RARE METAL OXIDE MINERALIZATIONS RELATED TO TWO NEOPROTEROZOIC TOURMALINE GRANITES FROM THE INTERFERENCE ZONE OF THE RIBEIRA AND BRASÍLIA BELTS, MINAS GERAIS, BRAZIL

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Resumo MINERALIZAÇÕES EM METAIS RAROS RELACIONADAS A TURMALINA GRANITOS NEOPROTEROZOICOS, DA ZONA DE INTERFERÊNCIA DAS FAIXAS RIBEIRA E BRASÍLIA, MINAS GERAIS, BRASIL Os turmalina granitos Itanhandu e Capivara afloram na porção sudeste do Estado de Minas Gerais. Esses granitos encontram-se encaixados em leucognaisses migmatíticos correlacionados a Megasequência Andrelândia e afloram na zona de interferência entre as faixas Ribeira e Brasília, ambas desenvolvidas durante a orogenia neoproterozóica brasileira. Dados geológicos apontam feições sintectônicas, enquanto os geoquímicos para um magma cálcio-alcalino e peraluminoso (tipo-S). As idades ²⁰⁷Pb/²⁰⁶Pb (evaporação de Pb em monocristal de zircão) de 605 ± 11 Ma do Granito Capivara e de 649 ± 6 Ma do Granito Itanhandu possibilitam a correlação dos mesmos, respectivamente, aos eventos metamórficos das faixas Ribeira e Brasília. Três conjuntos de corpos pegmatíticos ocorrem nas imediações do Granito Capivara e mostram texturas heterogêneas (PG-1 e PG-2) e homogêneas (PG-3). Estudos realizados em minerais de Nb-Ta-Sn apontaram para a presença de dois tipos distintos de associações minerais nas áreas de Itanhandu e Itamonte (Monte Belo-Capivara). Na área de Monte Belo a columbita-tantalita é zonada com núcleo tantalífero e bordas niobíferas, e possui inclusões de cassiterita, tantalita rica em chumbo, tantalita, microlita, zircão e uraninita. Na área de Itanhandu a principal fase mineral tantalífera-niobífera é homogênea e mais enriquecida em Ti e Sc correspondendo, provavelmente, a uma ixiolita. Suas inclusões são ilmenorutilo, cassiterita, columbita-tantalita, rutilo tantalífero, pirocloro e uraninita. Foram identificadas duas gerações composicionalmente distintas de cassiterita, predominando um conteúdo mais elevado de Ta₂O₅ (1,8% em peso) nos cristais de Monte Belo-Capivara. A cassiterita de Itanhandu tem inclusões de ilmenorutilo, columbita-tantalita rica em Ti e Sc (possível ixiolita) enquanto a de Monte Belo-Capivara apresenta pirita, zircão, tantalita rica em chumbo, pirocloro e pequenos grãos zonados de columbita-tantalita com núcleo niobífero e borda tantalífera.

Palavras-chave: turmalina granito, pegmatito, columbita-tantalita, cassiterita, faixas Ribeira e Brasília, Brasil.

Abstract Tin and tantalum mineralizations related to two S-type granites are located in southern Minas Gerais State, Brazil. The granitic bodies, named Capivara and Itanhandu granites, are slightly foliated tourmaline granites cropping out in the interference zone of the Brasília and Ribeira belts, developed during the Neoproterozoic Brazilian Orogeny. They are hosted by a migmatitic leucogneiss derived from the Andrelândia Megasequence. Geochemical and geological data point to calcalkaline, peraluminous (S-type), syn-tectonic and parautochthonous characteristics. The geochemical features and the ²⁰⁷Pb/²⁰⁶Pb zircon ages of the Capivara (605 ± 11 Ma) and Itanhandu (649 ± 6 Ma) granites probably relate these bodies to the metamorphism of the Ribeira and Brasília belts, respectively. Three distinct groups of pegmatites showing heterogeneous (PG-1 and PG-2) and homogeneous (PG-3) textures linked to the Capivara granite are concentrated around the body. From SEM-EDS studies two distinct kinds of Nb-Ta-bearing minerals and cassiterite were identified in the Itanhandu and Itamonte (Monte Belo-Capivara) areas. The Monte Belo-Capivara columbite-tantalite consists of a zoned oxide, with a tantaliferous core and a niobiferous rim. Its inclusions are cassiterite, plumbotantalite, tantalite, microlite, zircon and uraninite. The Itanhandu columbite-tantalite is a homogeneous, non zoned Sc and Ti-rich oxide, that may also be ixiolite. Its inclusions are ilmenorutile, columbite-tantalite, tantaliferous rutile, pyrochlore, uraninite and cassiterite. Two generations of cassiterite were identified in the Itanhandu and Itamonte (Monte Belo-Capivara) areas. The Monte Belo-Capivara cassiterite is Ta-enriched (1.8 % Ta₂O₅), compared to the Itanhandu one (0.7% Ta₂O₅). The inclusions in the Itanhandu cassiterite are ilmenorutile and Ti-Sc columbite-tantalite (possibly ixiolite) and in the Monte Belo-Capivara cassiterite they are pyrite, zircon, plumbotantalite, pyrochlore and small zoned crystals of columbite-tantalite with niobiferous core and a tantaliferous rim.

Keywords: tourmaline granite, pegmatite, columbite-tantalite, cassiterite, Ribeira and Brasília belts, Brazil.

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INTRODUCTION During the Neoproterozoic Brasiliano Orogeny abundant and diversified acid plutonism originated syn to post-tectonic batholiths and plutons, emplaced in the crust located in the southeast region of Brazil. Regional prospective surveys (Penha 1992, Pereira *et al.* 1992, 1994a, 1994b, 1997, Pereira 2001) revealed columbite-tantalite and/or cassiterite mineralizations distributed over several districts of Rio de Janeiro, São Paulo and Minas Gerais states, mainly along the upper valley of the Rio Grande river, southern portion of Minas Gerais State and along the medium valley of the Paraíba do Sul river at the junction between São Paulo and Rio de Janeiro states. In southern Minas Gerais State, cassiterite and columbite-tantalite were identified in the stream sediments (heavy pan) of the Itanhandu and Itamonte (Monte Belo-Capivara) areas. In both areas tin and tantalum mineralizations are in close relationship with the Itanhandu and Capivara granitic bodies. The geochemical characterization of these granites and their associated rare metal mineralizations constitutes a first approach for a better definition of the metallogenetic potentiality of tourmaline granites found in southern Minas Gerais State and adjacent areas.

GEOLOGICAL SETTING The focused area is located in the interference zone between the Brasília and Ribeira belts, generated during the Neoproterozoic Brasiliano Orogeny (Trouw *et al.* 2000). Recent works have considered the country rocks of the Itamonte and Itanhandu granites as part of the Andrelândia Megasequence (Fig. 1), predominantly composed of metasedimentary rocks (Ribeiro *et al.* 1995, Paciullo 1997, Pereira 2001). These rocks were metamorphosed under moderate pressures, under a P-T conditions compatible with crustal collision. Large scale melting and migmatization of the metasedimentary rocks occurred in the area, culminating with the generation of extensive leucogranitic bodies (Junho 1995).

The host rocks of the Itanhandu and Capivara tourmaline granites are migmatitic biotite gneisses and heterogeneous migmatitic leucogneisses. They display predominantly stromatic structures, represented by three different compositional layers: the aplitic and/or pegmatitic gneissic leucosome; the biotite-quartz melanosome; and the fine-grained granodioritic gneiss mesosome (Almeida 1996).

Figure 1 - Tectonic map of the middle Paraíba do Sul and upper Rio Grande rivers area (Modified of Pereira *et al.* 2002a). I – Paraíba do Sul Klippe; II – Embu Domain; III – Juiz de Fora Thrust System; IV – Socorro-Guaxupé Thrust Nappe; V – Andrelândia Thrust System; VI – Neoproterozoic Porphyritic Granites: Mr = Maromba; Ps = Pedra Selada; Ma = Marins; Me = Mendanha (592 ± 5 Ma); Si = Silveiras; Im = Itamonte; Qc = Quebra Cangalha; Sjb = São José do Barreiro (603 ± 3 Ma); Rt = Rio Turvo; Tq = Taquaral; Fu = Funil (584 ± 5 Ma); Rb – Rio Bravo; VII – Neoproterozoic Tourmaline Granites: It = Itanhandu (649 ± 6 Ma) Cp = Capivara (605 ± 11 Ma); VIII – Mesozoic Alkaline Massifs: Pq – Passa Quatro; Ita = Itatiaia; IX – Paleogene Sedimentary Basins: RsB = Resende Basin; TaB = Taubaté Basin. Legend: Csz = Cubatão Shear Zone; Afsz = Alto da Fartura Shear Zone; RJ = Rio de Janeiro state; SP = São Paulo state; MG = Minas Gerais state.

Zircon grains of an heterogeneous migmatite from the vicinity of the city of Carvalhos were analysed by the $^{207}\text{Pb}/^{206}\text{Pb}$ evaporation technique at the Para Iso Laboratory, Universidade Federal do Pará. The obtained paleoproterozoic age of 2.05 Ga

(Fig. 2 and Table 1) led us to interpret part of the migmatitic rocks of the region as possible basement of the Andrelândia Megasequence. It must be stressed that such dated migmatite crops out far from the area of occurrence of the granites focused in

Figure 2 - Age (Y) x evaporation step (X) of zircon crystals of migmatitic leucogneiss from the vicinity of Carvalhos city. (•) Block of isotopic ratio considered for age calculation; (□) eliminated block; (x) eliminated block: isotopic ratio $^{204}\text{Pb}/^{206}\text{Pb} > 0.0004$; 2σ error.

Table 1 - $^{207}\text{Pb}/^{206}\text{Pb}$ apparent ages for zircon crystals of the migmatitic leucogneiss from the vicinity of Carvalhos city. Uncertainties are given at 2σ . * = step not considered for age calculation; # = $^{204}\text{Pb}/^{206}\text{Pb} > 0.0004$; ** = $^{207}\text{Pb}/^{206}\text{Pb}$ ratio correct for common Pb contamination.

Zircon	Temp. Evaporation	Number of ratios	$^{204}\text{Pb}/^{206}\text{Pb}$	2σ	$^{208}\text{Pb}/^{206}\text{Pb}$	2σ	$^{207}\text{Pb}/^{206}\text{Pb}$	2σ	$^{207}\text{Pb}/^{206}\text{Pb}$ **	2σ	Age
5	*1500	34	0.000102	6	0.13390	107	0.12531	51	0.12390	49	2014 ± 7
	1550	40	0.000116	10	0.14253	110	0.12857	54	0.12699	39	2057 ± 5
6	#1450	30	0.000591	113	0.13002	189	0.12719	65	0.11834	111	1931 ± 17
	1500	38	0.000103	19	0.12197	74	0.12827	40	0.12682	22	2055 ± 3
7	*1500	8	0.000018	22	0.12452	116	0.12429	316	0.12405	317	2016 ± 45
	1550	26	0.000027	8	0.16578	70	0.12687	21	0.12658	21	2051 ± 3
9	*1450	26	0.000112	10	0.08176	30	0.10898	43	0.10743	42	1757 ± 7
	1500	34	0.000052	7	0.14260	92	0.12759	21	0.12693	22	2056 ± 3
	1550	30	0.000034	9	0.15414	66	0.12768	34	0.12715	33	2059 ± 5
12	*1450	6	0.000112	38	0.12068	133	0.11825	47	0.11674	69	1907 ± 11
	*1475	36	0.000048	5	0.13446	152	0.12347	18	0.12279	18	1997 ± 3
	1500	34	0.000071	10	0.14600	57	0.12704	32	0.12606	28	2044 ± 4
mean											2053 ± 4

this paper.

The single zircon Pb-evaporation technique (Pb-Pb in zircon) was used for the geochronological determinations, on a Finnigan MAT 262 thermal ionization mass spectrometer. Pb signal was collected by peak hopping in the order 206, 207, 208, 206, 207, 204 along 10 mass scans, defining one block of data with 18 $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. Outliers were eliminated using Dixon's test. The average $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of each step was determined based on five blocks, or until the intensity beam was sufficient for a reliable analysis. The $^{207}\text{Pb}/^{206}\text{Pb}$ ratio was measured in three steps of evaporation at temperatures of 1450, 1500 and 1550°C. Usually, the average $^{207}\text{Pb}/^{206}\text{Pb}$ ratio obtained in the highest evaporation temperature, in each zircon, was considered for age calculation. However, the ages of the lower temperature steps were also considered when they overlapped within the error with those ages obtained at the highest evaporation temperature. The ages were calculated with 2σ error and common Pb correction was done for those blocks where the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios were lower than 0.0004, using an appropriate age value derived from the model of Stacey & Kramers (1975).

TOURMALINE GRANITES The Itanhandu and Capivara tourmaline granites crop out near the Passa Quatro and Itatiaia alkaline intrusions (Fig. 1). They are phaneritic, medium to coarse-grained, holocrystalline and dominantly hololeucocratic. Their textures vary from equigranular to the predominant porphyritic inequigranular. They contain plagioclase and microcline crystals ranging from 1.0 mm to 5.0 cm long, and show a slight foliation marked by muscovite and biotite orientations. The contacts with

the country migmatitic units may be abrupt and discordant as well as transitional and concordant.

The Itanhandu tourmaline granite shows fine to medium-grained and coarse-grained porphyritic facies, the latter bearing centimetric microcline phenocrysts. The Capivara tourmaline Granite has two mineralogical facies. The Monte Belo facies is a muscovite granite with a pegmatitic subfacies (a possible stockscheider) and the Dois Irmãos facies corresponds to a biotite granite (Almeida 1996). This granite was probably altered during a hydrothermal activity in the late to post-magmatic stage, causing its wide spread kaolinization.

The essential mineralogy of the Itanhandu and Capivara tourmaline granites is quartz, plagioclase and microcline with smaller amounts of muscovite, biotite, tourmaline, garnet, monazite and opaque minerals. The porphyritic types have perthitic microcline megacrystals surrounded by a granular matrix composed essentially of plagioclase, quartz and microcline. Muscovite appears as small grains cutting or replacing, partially or totally, the biotite. Biotite commonly presents metamictic halos caused by zircon and monazite inclusions.

Fourteen samples of the tourmaline granites were analyzed for major and trace elements at the Lakefield-Geosol Laboratory (Belo Horizonte, Brazil). The loss on ignition was measured after heating the rock powder at 1000°C for 1 hour. The major elements (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CaO , K_2O and P_2O_5) were detected on lithium tetraborate fused pellets and the trace elements were

Table 2 - Major (wt%) and trace elements (in ppm) of the Capivara tourmaline Granite.

	C-88	C-76	C-70	C-61a	C-03a	C-15a	C-133a	C-137	C-137a
SiO_2	72.94	73.30	74.0	71.22	72.6	74.7	71.89	71.0	71.22
TiO_2	0.12	0.06	0.05	0.12	0.20	0.10	0.17	0.17	0.18
Al_2O_3	15.20	15.30	14.80	15.30	14.50	13.90	14.82	15.30	15.43
Fe_2O_3	1.00	0.78	0.19	1.00	0.95	0.52	1.30	1.00	1.37
FeO	-	0.69	1.00	0.85	0.97	0.80	-	0.85	-
MnO	0.11	0.11	0.13	0.90	0.01	0.07	0.11	0.09	0.09
MgO	0.24	0.12	0.10	0.42	0.27	0.10	0.29	0.42	0.31
CaO	0.67	0.57	0.37	0.69	0.93	0.72	0.80	0.69	0.60
Na_2O	3.03	3.00	3.50	2.50	2.80	3.40	2.90	2.50	2.71
K_2O	4.99	4.40	4.30	5.20	5.20	4.80	5.74	5.20	5.15
P_2O_5	0.12	0.06	0.05	0.10	0.05	0.05	0.10	0.10	0.11
LOI	1.44	1.30	1.37	2.03	1.27	0.62	1.00	2.57	1.93
Total	99.86	99.69	99.86	100.2	99.75	99.78	99.12	99.89	99.10
Rb	243	340	330	293	240	360	260	351	345
Ba	375	220	75	457	590	260	610	380	358
Sr	87	77	45	76	160	89	101	92	63
Y	7	18	11	14	8	18	8	3	9
Nb	15	19	10	16	15	20	12	8	13
F	-	67	45	-	37	43	-	53	-
Sn	7	-	-	8	-	-	8	-	18
U	6	10	10	8	10	10	11	10	8
Th	5	5	5	19	30	18	29	25	22
La	-	3.14	5.31	-	32.0	17.09	-	24.39	-
Ce	-	13.14	9.15	-	83.52	31.82	-	69.32	-
Nd	-	3.45	3.05	-	24.78	12.82	-	22.79	-
Sm	-	1.13	0.75	-	4.59	2.37	-	4.14	-
Eu	-	0.22	0.14	-	0.64	0.29	-	0.49	-
Gd	-	1.28	0.67	-	2.92	1.81	-	2.49	-
Dy	-	1.43	0.91	-	1.51	1.48	-	1.43	-
Ho	-	0.29	0.21	-	0.26	0.28	-	0.24	-
Er	-	0.81	1.13	-	0.51	0.69	-	0.56	-
Yb	-	-	-	-	0.50	0.54	-	0.35	-
Lu	-	0.16	0.17	-	0.07	0.10	-	0.07	-

Table 3 - Major (wt%) and trace elements (in ppm) of the Itanhandu tourmaline Granite.

	IT-01	IT-02	IT-MD	IT-10	IT-11MD
SiO_2	73.70	74.50	72.90	73.10	73.70
TiO_2	0.03	0.02	0.02	0.03	0.02
Al_2O_3	15.40	14.90	16.10	15.60	15.10
Fe_2O_3	0.09	0.11	0.04	0.17	0.58
FeO	0.14	0.14	0.28	0.28	0.42
MnO	0.08	0.01	0.01	0.07	0.02
MgO	0.09	0.11	0.14	0.15	0.20
CaO	0.37	0.51	0.82	0.39	0.48
Na_2O	3.30	5.00	5.60	3.60	4.80
K_2O	5.60	4.40	2.90	5.40	3.40
P_2O_5	0.06	0.07	0.07	0.06	0.07
LOI	0.50	0.37	0.72	1.38	0.88
Total	99.36	100.14	99.6	100.23	99.67
Rb	334	326	132	373	197
Ba	58	13	16	100	36
Sr	32	21	22	34	20
Y	21	23	11	9	4
Nb	13	30	9	12	9
F	115	85	75	110	70
Sn	<5	<5	<5	-	-
Li	20	12	16	-	-
U	<10	<10	<10	-	-
Th	<5	<5	<5	-	-
La	3.56	2.75	3.10	-	-
Ce	7.27	6.25	6.46	-	-
Nd	3.44	2.97	2.82	-	-
Sm	1.27	1.08	0.77	-	-
Eu	0.124	0.07	0.05	-	-
Gd	1.51	1.50	0.90	-	-
Dy	1.70	1.72	1.08	-	-
Ho	0.31	0.29	0.24	-	-
Er	0.87	0.69	0.49	-	-
Yb	0.90	0.60	0.44	-	-
Lu	0.12	0.08	0.05	-	-

dosed on pellets of rock powder pressed with wax agglutinate. They were analysed by the X ray Fluorescence spectrometry technique. The rare earth elements were detected by ICP-AS spectrometry, after pre-concentration in a cationic changing

column. The results are presented in Tables 2 and 3..

The tourmaline granites show a calcalkaline signature with a peraluminous character (Figures 3 and 4) and the agpaite index varies from 1.08 in the low muscovite types to 1.45 in the more

Figure 3 - AFM diagram (Irvine & Baragar 1971) for Itanhandu and Capivara tourmaline granites. Symbols: cross – Itanhandu tourmaline Granite; open circle – Capivara tourmaline Granite

Figure 4 - $[Al_2O_3 / (CaO + Na_2O + K_2O)]_{mol} \times [Al_2O_3 / (Na_2O + K_2O)]_{mol}$ diagram (Maniar & Picolli 1989) for Itanhandu and Capivara tourmaline granites. Symbols as in Fig. 3.

Figure 5 - Harker diagrams for Itanhandu and Capivara tourmaline granites. Symbols as in Fig. 3.

Figure 6 - Rb x Y+Nb diagram (Pearce et al. 1984) of the Itanhandu and Capivara tourmaline granites. Symbols as in Fig. 3. Syn-COLG – Syn-collisional; VAG – Volcanic arc-granite; ORG – Ocean ridge granite; WPG – Within plate granite.

muscovitic ones. Some samples from the Capivara tourmaline Granite are strongly peraluminous.

The major and trace element behaviour clearly separates the granites, as shown in the Harker diagrams (Fig. 5). The Capivara tourmaline granite has higher $\text{Fe}_2\text{O}_3(\text{t})$, TiO_2 , MgO , CaO , MnO , P_2O_5 , Ba and Sr values than the Itanhandu tourmaline granite, contrasting with its lower Na_2O contents (Tables 2 and 3).

The Y+Nb x Rb diagram points to the syn-collisional character of these bodies (Fig. 6). The Capivara tourmaline granite shows a considerable higher REE content when compared to the Itanhandu tourmaline granite. The REE diagram highlights the different patterns for the Itanhandu and Capivara tourmaline granites. The former shows a flat pattern, with a strong negative Eu anomaly and the later has a more accentuated fractionated pattern with slightly negative Eu anomaly (Fig. 7). The accessory phases of the Capivara Granite must contain important light and intermediate REE enriched minerals. Probably the REE contents were controlled by feldspar, monazite, apatite, garnet and zircon crystallization.

The geochemical differences observed between the granites, as described above, may suggest a heterogeneous source for the rocks, probably related to the modal compositional variation of the protholites.

Minimum ages of crystallization (Pb evaporation in zircon) for the Itanhandu (649 ± 6 Ma) and Capivara (605 ± 11 Ma) tourmaline granites connect these bodies, respectively, to the Brasília and Ribeira metamorphism of the Neoproterozoic Brasileiro Orogeny (Pereira et al. 2002a).

PEGMATITES Three distinct groups of pegmatites spatially related to the Capivara tourmaline Granite are present in the Itamonte (Monte Belo-Capivara) area. They are hosted by the supracrustal

Figure 7 - Chondrite normalized REE diagram (Boynton 1984) of the Itanhandu and Capivara tourmaline granites. Symbols: cross – Itanhandu tourmaline granite; filled circle – Capivara tourmaline granite

rocks in the neighborhood of the granitic body and inside the granite.

Two of the pegmatites (PG-1 and PG-2 suites) are heterogeneous and zoned, showing a quartz core between quartz, feldspar and muscovite wall zones. The other group (PG-3 suite) has a homogeneous mineral distribution. Generally, the pegmatitic bodies are short and narrow, mostly less than 1 m in thickness, and strongly weathered. Pegmatites are rare in the Itanhandu area.

The mineral assemblage of the pegmatites is quartz, feldspar, muscovite, zircon, tourmaline, monazite, xenotime, rutile, garnet, ilmenite, kyanite and sillimanite ($\pm$ columbite-tantalite, $\pm$ cassiterite). Li and Be minerals are lacking in the pegmatites. Columbite-tantalite was detected in both the PG-1 heterogeneous and the PG-3 homogeneous pegmatites. Cassiterite was identified only in PG-3.

The weathered pegmatites (saprolitic rocks) were washed and panned and the heavy minerals were chemically analyzed by optical emission spectrography (Table 4). The PG-1 pegmatites show higher Mn, B, Nb and Zn values when compared to PG-2. The PG-3 pegmatites have Sn and Pb contents higher than PG-1 and PG-2 pegmatites.

The temporal relationship between granitic bodies and mineralization were not determined, but a probable genetic linkage between the Capivara and Itanhandu tourmaline granites and the cassiterite and columbite-tantalite mineralizations is considered in this paper. The chemical fractionation process which contribute to enrichment of rare metals in granitic magmas may be result in the formation of mineralization hosted by granites and pegmatites (Pollard 1995, Suwimonprecha et al. 1995).

OXIDE MINERALS: COLUMBITE-TANTALITE AND CASSITERITE Columbite-tantalite is the main Nb and Ta-bearing mineral in the Itanhandu and Itamonte (Monte Belo-Capivara) areas. Tabular crystals or elongated laths picked up in the heavy pan

Table 4 - Optical Emission Spectrography semiquantitative analyses of heavy pan pegmatite minerals from Itamonte (Monte Belo-Capivara) area.

Pegmatitic suites	Mn	B	Nb	V	Y	La	Zr	Sn	Zn	Pb
Heterogeneous PG-1	5000	2000	2000	10	50	20	150	50	1000	15
Heterogeneous PG-2	1500	100	10	10	200	70	1000	20	-	10
Homogeneous PG-3	5000	2000	2000	10	150	20	150	1000	-	150

Analyses by LAMIN – CPRM; (-): not detected

Table 5 - SEM-EDS analysis of columbite-tantalite from Itanhandu and Itamonte (Monte Belo – Capivara) areas.

	Itanhandu area (3)	Monte Belo-Capivara (2)	
		zoned grain	
		rim	core
Sc ₂ O ₃	1.5	-	4.3
TiO ₂	5.2	0.3	2.0
MnO	7.5	5.6	6.2
Fe ₂ O ₃	9.7	13.5	9.8
Nb ₂ O ₅	57.5	60.6	37.8
Ta ₂ O ₅	17.6	19.1	39.0
SnO ₂	0.6	-	0.4
PbO	0.4	1.1	0.5
UO ₃	-	-	-
total %	100.0	100.2	100.0

(2): number of grains (-): not detected

assemblages are the most common shapes of this mineral. Its grain size usually ranges from 0.125 to 0.50 mm in the Itanhandu area whereas larger crystals, up to 1.5 mm, occur in the Itamonte (Monte Belo-Capivara) area. The energy dispersion (EDS) analyses were carried out at the Centre for Mineral Technology (CETEM), Rio de Janeiro, using a LEO S440 SEM coupled to a Link ISIS L300 EDS system, with SiLi Pentafet detector, ultrathin ATW II window and 133 eV resolution at 5,9 keV. Element profiles were generated from analysis of certified standards provided by *Micro-Analysis Consultants Limited* (standart block # 3890), under the same analytical conditions. Calibration was performed every 30 minutes using a certified 99,995% cobalt standard. Acquisition time for standards and analysed samples was kept on 100 s plus dead time correction, at process time 4. ZAF corrections were performed by SEMQUANT software from Oxford.

The compositions of columbite-tantalite (Tables 5 and 6) and of their associated inclusions and exsolutions define two suites for this mineral: an Itanhandu niobium-titanium-rich type and an Itamonte (Monte Belo-Capivara) tantalum-rich type (Pereira *et al.*

Table 6 – SEM-EDS analysis of columbite-tantalite hosted in cassiterite from Itanhandu and Itamonte (Monte Belo – Capivara) areas.

	Itanhandu area (4)	Monte Belo-Capivara area (2)	
		zoned grain	
		rim	core
Sc ₂ O ₃	1.6	4.7	-
TiO ₂	4.2	1.4	1.3
MnO	6.0	3.1	6.0
Fe ₂ O ₃	10.9	9.6	9.6
Nb ₂ O ₅	54.6	10.8	25.2
Ta ₂ O ₅	21.3	58.6	57.4
SnO ₂	1.2	11.8	0.4
PbO	-	-	0.3
Total %	99.8	100.0	100.2

(4): number of analyses; - : not detected.

2002b)

Two generations of columbite-tantalite can be identified in the Itanhandu area: an early generation of common columbite-tantalite, hosted in the later Ti-Sc rich columbite-tantalite. The latter may be an ixiolite, on the basis of its Ti and Sc contents (Table 5). It is a non-zoned mineral and its exsolutions and mineral inclusions are ilmenorutile, cassiterite (Fig. 8), columbite-tantalite, pyrochlore, uraninite and tantaliferous rutile (Table 7). According to Cerný *et al.* (1998), titanium enriched members of the columbite group commonly contain exsolved niobian-tantalian rutile. Dominance of Nb over Ta in niobian-tantalian rutile is universal (Suwimonprecha *et al.* 1995). In fact, in the Itanhandu area the ilmenorutile exsolutions dominate over the tantalum-rich rutile, both hosted by the Ti-rich columbite-tantalite.

The columbite-tantalite of the Itamonte area (Monte Belo-Capivara) usually contains minor Ti (Tables 5 and 6), and presents irregular oscillatory or broad oscillatory zones (Fig. 9) parallel to (010). Such broad zones are related to the reversed type (Lahti 1987), with a tantalum-rich core and a high niobium rim (Figs. 9 and

Figure 8 – Cassiterite (Cas) and ilmenorutile (Ir) inclusions in the Ti-rich columbite-tantalite (Ti-col) from Itanhandu area.

Table 7 - Mineral inclusions and exsolutions hosted in columbite-tantalite and cassiterite from Itanhandu and Itamonte (Monte Belo – Capivara) areas.

Mineral	columbite /tantalite	cassiterite
columbite-tantalite	■	■
tantalite	■	-
pyrochlore	■	■
plumbotantalite	■	■
cassiterite	■	-
ilmenorutile	■	■
tantalian rutile	■	-
zircon	■	■
uraninite	■	-
microlite	■	-
ixiolite	-	■
pyrite	-	■

- not determined.

10). The inclusions found in the minerals are cassiterite, microlite, plumbotantalite, tantalite, zircon and uraninite (Table 7). In the Itamonte (Monte Belo-Capivara) area there are also two generations of Nb-Ta minerals, an early generation of plumbotantalite and tantalite, hosted by a later zoned columbite-tantalite with Ta-rich core and Nb-rich rim.

Cassiterite is common in both areas, and frequently forms euhedral crystals up to 0.5 mm large, exhibiting dark brown colour. The cassiterite presents a narrow compositional range: 99.3% (wt) SnO_2 in the Itanhandu granite, and 97.9% (wt) SnO_2 in the Monte Belo-Capivara type (Table 8). The Monte Belo-Capivara type is more Nb- and Ta-rich (0.3% Nb_2O_5 and 1.8% Ta_2O_5) than the cassiterite of the Itanhandu area (no Nb_2O_5 detected, and 0.7% Ta_2O_5). Ilmenorutile and Ti-Sc columbite-tantalite (ixiolite?) are the inclusions observed in the cassiterite from Itanhandu (Table 7).

Figure 9 - Broad oscillatory zones parallel to (010) in columbite-tantalite of the Itamonte (Monte Belo-Capivara) area. Core is tantalite (Ta) and rim is columbite (Col). Inclusions of uraninite (Ur) and zircon (Zr).

Figure 10 - Broad oscillatory zones in columbite-tantalite of Itamonte (Monte Belo-Capivara) area. Core is tantalite (Ta) and rim is columbite (Nb).

The cassiterite from Itamonte (Monte Belo-Capivara) area shows inclusions of pyrite, zircon, plumbotantalite, pyrochlore and of small zoned crystals of columbite-tantalite with a niobiferous core and a tantaliferous rim (Table 7).

Cassiterite grains of the Itanhandu area host and are hosted by the Ti-rich columbite-tantalite (ixiolite)

OXIDE MINERALS: CONCLUDING REMARKS The cassiterite and the columbite-tantalite of the Itamonte (Monte Belo-Capivara) area are derived from pegmatites. The cassiterite contains $\text{Ta}_2\text{O}_5 > \text{Nb}_2\text{O}_5$, and these elements are incorporated in the cassiterite structure. According to Foord (1982), cassiterite containing higher Ta than Nb contents may indicate the presence of Ta mineralization associated to pegmatites. The cassiterite crystals of the Itamonte (Monte Belo-Capivara) area are characterized by abundant mineral inclusions. The tantaliferous columbite-tantalite of the Itamonte (Monte Belo-Capivara) area may be related to a more evolved pegmatite. According to Cerný & Ercit (1985), the Ta/Nb ratio increases during fractionation of the pegmatitic fluid.

The origin of the heavy pan cassiterite from Itanhandu area is still doubtful, but the ilmenorutile inclusions may be related to a quartz-sulfide genetic type, as reported by Murciego *et al.* (1987) in Western Spain. Abella *et al.* (1995) considered the Nb and Ta rutile present at the border and wall of pegmatites from the Cap de Creus area (Spain) as being due to host rock assimilation. The same process was related to the Sb and Ti enrichment of pyrochlore group minerals in the Canadian Separation Rapids pegmatite group

Table 8 - SEM-EDS analysis of cassiterite from Itanhandu and Itamonte (Monte Belo - Capivara) areas.

	Itanhandu (4)	Itamonte (4)
SnO_2	99.3	97.9
Ta_2O_5	0.7	1.8
Nb_2O_5	-	0.4
total %	100.0	100.1

(4): number of analyses; -: not detected

Figure 11 - Ilmenorutile (IR) with exsolutions of columbite-tantalite in contact with cassiterite (Cas) grain of the Itanhandu area.

(Tindle & Breaks 1998). It seems that host rock assimilation may also have contributed to the formation of the ilmenorutile mineralization and to the Ti enrichment of the columbite-tantalite of the Itanhandu area (Fig. 11). In fact, the Andrelândia Depositional Sequence country rocks are rich in rutile and ilmenite, and thin (up to 5 cm) layers of a mixture of Ti and Fe oxides (named "carranquita") are quite common in specific stratigraphic horizons

CONCLUSIONS Tin and tantalum mineralizations are related to the Neoproterozoic Itanhandu and Capivara tourmaline granites, hosted in the migmatitic units of the Andrelândia Megasequence. These bodies are phaneritic, leucocratic, weakly foliated and have calcalkaline, peraluminous (S-type) and parautochthonous characteristics. The geochemical differences between the granites may suggest a heterogeneous source for the rocks, probably

derived from the different migmatitic country rocks by partial melting. Their $Pb^{207}/^{206}Pb$ zircon minimum ages (evaporation technique) relates them to the Ribeira (Capivara tourmaline granite) and Brasília (Itanhandu tourmaline granite) belts.

Columbite-tantalite is the major Nb- and Ta-bearing mineral present in the Itanhandu and Itamonte (Monte Belo-Capivara) areas. In the Itamonte (Monte Belo-Capivara) area the oxide minerals are related to the heterogeneous (PG-1) tantalite-bearing and homogeneous (PG-3) tantalite-cassiterite bearing pegmatites. In the Itanhandu area the origin of the cassiterite is still uncertain.

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References

- Abellaa P.A., Corbella C.M., Draper J.C.M. 1995. Nb-Ta minerals from the Cap de Creus pegmatite field, eastern Pyrenees: distribution and geochemical trends. *Mineral. Petrol.*, **55**:53-69.
- Almeira M.E. 1996. *Geologia, petrografia e geoquímica preliminar do leucogranito Capivara, Itamonte (MG)*. Dissertação de Mestrado, Departamento de Geologia, Universidade Federal do Rio de Janeiro, 132 p.
- Boynton W.V. 1984. Cosmochemistry of the rare earth element: meteorite studies. In: P. Henderson (ed.) *Rare Earth Element Geochemistry*. Elsevier, Amsterdam, pp.: 63-114.
- Cerny P. & Ercit T.S. 1985. Some recent advances in the mineralogy and geocemistry of Nb and Ta in rare-element granitic pegmatites. *Bull. Mineral.*, **108**:499-532.
- Cerny Y P., Ercit T.S., Wise M.A., Chapmam R., Bick H.M. 1998. Compositional, structural and phase relationships in titanian ixiolite and titanian columbite-tantalite. *Can. Miner.*, **36**:547-561.
- Foord E.E. 1982. Minerals of tin, titanium, niobium and tantalum in granitic pegmatites. In: P. Cerný (ed.) *Granite pegmatites in Science and Industry*. Mineralogical Association of Canada Short Course Handbook, 8, Friesen Printers, pp.:187-238.
- Junho M.C.B. 1995. Leucogranites and related migmatites, southern Minas Gerais and southwestern Rio de Janeiro states, Brazil. *An. Acad. Bras. Ciênc.*, **67**:497-515.
- Irvine T.N. & Baragar W.R.A. 1971. A guide to the chemical classification of the common volcanic rocks. *Can. J. Earth Sc.*, **8**:523-548.
- Lahti S.I. 1987. Zoning in columbite-tantalite crystals from the granitic pegmatites of the Erjarvi area, southern Finland. *Geochim. Cosmoch. Acta*, **51**:505-517.
- Maniar P.D. & Picolli P.M. 1989. Tectonic discrimination of granitoids. *Geol. Soc. Amer. Bull.*, **101**:635-643.
- Murciego A., García Sanches A., Martín Pozas J.M. 1987. Microinclusiones de cassiteritas de distintos tipos de yacimientos del centro-oeste de España. *Cuadernos do Labor. Geol. de Laxe*, **12**:273-288.
- Paciullo F.V.P. 1997. *A sequência deposicional Andrelândia*. Tese de Doutorado, Departamento de Geologia, Universidade Federal do Rio de Janeiro, 245 p.
- Pearce J.A., Harris N.B.W., Tindle A.G. 1984. Trace element discrimination diagrams for the tectonic interpretation of granitic rocks. *J. Petrol.*, **25**:956-983.
- Penha U.C. 1992. Prospecção geoquímica em terreno transcorrente. O exemplo do sul de Minas Gerais. In: SBG, Congr. Bras. Geol., **37**, *Bol. Res. Exp.*, p. 239-240.
- Pereira R.M. 2001. *Caracterização geocronológica, geoquímica, geofísica e metalogênica de alguns plutonitos graníticos da região do médio rio Paraíba do Sul e alto Rio Grande, segmento central da Faixa Ribeira*. Tese de Doutorado, Departamento de Geologia, Universidade Federal do Rio de Janeiro, 213 p.
- Pereira R.M., Moreira M.M., Santos R.A., Neves J.L.P. 1992. Geologia e mineralogia do Granito capivara, município de Itamonte, Minas Gerais. In: SBG, Congr. Bras. Geol., **37**, *Bol. Res. Exp.*, p. 215.
- Pereira R.M., Neves J.L.P., Ávila C.A. 1994a. Alguns corpos graníticos da região limítrofe aos estados de São Paulo - Minas Gerais - Rio de Janeiro e suas mineralizações associadas. In: SBG, Congr. Bras. Geol., **38**, *Bol. Res. Exp.*, p. 42-43.
- Pereira R.M., Santos R.A., Neves J.L.P. 1994b. Prospecção à bateia na borda oriental da região sudeste do Brasil: Primeiros resultados. In: SBG, Congr. Bras. Geol., **38**, *Bol. Res. Exp.*, p. 197-198.
- Pereira R.M., Filgueiras S.A., Oliveira A. 1997. Cassiterita associada às rochas graníticas do médio rio Paraíba do Sul, Estado de São Paulo. In: SBG, Simp. Geol. Sudeste, **5**, *Atas*, p. 420-421.
- Pereira R.M., Moura C.A.V., Junho M.C.B. 2002a. Single zircon Pb-evaporation age of some granitic plutons in the central part of the Ribeira Belt, southeastern Brazil. *Rev. Bras. Geoc.*, **32**:327-334.
- Pereira R.M., Neumann R., Netto A.M. 2002b. Investigação química e mineralógica de cassiterita e columbita-tantalita do sudeste do Brasil por microscopia eletrônica de varredura. *Geoquim. Brasil*, **16**:17-23.
- Pollard P.J. 1995. Geology of rare metal deposits: An introduction and overview. *Econ. Geol.*, **90**:489-494.
- Ribeiro A., Trouw R.A.J., Andreis R.R., Paciullo F.V.P., Valença J.G. 1995. Evolução das bacias Proterozóicas e o termo -tectonismo brasileiro na margem sul do Craton do São Francisco. *Rev. Bras. Geoc.*, **25**:235-248.

- Stacey J.S. & Kramer J.D. 1975. Approximation of terrestrial lead isotope by a two-stage model. *Earth Planet. Sci. Letters*, **26**:207-221.
- Suwimonprecha P., Cerney P., Friedrich G. 1995. Rare metal mineralization related to granites and pegmatites, Phuket, Thailand. *Econ. Geol.*, **90**:603-615.
- Tindle A.G. & Breaks F.W. 1998. Oxide minerals of the Separation Rapids granitic pegmatitic group, northwestern Ontario. *Can. Miner.*, **36**:609-635.
- Trouw R.A.J., Heilbron M., Robeiro A., Paciullo F., Valeriano C., Almeida J., Tupinambá M., Amdreis R. 2000. The central segment of the Ribeira Belt. In: U.G. Cordani, E.J. Milani, A. Thomaz Filho, D.A. Campos (eds.) *Tectonic Evolution of South America*. International Geological Congress, 31, pp.: 287-310.

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