealing-recovery cycles and differs from the trends of primary crystallization. In the columbite-tantalite/tapiolite quadrilateral, Ta/Nb variation shows a much greater magnitude than Mn/Fe and drifts at low Mn. At the paragenetic evolution, compositional trends crossing the graphic hiatus between columbite – tantalite and tapiolite are expressed in disordered phases with Ti (disordered Fe-columbite, ti-ixiolite, ilmenorutile and struverite) plotted inside the transition gap. From a crystallographic point of view, tapiolite (with tri-rutile type structure) has higher affinity with the rutile structure. The columbite-tantalite has greater affinity with the orthorhombic α-PbO_2. The conditions of tapiolite-(columbite-tantalite) transition are still poorly known, mainly concerning high pressure sub-crustal environments, although it is possible under high pressure experimental conditions. The work of Turnock (1966) suggests an increase of tapiolite stability at higher temperature (extending its compositional variability). That transition is considered to be a part of a broader sequence of increasing pressure and decreasing temperature: rutile (tetragonal) => □-PbO_2 (orthorhombic) => baddeleyte (monoclinic), which respects the geometry of columbite – tapiolite gap in the columbite-tantalite-tapiolite quadrilateral.

In the evolution of early Variscan pegmatoids, paragenesis and crystalchemistry seems to register the following succession depending on multistage variation of pressure and temperature: rutile => Ti minerals (struverite and ilmenorutile - struverite predominates by preferential release of Ta) => tri-rutile as tapiolite => α-PbO_2 as columbite - tantalite. The Variscan D_1-D_2 metamorphic and deformational context promotes annealing and preferential release of Ta from Ti precursors (possibly ilmenite, rutile or anatase) in the crystalline recovery. The paragenetic succession expressing Ta remobilization traces efficiently the progressive deformation (Fig. 4A). The exudation and release of molecules with high Ta materialize deltoid trails and sigmoid and acicular strain fringes, formulated by rotation, simple brittle-ductile shear and stretching (Fig. 4B). Once established, the Nb-Ta phases remain in equilibrium even at high heat release related to granites emplacement and evolution.

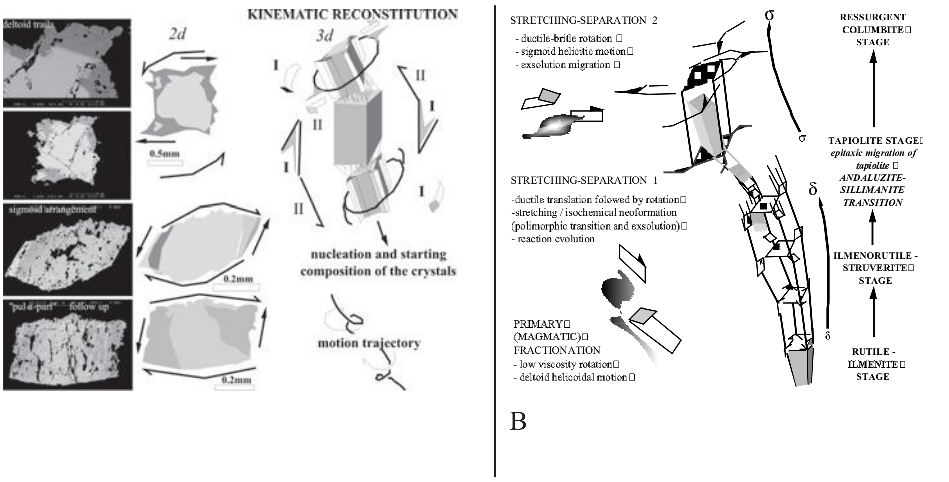

Figure 4 - Progressive deformation geometries in almost basal sections of elongated prismatic crystals and cinematic reconstitution (2d deduced from SEM-BE).

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