Nb-Ta Oxide Minerals of Alluvial Placers from the Sunsás Belt, Precambrian Shield of Bolivia

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Abstract. The mineralogy of Nb-Ta oxide minerals from alluvial placers origin from rare-element pegmatites in the Sunsás Belt, Precambrian shield of Bolivia, was studied. In the studied placer deposits columbite group minerals are the most abundant Nb-Ta bearing minerals. Most compositions of this group belong to manganocolumbite, although ferrocolumbite and manganotantalite also exist. Columbite crystals exhibit oscillatory and irregular zoning. The Ta /(Ta+Nb ratio ranges from 0.08 to 0.5 and The Mn/Mn+Fe ratio is between 0.31 and 0.89. Subsolidus replacements in fractures and rims of the columbite group minerals formed polycrase, fersmite, pyrochlore, and microlite. Strüverite and ilmenorutile occur as other Nb-Ta bearing phases.

Keywords. Columbite group, Niobium, Tantalum, Bolivia

1 Introduction

Niobium and tantalum are becoming increasingly important by their applications in high technology. They are considered as strategic metals by several international organizations as then European Comission (Chakhmouradian et al. 2015). The main sources of tantalum and niobium are leucogranites and granitic pegmatites.

In eastern Bolivia there are abundant Precambrian granites and rare element pegmatites that, although they have been considered of potential for tantalum (Arce-Burgoa and Goldfarb 2009), have not been studied before. In addition, the weathering of these rocks produced alluvial placers of tantalum and niobium. Tantalum and niobium were mined in the Concepción and San Ignacio pegmatites (Berrangé 1982) and nowdays several placers are being exploited.

In the present study we present a preliminary mineralogical characterisation of Nb-Ta minerals from alluvial placers located in the Sunsás belt, eastern part of the Santa Cruz department, Bolivia.

2 Geological setting

The eastern half of Bolivia is constituted by a Precambrian shield that forms the southwestern part of the Amazonian craton. This area is divided into the Sunsás-Aguapeí and Rodonia-San Ignacio provinces. In turn, the Sunsás-Aguapeí province comprises the Sunsás belt, located to the west, and the Aguapeí belt, in the east (Fig. 1).

The Sunsás belt is constituted the extensive milonitic zones or tectonic fronts of Santa Catalina, Rio Negro and San Diablo (Teixeira et al 2010). The basement consists mainly of schists and gneisses that are followed by Mesoproterozoic granitic rocks and Neo-Mesoproterozoic granites and pegmatites from the Sunsás suite. Tertiary laterites and Quaternary alluvial basin deposits cover extensive areas (Arce-Burgoa and Goldfarb 2009).

Several rare-element granitic pegmatite fields occur in this area, being the most known those from La Bella, Ascencion de Guarayos, San Ignacio, Concepción, San Javier and San Ramón. The weathering of these pegmatites produced alluvial placers of tantalum, Titanium and Tin.

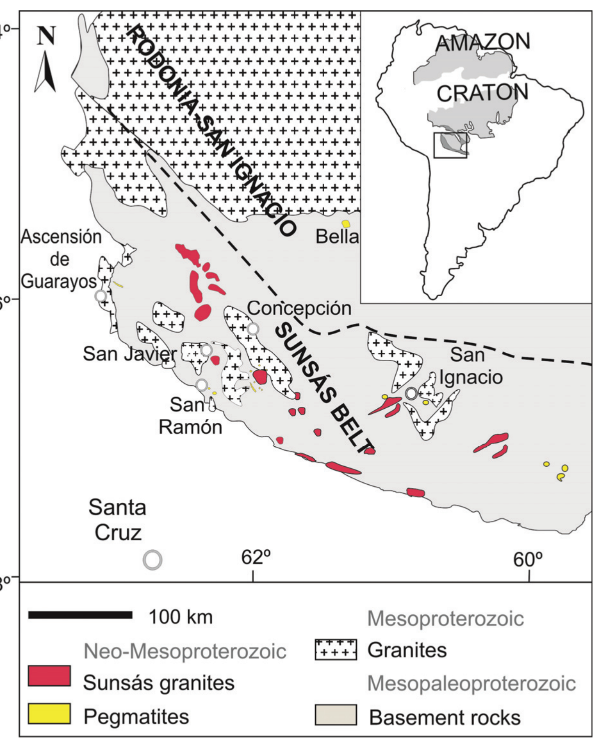

Figure 1. Location of The sSunsás belt and the main pegmatites of the area (modified from Litherland et al. 1986 and Bettencourt et al. 2010).

3 Mineralogy of Nb-Ta oxide minerals

Scanning electron microscopy with energy-dispersive spectral analysis (SEM–EDS) was used in the back-scattered electron mode (BSE). Electron microprobe analyses (EMPA) were performed in the Centres Cientifics i Tecnològics de la Universitat de Barcelona using a JEOL JXA-8230 electron microprobe.

Most grains of the Nb-Ta bearing minerals belong to the columbite group. Columbite-tantalite usually occurs as subhedral tabular dark brown crystals up to 1 cm in size. These crystals in backscattering observation are homogeneous or zoned, showing alternances of oscillatory light Ta-rich and dark Nb-rich bands. Irregular patchy zoning is also present (Fig. 2); it is interpreted as product of the interaction of late fluids (Alfonso et al. 1995; Tindle and Breaks 2000).

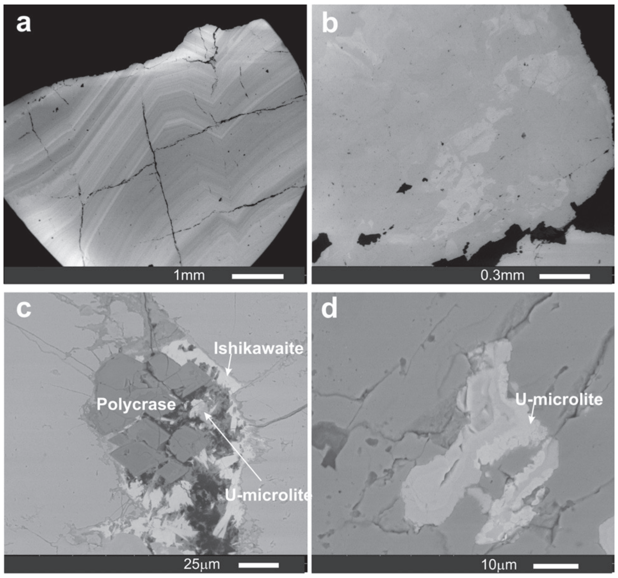

Figure 2. Backscattered electron images of columbite-tantalite grains from the placers of the Sunsás belt. (a) Crystal with oscillatory compositional growth zoning; (b) crystal with irregular zoning, (c) columbite crystal with polycrase, ishikawaite and microlite. A thin film of fersmite surrounds the ensemble. (d) a zoned microlite growth in columbite with a late rim of U-microlite.

Late fluids during the formation of pegmatites produced replacement of columbite-tantalite crystals mainly located along fractures or in the rims. In the early stages of replacement a Nb, Ti rich phase formed in substitution of Columbite. These are phases typical of the early stages of pegmatite fluids crystallization. Thus, here a reverse trend has occurred, similarly as the previously observed in other grains from pegmatites (eg. Beurlen et al. 2008). In the central parts of fractures U-rich minerals and Ta-rich pyrochlore group minerals were formed (Fig. 3).

4 Mineral chemistry of Nb-Ta oxide minerals

4.1 Columbite group

About 300 electron microprobe analyses were obtained from columbite group grains. Columbite group minerals have a general formula of $(Fe,Mn)(Nb,Ta)_2O_6$. Most of the analysed crystals of the Sunsás belt are manganocolumbite although ferrocolumbite and mangano-tantalite also occur (Fig. 3).

The Mn/(Fe+Mn) ratio in the placer deposits ranges from 0.31to 0.89 and the Ta/((Nb+Ta) ratio vary between 0.08 and 0.55. Whereas, in most individual crystals there is a narrow variation in the Mn/(Fe+Mn) ratio and a greater variation in the Ta/((Nb+Ta) ratio.

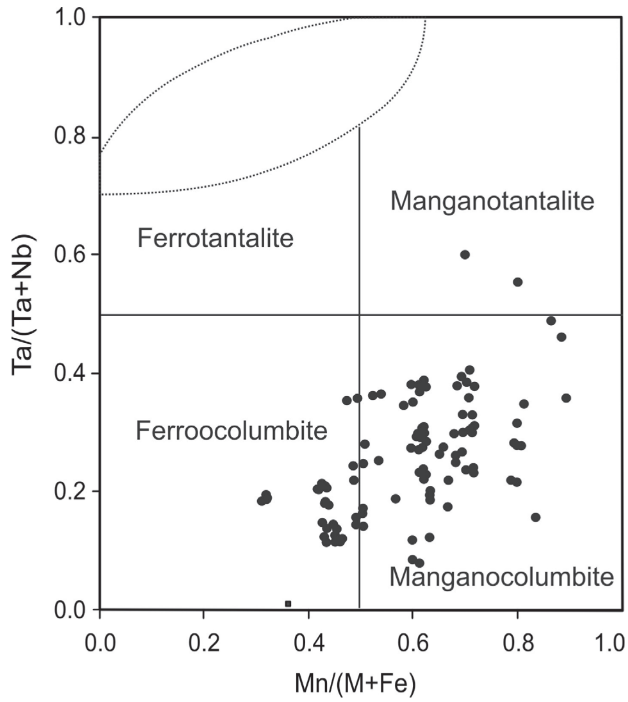

Figure 3. Quadrilater diagram of columbite group minerals from the placers of the Sunsás belt.

Minor elements in substitution of Ta and Nb are Ti, W and Sn. Ti can reach up to 2.09 wt% TiO_2, W up to 1.88 wt% WO_3 and Sn up to 0.32 wt% SnO_2, and usually it is lower than 0.1 wt%. The Sn and Y content decrease with the increase of the Ta/(Nb+Ta) ratio but Ti and W are not correlated with tantalum.

The chemical composition of columbite group minerals (Fig. 3) suggests an evolutionary trend indicative of a moderate degree of fractionation of the parent pegmatites. Similar trends are produced by pegmatites of a medium degree of evolution, as the Beryl-Columbite-Phospate subtype (Černý 1992).

4.2 Pyrochlore supergroup

Pyrochlore supergroup minerals have a varied composition with formula $A_{2-m}\ B_2\ X_{6-w}\ Y_{1-n}$. The A site can be Na, Ca, Ag, Mn, Sr, Ba, Fe, Pb, Sn, Sb, Bi, Y, REE, Sc, U, Th, □, or H2O. B site is Ta, Nb, Ti, Sb, W, V, Sn, Zr, Hf, Fe, Mg, Al and Si. X and Y are anions (Atencio et al 2010).

The chemical composition of the pyrochlore supergroup minerals from the Sunsás placer deposits is varied. Microlite is the most common mineral of this group. Pyrochlore also occur in very minor amounts (Fig. 4). In all cases the content of Pb, Sb and Bi was negligible. Ta/(Nb+Ta) values in microlite vary from 0.75 to 0.91 and Ti content vary from 0.14 to 0.56 apfu (Fig. 4). The most abundant cation in A site is Ca, with 0.87 to 1.24 apfu; Na attains from 0.43 to 0.79 apfu. The U content decreases with the Ta/(Nb+Ta) ratio; it can reach up to 0.31 apfu and Th can be up to 0.01 apfu. Sn can reach up to 0.06 apfu.and W, up to 0.01 apfu. Fluorine has not been analysed because it was not detected with SEM-EDS.

4.3 Other Nb-Ta minerals

Fersmite (AB_2X_{6-w} Y_{1-n}) occurs along the contact of columbite and microlite. B site is Nb, from 1.53 to 1.71 apfu, Ta, from 0.25 to 0.39 apfu and Ti, up to 0.09 apfu (Table 1). A site is mainly occupied by Ca, with 0.67 to 1.05 apfu. Y can reach up to 0.08 apfu.

The contact between fersmite and columbite is diffuse, suggesting that this mineral formed by replacement of columbite during a late stage. Fersmite from other locations also has this metasomatic origin (Uher et al. 1998; Chakhmouradian et al. 2015).

Table 1. Composition of microlite and fersmite from the Sunsás placers. Structural formulas were calculated for B site=2.

	SR-2-1	SR-2-3	SR-2-2a	SR-2-2b
Oxide	Microlite	Microlite	Microlite	Fersmite
WO_3	0.52	0.40	0.32	0.58
Nb_2O_5	4.81	7.33	12.55	56.02
Ta_2O_5	54.36	68.39	61.51	23.33
TiO_2	6.32	2.05	1.55	0.44
UO_2	16.26	1.08	5.54	0.00
ThO_2	0.32	0.00	0.13	0.00
CaO	10.02	13.28	12.02	12.53
Y_2O_3	0.00	0.00	0.00	0.17
SnO2	1.17	0.73	0.10	0.01
Na_2O	3.29	4.51	4.38	0.00
FeO	0.17	0.17	0.07	2.36
MnO	0.26	0.21	0.10	0.85
OH^-	1.67	1.79	1.77	2.41
Tot	98.65	99.53	99.72	98.13
U^{4+}	0.32	0.02	0.10	0.00
Th^{4+}	0.01	0.00	0.00	0.00
Y3+	0.00	0.00	0.00	0.01
Ca	0.96	1.19	1.09	0.84
Na	0.57	0.73	0.72	0.00
Fe2+	0.01	0.01	0.00	0.12
Mn^{2+}	0.02	0.01	0.01	0.04
∑A site	1.90	1.97	1.92	1.01
W	0.01	0.01	0.01	0.01
Nb	0.19	0.28	0.48	1.58
Ta	1.32	1.56	1.41	0.39
Sn^{4+}	0.04	0.02	0.00	0.00
Ti	0.43	0.13	0.10	0.02
∑B site	2.00	2.00	2.00	2.00
Ta/(Ta+Nb)	0.87	0.85	0.75	0.20

Ishikawaite, the U-rich member of the samarskite-group minerals, is a relatively common mineral that occurs as late crystals located in fractures close to microlite. The structural formula of a representative grain is $U_{0.86}Ca_{0.28}Fe_{0.02}Mn_{0.01}Na_{0.01}Nb_{0.60}Ta_{0.06}Ti_{0.16}O_4$. This mineral can present up to 3.84 wt.% of ThO_2.

Polycrase (AB_2O_6), is the only Y-rich phase commonly present in the replacements. The A site is mainly occupied by Y, up to 0.40 apfu and U, between 0.14 and 0.32 apfu. The B site has between 0.71 to 1.23 apfu of Ti. Nb ranges from 0.32 to 0.75 apfu and Ta from 0.40 to 0.70 apfu.. The Ta/(Nb+Ta) ratio is 0.44 - 0.60.

Nb-Ta rich rutile occurs mainly as ilmenorutile, strüverite also occurs, with up to 16 wt% of Ta_2O_5. They constitute small minerals replacing columbite-tantalite

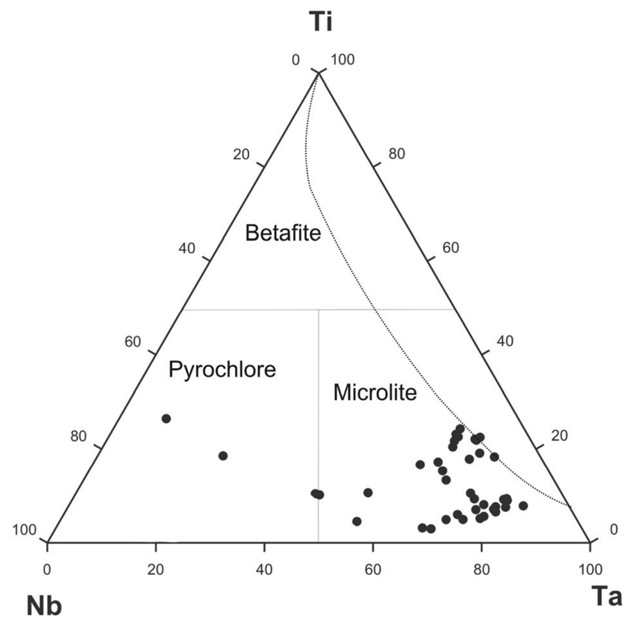

Figure 4. Ti-Nb-Ta diagram of the pyrochlore supergroup from the placers of the Sunsás belt. The dotted line represents a compositional gap of the group according to Atencio et al. (2010).

5 Conclusions

The main Nb-Ta rich mineral in the placers originated from the pegmatites of the Sunsás belt is manganocolumbite. Columbite from placers of the Sunsás belt is homogeneous or has oscillatory zoning. Patchy zoning is less abundant. Zoning is related with variation in the Ta/(Nb+Ta) ratio. Late processes replace columbite group minerals by fersmite and formed policrase and microlite.

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