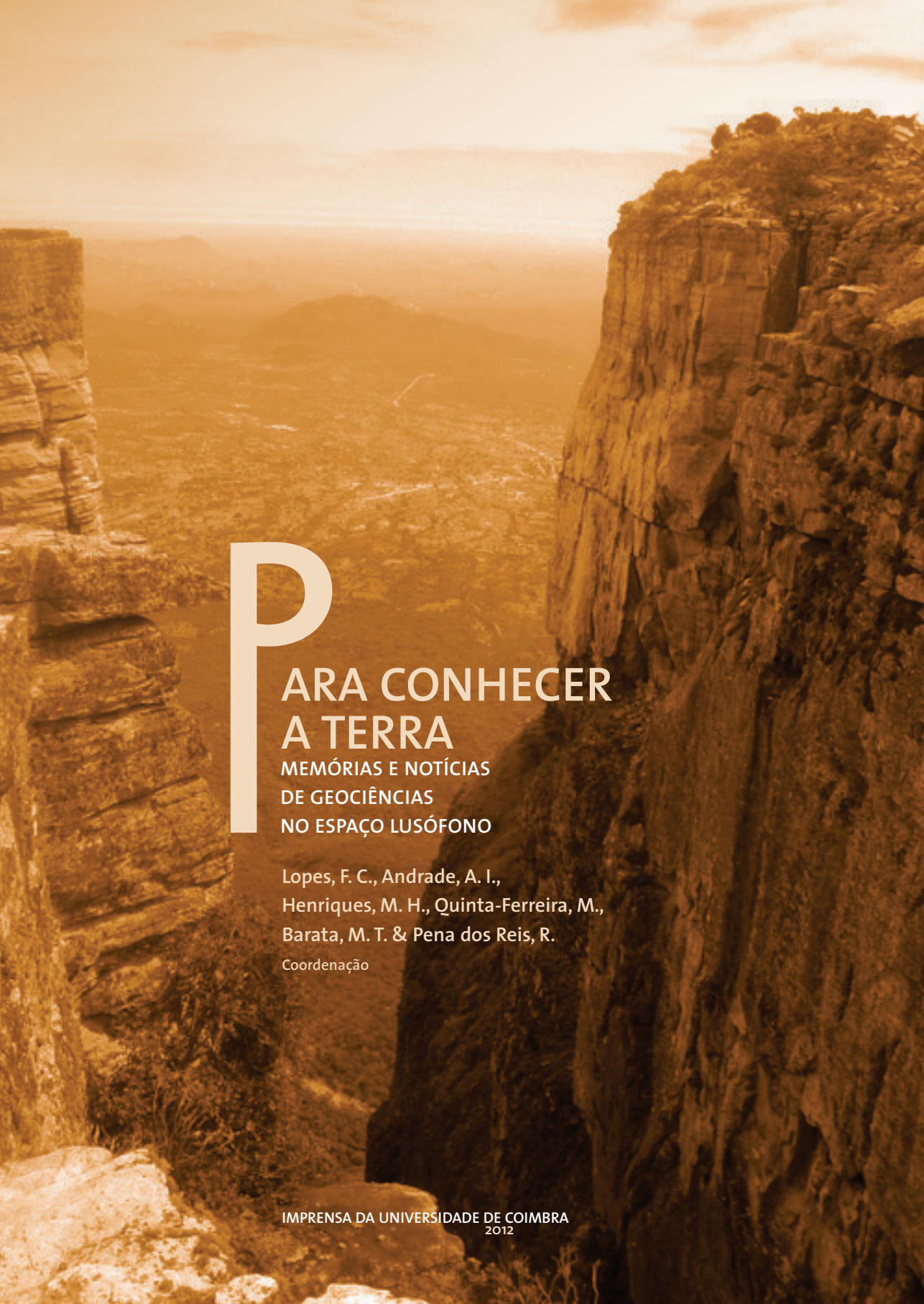

PARA CONHECER A TERRA

MEMÓRIAS E NOTÍCIAS DE GEOCIÊNCIAS NO ESPAÇO LUSÓFONO

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THE SECONDARY PHOSPHATE MINERALS FROM CONSELHEIRO PENA PEGMATITE DISTRICT (MINAS GERAIS, BRAZIL): SUBSTITUTIONS OF TRIPHYLITE AND MONTEBRASITE

OS FOSFATOS SECUNDÁRIOS DO DISTRITO PEGMATÍTICO DE CONSELHEIRO PENA (MINAS GERAIS, BRAZIL): SUBSTITUIÇÕES DE TRIFILITA E MONTEBRASITA

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Abstract – The Eastern Brazilian Pegmatite Province encompasses a region near 150,000km^2 large, mainly in the Minas Gerais State. In this context, the Conselheiro Pena pegmatite district in middle Doce River basin covers part of the Conselheiro Pena and Galiléia counties. Such district is inserted in the domains of Araçuaí fold belt, developed in the eastern margin of the São Francisco craton during the Brasiliano orogenic cycle (630-490My); main regional rocks are proterozoic metasediments of the Rio Doce Group intruded by several granitic suites of Neoproterozoic to Cambrian ages. Pegmatite bodies generally display a complex zoning and diversified mineralogy, where their lithium minerals occur in two groups related to a montebrasite and triphylite primary mineralogy. Triphylite-bearing pegmatites developed secondary phosphates replacing partially/completely the triphylite-lithiophylite assemblage, comprising mainly iron and manganese phosphates, resulting in a complex mineralogical paragenesis that include sicklerite-ferrisickerite, heterosite-purpurite, frondelite-rockbrigeite, hureaulite, reddingite, barbosalite, gormanite, phosphosiderite-strengite, variscite, cyrilovite and vivianite. In relation to the montebrasite-rich pegmatites, the primary mineral occurs associated with

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fluorapatite, hydroxylherderite, brazilianite, beryllonite, eosphorite, siderite, greinfeinstenite, zanazziite, goyazite and crandalite. Other two types of secondary montebrasite also can be found in substitution bodies, showing lower-F content. Such pegmatite groups are mainly related to the Urucum granitic suite that composes the G2 granitic "supersuite"; they are distributed in a north-south trend around the Urucum pluton, in central portion of the district. The distribution of pegmatites of triphylite or montebrasite groups seems to be related to differentiation process, and can be used as a prospective guide for lithium minerals.

Keywords – Pegmatite; Triphylite; Montebrasite; Lithium

Resumo *– A Província Pegmatítica Oriental Brasileira envolve uma extensa região com cerca de 150.000km², principalmente no estado de Minas Gerais. Nesse contexto, o Distrito Pegmatítico de Conselheiro Pena, no médio vale do Rio Doce, abrange parte dos municípios de Conselheiro Pena-Galiléia. Tal distrito encontra-se nos domínios da Faixa de Dobramentos Araçuaí, desenvolvida na margem leste do Cráton São Francisco no ciclo orogênico Brasiliano (630-490Ma). As principais rochas da região são metassedimentos proterozoicos do Grupo Rio Doce, intrudidos por diversas suítes graníticas de idades neoproterozoica/cambriana. Os corpos pegmatíticos geralmente possuem um zonamento complexo e uma mineralogia diversificada, onde os minerais de lítio ocorrem em dois grupos relacionados à presença de montebrasita ou trifilita como minerais primários. Os pegmatitos com trifilita desenvolveram fosfatos secundários substituindo parcial/totalmente a assembléia trifilita-litiofilita, compreendendo principalmente fosfatos de Fe/Mn, que resultou numa paragênese mineralógica complexa que inclui sicklerita-ferrisickerita, heterosita-purpurita, frondelita-rockbrigeita, hureaulita, reddingita, barbosalita, gormanita, fosfosiderita-strengita, variscita, cyrilovita e vivianita. Quanto aos pegmatitos com montebrasita, o mineral primário ocorre associado com fluorapatita, hydroxylherderita, brazilianita, beryllonita, eosforita, siderita, greinfeinstenita, zanazziita, goiasita e crandalita. Outros dois tipos de montebrasita secundária, com baixo flúor, também são encontrados nos corpos de substituição. Tais grupos de pegmatitos estão principalmente relacionados à Suíte Granítica Urucum, que compõe a "supersuíte" granítica G2; eles ocorrem distribuídos num trend norte-sul, nos arredores do pluton Urucum, parte central do distrito. A distribuição dos pegmatitos dos grupos a trifilita ou a montebrasita é relacionada a processos de diferenciação, e pode ser utilizada como guia prospectivo para minerais de lítio.*

Palavras-chave *– Pegmatito; Trifilita; Montebrasita; Lítio*

1 – Introduction

Triphylite-lithiophylite, amblygonite-montebrasite, spodumene and polylithionite-trilithionite (lepidolite) are the dominant lithium minerals in granitic pegmatites. Lithium is an important and strategic mineral resource. In high technological material industry, it is used in aluminum-alloys for the aerospace equipments, in ceramics and lubricants. In the pharmaceutics industry is an important issue in psycho-therapeutics medicaments

and, recently, with the environmental tendency to decrease the petroleum consume, it becomes as an essential issue in an increasing battery market.

The most important lithium world deposits are related to continental brines, especially which located in Bolivia (Salar de Uyuni), Chile (Salar de Atacama) and Argentina (Atacama Desert) and pegmatites (Australia). In Australia, the most important deposits are related to granitic pegmatites of New South Wales, especially associated to the phosphate amblygonite (LISHMUND, 1982). In Brazil, lithium minerals occur in pegmatites of the Borborema Pegmatite Province (BPP), in the Paraíba and Rio Grande do Norte states and in the Eastern Brazilian Pegmatite Province (EBP), in the east and northeast of Minas Gerais and minor proportions in Bahia, Espírito Santo and Rio de Janeiro states.

The only mine in activity in Brazil and responsible for 100% of the Brazilian production is the spodumene rich pegmatite of Cachoeira in Araçuaí county, North of Minas Gerais. With the perspective of improvement of the lithium consumption, others pegmatites will be targets of geological investigation, and other minerals in addition to spodumene will be applied to the lithium production.

The Eastern Brazilian Pegmatite Province (EBP) encompasses a very large region of about 150,000 km^2, from Bahia to Rio de Janeiro states, but more than 90% of its whole area is located in eastern Minas Gerais State. In such context, the Conselheiro Pena pegmatite district is located in the northeast portion of the Minas Gerais state, ca. 360 km from Belo Horizonte city (the state capital). It is inserted in the middle Doce River basin, covering part of the municipalities of Conselheiro Pena, Mendes Pimentel, Divino das Laranjeiras and Galiléia, including an area of about 5,000 km^2 (Fig. 1).

Pegmatites of EBP region were worldwide known in the 1940 decade, after the production of industrial minerals to supply the military industry during the Second World War, as well as gemological minerals and species for the collectors market. Particularly in the Conselheiro Pena district, also occur a large number of rare minerals, including minerals that were first described in the region. In Divino das Laranjeiras were described brazilianite, scorzalite and souzalite, in the Córrego Frio pegmatite (POUGH & HENDERSON, 1945; PECORA & FAHEY, 1949), atencioite (CHUKANOV *et al*., 2006) and qingheiite-(Fe^{2+}) (HATERT *et al*., 2010). Matioliite was described from the Gentil Pegmatite, in Mendes Pimentel county by ATENCIO *et al*. (2006). In Galiléia were described barbosalite, faheyite, frondelite, lipscombite, moraesite, tavorite, arrojadite-(PbFe) and ruifrancoite from Sapucaia pegmatite, locally called "Lavra Proberil" (CASSEDANE & BATISTA, 1999; CHOPIN *et al*., 2006; ATENCIO *et al*., 2007); coutinhoite from Urucum pegmatite (ATENCIO *et al*., 2004a); and lindbergite from Boca Rica pegmatite (ATENCIO *et al*., 2004b).

Mineralogical studies published by CHAVES *et al*. (2005) and SCHOLZ *et al*. (2011) have classified the pegmatites from Conselheiro Pena Pegmatite District concerning their mineralogy with emphasis on lithium minerals. The lithium-rich pegmatites were divided based on the main primary lithium mineralogy.

The aims of this article are to establish a relation between the chemical composition of the primary phosphates triphylite and montebrasite and the secondary phosphate mineralogy in the pegmatites from Conselheiro Pena District. A second objective is to

determine the characteristic mineralogy and the relation to the primary mineralogy. This information can be applied to prepare a regional prospective guide for lithium-bearing pegmatites.

2 – Geological setting

The Conselheiro Pena pegmatite district is inserted in the domains of Araçuaí fold belt (ALMEIDA, 1977), that is a mobile belt developed in the eastern margin of the São Francisco craton during the Brasiliano orogenic cycle (630-490 My). Geologic units in this belt show structural direction north-south in Minas Gerais state, changing to east-west direction in southern Bahia state.

In the studied region mainly occur granitoid rocks of several suites, as Urucum and Palmital of Eocambrian to Paleozoic age, and Galileia of Neoproterozoic age (NALINI JR *et al.*, 2000), as well as gneiss, schist, quartzite, and calcosilicate rock of Neoproterozoic age, like the Tumiritinga and São Tomé formations, of Rio Doce Group (Fig. 1). The main regional structure seems to be a mega synclinorium that has basically north-south direction, where metasediments are found in syncline parts of this structure, while in adjacent anticline parts granitoid rocks occur. Ages of the pegmatite bodies are about 580 My (NALINI, 1997), and are related to granite G2 supersuite (PEDROSA-SOARES *et al.*, 2001) intrusive in the metasediment units. They consist mostly of S-type peraluminous granites and minor metaluminous granites, generated during the syn-collisional stage of Araçuaí orogen.

The Conselheiro Pena district is one of the seven pegmatite districts that subdivide the EPB in Minas Gerais state. Granites and pegmatites were mainly emplaced along high-angle-dip strike-slip shear zones (NALINI, 1997). The important pegmatites are generally external bodies hosted by amphibolite facies rocks, like sillimanite-staurolite-garnet-mica schist with intercalations of calcsilicate rock, metagraywacke and quartzite of the São Tomé Formation. NETTO *et al.* (1998) reported mining activities in 205 pegmatites of the Conselheiro Pena district, many of them large (15 to 50 m thick) to very large (> 50 m thick) bodies.

Pegmatite bodies are tabular- or lens-shaped, and a few are irregular-shaped balloons. They generally display complex zoning and diversified mineralogy. The Conselheiro Pena district is characterized by remarkable phosphate assemblages, such as those of the Sapucaia pegmatite (LINDBERG & PECORA, 1958; CASSEDANNE, 1983), also including the famous brazilianite of the Córrego Frio area (POUGH & HENDERSON, 1945). Triphylite and montebrasite are the main primary phosphates that formed dozens of metasomatic and secondary phosphates, such as eosphorite, hureaulite, reddingite, variscite, vivianite and frondelite (CHAVES & SCHOLZ, 2008; SCHOLZ *et al.*, 2008).

In the past, this district was very important for the production of gem-quality tourmaline, morganite, aquamarine and kunzite, besides industrial minerals, such as microcline, albite, muscovite and beryl ore. Nowadays, these pegmatites are mined for industrial feldspar, mainly microcline, besides gemological, collection and rare minerals. The Fig. 1 shows the geological map of the region, including the locations of the triphylite and montebrasite-rich pegmatites.

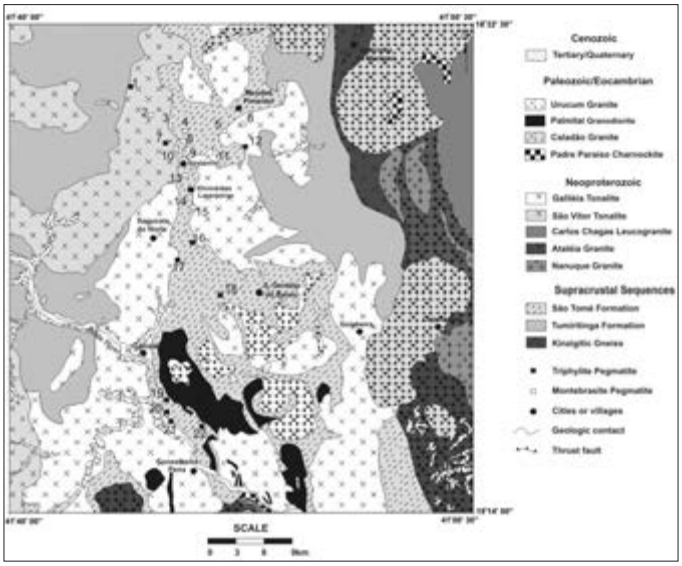

Fig. 1 – Geology and location of the triphylite and montebrasite rich pegmatites from Conselheiro Pena district (after NETTO *et al.*, 1998; SCHOLZ *et al.*, 2011).1 – Pomarolli I, 2 – João Firmino, 3 – Córrego Frio, 4 – Almerindo (or Piano), 5 – Indaiá, 6 – Boa Esperança (João Bobim), 7 – Pomarolli II, 8 – Roberto, 9 – Osvaldo Perin, 10 – Pomarolli III, 11 – Jove Lauriano, 12 – Gentil, 13 – Evaldo or Matinha, 14 – Boa Esperança I, 15 – Boa Esperança II, 16 – Boca Rica, 17 – Sapucaia, 18 – Sapucaia Proberil, 19 Rogério II, 20 – Marcelo, 21 – Bode, 22 – Cigana (or Jocão).

3 – Analytical procedures

Phosphate minerals were collected systematically from different pegmatite bodies. The samples have been studied by three methods:

1 Powder X-ray diffraction (XRD) – in the first stage of research, the phosphate mineral assemblage was determinate. The samples were phase analyzed in a Shimadzu XRD-6000 diffractometer using FeK_{α} radiation and a graphite monochromater. The 2θ range between 5° and 70° was scanned at a speed of 0.5 °/min.

2 Electron Microprobe Analysis – seven samples of brazilianite, five samples of montebrasite and four samples of triphylite were prepared in resin. These minerals were analyzed in the LMA (microanalysis laboratory) of the Physics Department of the Federal University of Minas Gerais, using a Jeol-jxa-8900R on WDS-mode electron microprobe equipped with four wavelength dispersive spectrometers, using an acceleration voltage of 15 kv and a beam current of 20 nA. The following standards were used: Al, An100; Fe and Mg, olivine; Mn, rhodonite; P and Ca, apatite Artimex; Na, albite; F, fluorite; and K, microcline;

3 Water content in the brazilianite was calculated from the losses of mass by thermogravimetric analysis carried out in the Magnesita S.A. laboratory. Water content in other minerals was calculated by stoichiometry.

4 – Phosphate mineralogy from the Conselheiro Pena pegmatite District

In relation to the pegmatite classification of CHAVES *et al.* (2005) and SCHOLZ *et al.* (2011) of the lithium pegmatites from Conselheiro Pena District, the two most representative groups are those related to montebrasite and triphylite primary mineralogy.

4.1 – Triphylite bearing pegmatites

The triphylite-rich pegmatites are hosted mainly in rocks of the São Tomé Formation and are mainly distributed in the central and south part of the area (Fig. 1), especially in the region around Galiléia and Conselheiro Pena. Pegmatites related to this group are poor in gem quality minerals, with rare occurrences of elbaite in the pegmatites Pomarolli I and II.

In the pegmatites of this group, secondary phosphates occurs replacing partially or completely the triphylite-lithiophylite assemblage. The mineralogy comprises several iron and manganese phosphates, resulting in a complex mineralogical paragenesis, that include sicklerite-ferrisickerite, lazulite-scorzalite, heterosite-purpurite, frondelite-rockbrigeite, hureaulite, reddingite, barbosalite, gormanite, phosphosiderite-strengite, variscite, cyrilovite, vivianite and metavivianite. Eosphorite, matioliite and fluorapatite are rare. Small amounts of secondary montebrasite also can be found (SCHNELLRATH *et al.*, 2010).

Chemical composition of two different triphylite crystals from Gentil and one lithiophilite from Jocão (or Cigana) pegmatites are presented in Table 1. The chemical content of lazulite, phosphosiderite and matioliite samples from Gentil pegmatite are also shown.

The chemical data in triphylite shows a high content of Fe in samples from Gentil pegmatite and higher content of Mn in sample from Cigana pegmatite, with predominance of lithiophilite end member, what can be related to a higher degree of differentiation of Cigana pegmatite in relation to Gentil pegmatite.

In this group, miarolitic cavities are rare, usually smaller than $0.01m^3$. In the cavities, muscovite, quartz, albite and a large number of secondary phosphates such as lithiophilite, eosphorite, gormanite and vivianite can be found Brazilianite is rare and was described in Gentil pegmatite associated with matioliite, crandalite and fluorapatite (CHAVES & SCHOLZ, 2008). A secondary montebrasite also occurs associated with greinfeinstenite and eosphorite.

Table 1 – Chemical composition in wt% of triphylite and of some other minerals that compose the paragenesis in triphylite type pegmatites. (GE and OR – Gentil, JO – Cigana or Jocão). Elements not analyzed are marked with (-).

Sample	Mineral Name	FeO	MnO	Al_2O_3	P_2O_5	MgO	Li_2O	H_2O	Total
GE-28	Triphylite	32.90	9.53	0.01	47.20	1.51	-	-	91.17
GE-21	Triphylite	32.26	9.43	0.00	47.90	1.47	-	-	91.11
JO-07	Lithiophylite	18.87	26.67	0.00	44.24	0.27	-	-	90.20
GE-23LA	Lazulite	1.79	0.00	30.91	48.51	11.78	0.00	5.96	99.00
GE-Fsid	Phosphosiderite	46.14	0.00	0.00	31.34	0.00	0.00	-	78.48
OR-01a	Matioliite	2.20	0.06	39.82	42,7	4.68	-	-	90.81

4.2 – Montebrasite bearing pegmatites

The montebrasite-rich pegmatites are hosted mainly in rocks of the São Tomé Formation. Pegmatites classified in this group are poor in gem quality minerals, with rare occurrences of elbaite in João Firmino and Matinha pegmatites. In this group of pegmatites, small amounts of triphylite and their secondary minerals also can be found as in Telírio pegmatite.

Primary montebrasite occurs associated with fluorapatite, hydroxylherderite, brazilianite, beryllonite, eosphorite, siderite, gerifensteinite, zanazziite, goyazite and crandalite. Other two types of secondary montebrasites also can be found in substitution bodies, and show lower fluorine content (SCHOLZ *et al.,* 2008) than the primary montebrasite, that shows fluorine content ranging 3.52% to 5.57% (Table 2); relevant cationic substitutions were not found. In this group of pegmatites, substitution bodies to late crystallization bodies are common, usually smaller than 0.1 m^3, covered by secondary montebrasite, muscovite, quartz, albite and others secondary phosphates. This type of pegmatite is the most important source for brazilianite. Chemical data of montebrasites are presented in Table 2.

Table 2 – Chemical composition in wt% of montebrasite and the most common minerals that compose the paragenesis in montebrasite type pegmatites. (JF – João Firmino, JL – Jove Lauriano, CF – Córrego Frio, PO – Pomarolli, TE – Telírio, RO – Roberto). Elements not analyzed are marked with (-). Elements calculated by stoichiometry (*).

Sample	Mineral Name	FeO	MnO	Na_2O	Al_2O_3	P_2O_5	Li_2O	F	H_2O	Total
JF-01b	Montebrasite	0.02	-	0.13	34.28	49.62	10.21*	3.86	-	96.52
JL-01b	Montebrasite	0.00	-	0.00	34.23	49.72	10.21*	3.52	-	96.27
CF-02	Montebrasite	0.00	-	0.00	34.35	50.16	10.21*	5.57	-	97.96
PO-01	Montebrasite	0.02	-	0.13	34.28	49.62	10.21*	4.91	-	97.33
CF-01	Brazilianite	0.02	-	7.17	43.15	40.95	-	-	8.92	100.22
TE-02	Brazilianite	0.09	-	7.09	43.22	40.86	-	-	8.42	99.68
RO-02	Eosphorite	10.40	18.38	0.01	23.56	31.93	-	-	-	85.09

5 – Concluding remarks

Two main groups of pegmatites with primary lithium minerals were indentified. The pegmatites related to the triphylite type are mainly distributed in the central and southern part of the Conselheiro Pena district. Secondary phosphates that occur associated to the triphylite are Fe and Mn rich and the most common are purpurite, hureaulite, reddingite, frondelite, phosphosiderite, gormanite and vivianite.

Main occurrences of montebrasite-rich pegmatites are located in the north portion of this region, near the locality of Linópolis. The most important mines are Córrego Frio, Telírio and João Firmino pegmatites. Brazilianite occurs associated with other secondary phosphates, including fluorapatite, beryllonite, secondary montebrasite, hydroxylherderite, eosphorite, and rare, greifensteinite, zanazziite, matioliite, gormanite, goyazite and crandalite.

Such pegmatites are mainly related to the Urucum suite that compose G2 granitic supersuite. These pegmatites are distributed in north-south trend around the Urucum pluton, located in central portion of the district. The distribution of pegmatites of triphylite and montebrasite types seems to be related to differentiation process. Pegmatites with montebrasite are important source of lithium, and in this work, the definition of two different areas with montebrasite at north and triphylite at south, can be used as a prospective guide.

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