

Article

# Nature and Evolution of Paleoproterozoic Sn and Rare Metal Albitites from Central Brazil: Constraints Based on Textural, Geochemical, Ar-Ar, and Oxygen Isotopes

Ana Rita F. Sirqueira <sup>1</sup>, Márcia A. Moura <sup>1,\*</sup>, Nilson F. Botelho <sup>1</sup> and T. Kurt Kyser <sup>2,†</sup>

<sup>1</sup> Instituto de Geociências, Universidade de Brasília, Campus Darcy Ribeiro, Brasília 70910-900, Brazil; ana\_rita\_felix@hotmail.com (A.R.F.S.); nilsonfb@unb.br (N.F.B.)

<sup>2</sup> Department of Geological Sciences and Geological Engineering, Queen's University, 36 Union Street, Kingston, ON K7L 3N6, Canada; kyser@geol.queensu.ca

\* Correspondence: mamoura@unb.br

† Professor T. Kurt Kyser, Fellow of the Royal Society of Canada and pioneering geochemist, died while teaching in Bermuda on 29 August 2017.

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**Abstract:** Economic and subeconomic concentrations of Sn, In, rare earth elements (REE), Ta, and Nb are known in Central Brazil, in the Goiás Tin Province. The Sn-P enriched albitites studied in this paper occur in sharp contact with peraluminous granites of the Aurumina Suite (2.0–2.17 Ga) and schists of the Archean to Paleoproterozoic Ticunzal Formation, as dikes or lenses from late-stage magma of the peraluminous magmatism, probably in granite cupolas. Geological, petrological, and isotopic studies were conducted. The albitites consist of albite, quartz, cassiterite, apatite, K-feldspar, and muscovite, and have magmatic texture, such as alignment of albite laths, and snowball texture in quartz, apatite, and cassiterite. They are enriched in Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, Sn, Ta, and Nb (Ta > Nb), and depleted in CaO, K<sub>2</sub>O, TiO<sub>2</sub>, MgO, Sr, Ba, Th, and REE. <sup>40</sup>Ar/<sup>39</sup>Ar in muscovite gave a plateau age of 1996.55 ± 13 Ma, interpreted as approaching the crystallization age. Oxygen isotope data in albite-cassiterite pairs resulted in an equilibrium temperature of 653–1016 °C and isotopic fluid composition of 8.66–9.72‰. They were formed by crystallization of a highly evolved and sodic granitic magma. This study has implications for Central Brazil's economic potential and offers better understanding of tin behavior in rare, evolved peraluminous granitic magmas.

**Keywords:** albitite; snowball texture; Tin; rare metals; Ar-Ar age; oxygen isotope; Brazil

## 1. Introduction

Albitites are uncommon rocks with usually more than 70–80% of albite. Most of the known albitites worldwide have their origin attributed to the action of hydrothermal fluids on granites [1–3]. In this case, quartz and K-feldspar are leached by Na-rich fluids, in an albitization process, which is sometimes related to greisenization from evolved granites [4,5]. More rarely, albitites are formed by direct crystallization from Na-rich magmas, generally related to specialized and rare-metal granites [6–9]. This type can be recognized by typical textures, such as albite inclusions along growth planes in quartz or other mineral, called *snowball texture*, or the alignment of albite laths in the rock matrix, which is interpreted as flow texture. In addition to textural studies, geochemical characterization of associated granites is crucial to distinguish sodic enrichment in the magmatic stage from metasomatic enrichment [7,9–11].

This paper aims to study albitites that occur in a restricted area, i.e., the Goiás Tin Province, located in Central Brazil [12]. Albitites occur as possible dikes or lenses of 1 to 2.5 m thick, cutting

peraluminous granites and graphite schists, or as albitite lenses. They have economic and subeconomic tin concentrations. This led to the exploitation by artisanal miners and the interest of mining companies for mineral exploration in the 1980s. However, there was no mine installation in the area.

### Geological Context

The study area is located within a region characterized by a geological evolution spanning from rhyacian to cryogenian times. In the region, there are schists and gneisses from the Paleoproterozoic Ticunzal Formation, the Aurumina Granitic Suite (2.17–2.12 Ga) [13–17], rift volcano-sedimentary rocks of the Arai Group, of ca. 1.77 Ga [12,18]; within-plate granites of the Goiás Tin Province, represented by the Pedra Branca Suite [9,12]; and Meso-Neoproterozoic sedimentary rocks of the Paranoá (1.2–0.9 Ga) and Bambuí groups (0.9–0.6 Ga; Figure 1A) [19]. The region was subjected to metamorphism and deformation in the Neoproterozoic (Brasiliano/Pan-African event).

The geological units identified in the study area are the Ticunzal Formation and the Aurumina Suite (Figure 1B). The Ticunzal Formation consists of graphite schist, mica-quartz schist, garnet-mica schist, and biotite gneiss. Its most striking feature is the presence of large amounts of graphite, which suggests a restricted marine sedimentary environment, warm and salt waters, with high biological activity. It is older than 2.17 Ga, the age of the oldest granitic intrusions of Aurumina Suite. Results of Sm-Nd isotopic data indicate model-age between 2.7 and 2.8 Ga for the metasedimentary package [13,20,21]. These lithologies are cut by granitic rocks attributed to the Aurumina Suite, which is generally divided in the following facies: muscovite granite, biotite-muscovite granite, tonalite, biotite granite and turmaline-muscovite granite. Pegmatites, albite granites and rare albitites are locally found. According to Botelho et al. [22], they are syn-collisional and S-type peraluminous Paleoproterozoic granites (2.12–2.17 Ga–zircon U-Pb), but recent data [14] show that the magmas of the Aurumina Suite were generated by the hybridization of mafic magmas and metasedimentary rocks, indicating that these peraluminous rocks are not true S-type granites.

This study was conducted in the Boa Vista and Pelotas artisanal mines. Geological, petrological and isotopic data from albitites and spatially associated-granites were integrated to constrain the genesis and evolution history of albitites. The study also intends to contribute to the literature on the petrogenesis and metallogenesis of evolved granitic systems rich in rare metals.

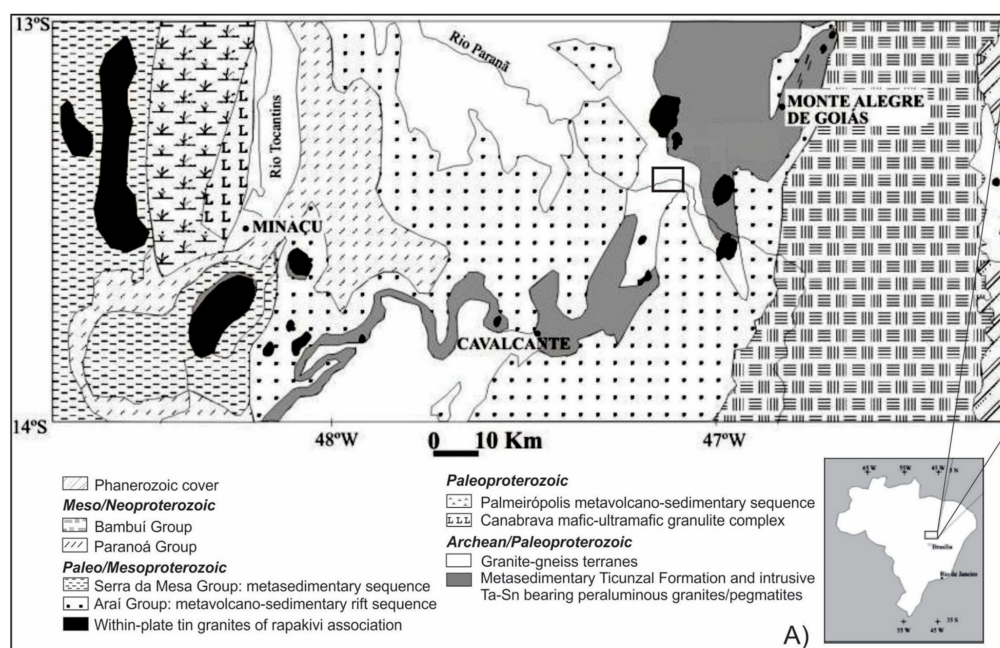
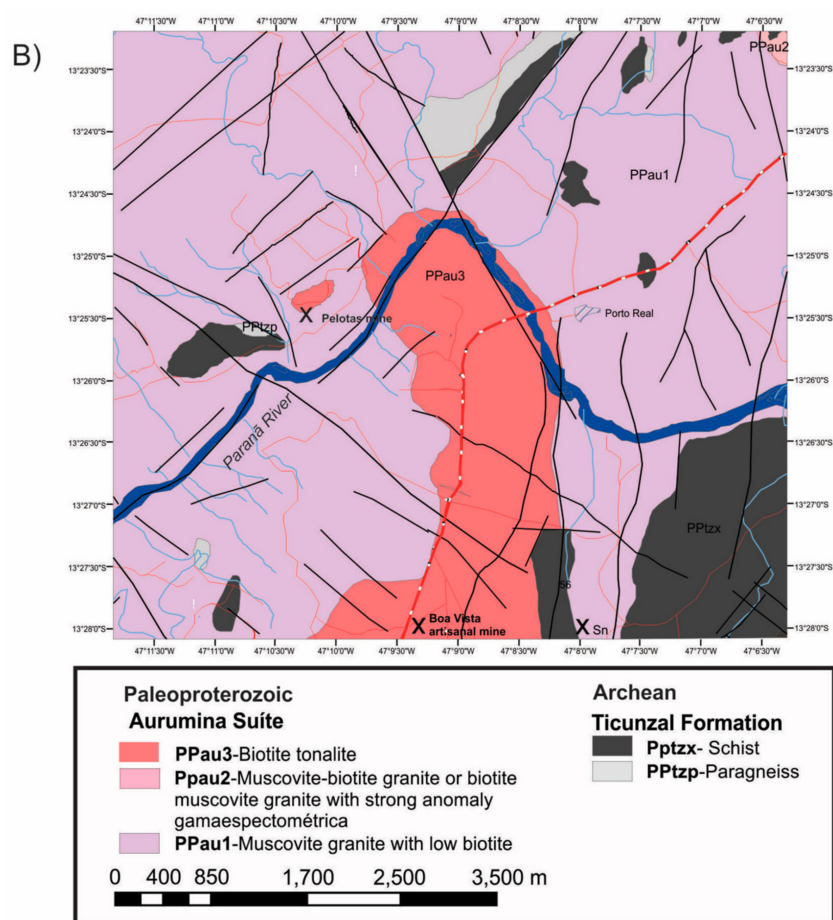


Figure 1. Cont.



**Figure 1.** Geological sketch maps of the study area: (A) a map of the Goiás Tin Province, with inset showing the approximate region of the study area; and (B) a map showing the location of the Pelotas and the Boa Vista artisanal mines [23].

## 2. Materials and Methods

Two field trips for geological studies and sample collection occurred. Eight drill holes from the Pelotas artisanal mine were sampled. Eighty-six thin sections from selected samples were studied. The petrographic studies were conducted in the Microscopy Laboratory of the Geoscience Institute at the University of Brasilia. The chemical analyses were performed at Acme Analytical Laboratories Ltd. (Vancouver, BC, Canada). Major elements ( $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ) were analysed by ICP-ES (inductively coupled plasma-emission spectrometry). Trace elements (Be, Rb, Cs, Ba, Sr, Ca, V, Sn, W, Ta, Nb, Th, U, Zr, Hf, Y, Sc), including rare earth elements, were analysed by ICP-MS (inductively coupled plasma-mass spectrometry). Cr and Co were analysed by the Leco method.

Mineral chemistry data were obtained from JXA-8230-Jeol electron microprobe (Jeol, Peabody, MA, USA), in the Electronic Microprobe Laboratory of the Geoscience Institute at the University of Brasilia. The standards were commercially supplied by CAMECA.

The  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronological analysis was performed in the Isotope Laboratory at Queen's University, Department of Geological Sciences and Geological Engineering, Ontario (Kingston, ON, Canada). There, 23 temperature steps were performed in primary muscovite from albitite of the Boa Vista Artisanal Mine. Mica was irradiated for 40 h in a McMaster-type nuclear reactor. An 8 W Lexel 3500 specific ion laser (Ar), a MAP 216 mass spectrometer, with a *Baur-Signer* source, and an electron multiplier were used. The measurements of argon isotopes were normalized to atmospheric  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio, using the ratios proposed by [24]. Ages were calculated relative to  $\text{Hb}_3\text{Gr}$  (hornblende) with

assigned age of 1072 Ma [24] using conventional 40 K decay constants [25,26]. The analytical precision of individual steps for calculation of the plateau was 0.5% at  $2\sigma$  level.

Stable isotope studies were performed on five samples of albitite, three on albitite from the Boa Vista Artisanal Mine and two on albitite from the Pelotas Artisanal Mine. Cassiterite and albite pairs were considered to be in paragenesis, based on petrographic study. The minerals were manually separated using a binocular loupe in the Geoscience Institute at the University of Brasilia: 5 mg of albite crystals and 3 mg of cassiterite crystals. The oxygen isotope analyses were performed in the laboratory of the Department of Geological Sciences and Geological Engineering at Queen's University (Kingston, ON, Canada). The oxygen isotopic compositions in albite and cassiterite pairs were measured using  $\text{BrF}_5$  by the method of Clayton and Mayeda [27]. Measurements of stable isotopes were performed using a Finnigan MAT 252 mass spectrometer. All values are expressed in ‰. Results were presented as  $\delta^{18}\text{O}$ , relatively to the VSMOW standard (Vienna Standard Mean Ocean Water). The analytical precision was of  $\pm 0.3\text{‰}$  for  $\delta^{18}\text{O}$  values. The isotopic equilibrium temperature for the quartz-cassiterite and cassiterite-water pairs was calculated according to Zheng [28]. The equation used to calculate the isotopic equilibrium temperature for the albite-water system was proposed by Bottinga and Javoy [29].

### 3. Geological Setting and Textural Relationships of Albitites

The granitic rocks and albitites described in the studied area are attributed to the Aurumina Suite. The granitic rocks are mainly represented by muscovite-biotite monzogranite and tonalite. The field relationships between the granites could not be defined, as some were identified only in drill holes.

The studied albitites occur as lenses or dikes spatially associated to tonalites and monzogranites, which sometimes contain xenoliths of graphitic schists or even individual graphite lamellae interpreted as xenocrystic inclusions. Schists also occur in contact with both albitites and granitic rocks. They constitute biotite-chlorite-quartz-graphite schist with garnet and graphite-muscovite-chlorite schist (Figure 2A–F).

The muscovite-biotite monzogranite is whitish-gray, medium to coarse-grained, composed of quartz, plagioclase  $\text{An}_{22-1}$ , orthoclase, muscovite and biotite; chalcopyrite, pyrite, garnet ( $\text{Al}_{80}\text{Py}_{12}\text{Sp}_4\text{Gr}_2$ ), and zircon are accessory minerals (Figure 2A,B,D). Tonalite is strongly altered near the albitites. It is whitish-grey to dark grey, composed of quartz (31–38%), altered plagioclase (48–58%), normally resulting in albite composition  $\text{An}_{10-3\%}$ , and microcline (3–5%) as essential minerals; biotite (1–2%) and muscovite (1–5%) as minor minerals (Figure 2E); and pyrite, chalcopyrite, zircon, and monazite as accessory minerals. Fine muscovite and zoisite/clinozoisite are the alteration minerals. Tonalites follow the modal criteria of classification from Streckeisen [30] nomenclature, and also the regional classification adopted by Botelho et al. [16] and Cuadros et al. [14].

Rare pegmatites and albite granite occur in the Pelotas Artisanal Mine, in contact with the granites and schists. They consist of quartz, K-feldspar, plagioclase, and muscovite.

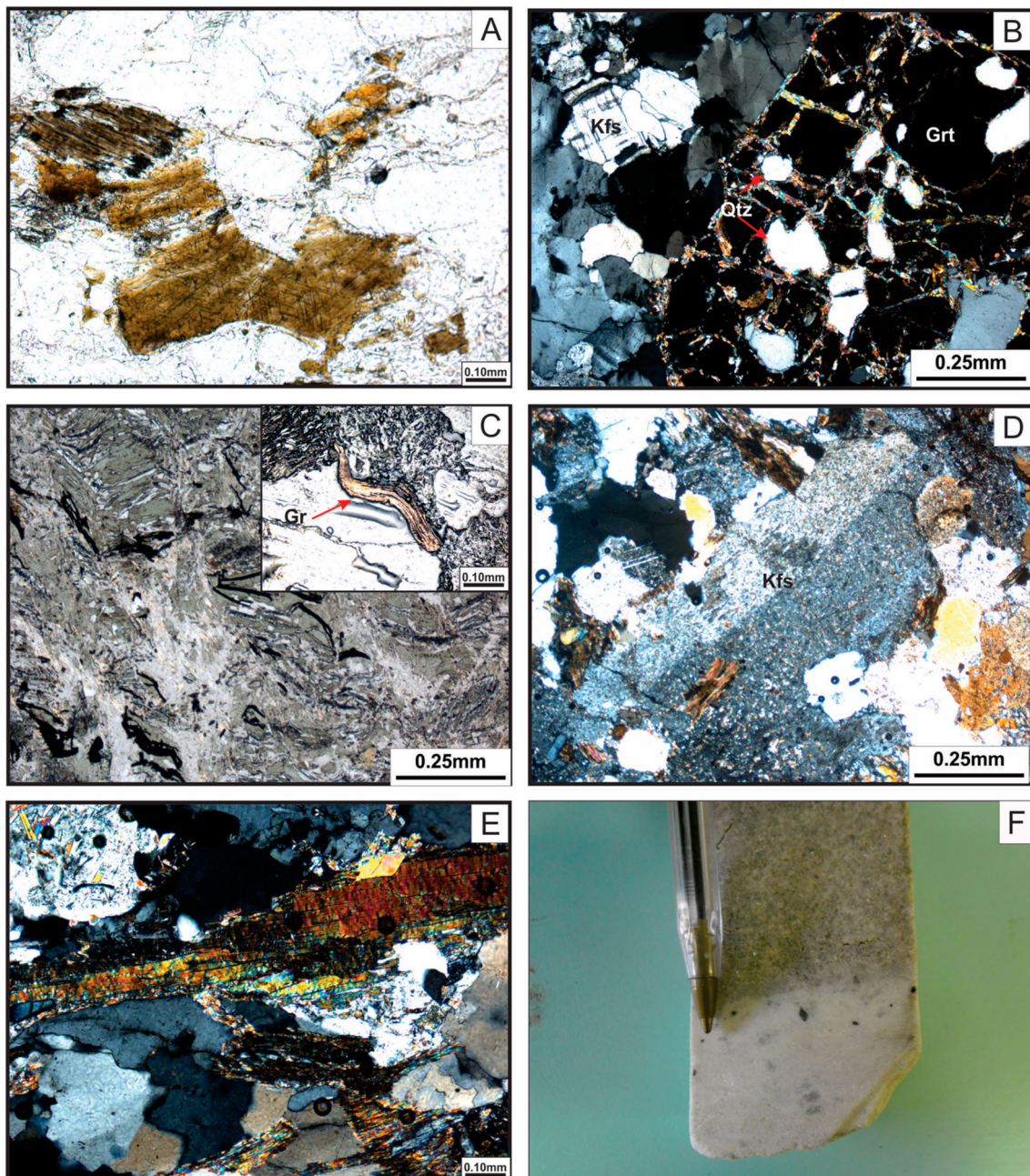
Albitites from both the Boa Vista and the Pelotas artisanal mines are quite similar. In Pelotas, sharp contact between albitite and other rocks is identified in drill-holes (Figure 2F). Albitites are white isotropic rocks, consisting of albite (90–91%), quartz (3–3.5%), cassiterite (1–2%), apatite (1–2%), K-feldspar (0–1%), and primary muscovite (2–4%) (Figure 3A–E).

Albite occurs either as subhedral to euhedral grains, ranging from 0.3 to 1 mm in size, comprising alignment of albite laths, interpreted as flow texture (Figure 3F), or as 0.3 mm euhedral to subhedral laths included in cassiterite and apatite crystals (Figure 3C–E). These Type-2 inclusions of albite crystals arranged almost regularly along growth zones of cassiterite and apatite describe the texture classified as snowball [31] (Figure 3D). Based on textural criteria, albite is interpreted as being of magmatic origin.

Apatite forms subhedral grains 1 to 5.5 mm in size. It occurs as interstitial mineral in most cases. In general, it presents randomly arranged albite lath inclusions. In some crystals, albite is arranged parallel to the apatite border, forming a texture similar to snowball (Figure 3C). It has fluorapatite chemical composition, with low REE content. Cassiterite has euhedral to subhedral habit and ranges from 0.5 to 5.0 mm in size. The crystals are often twinned and the pleochroism varies from reddish

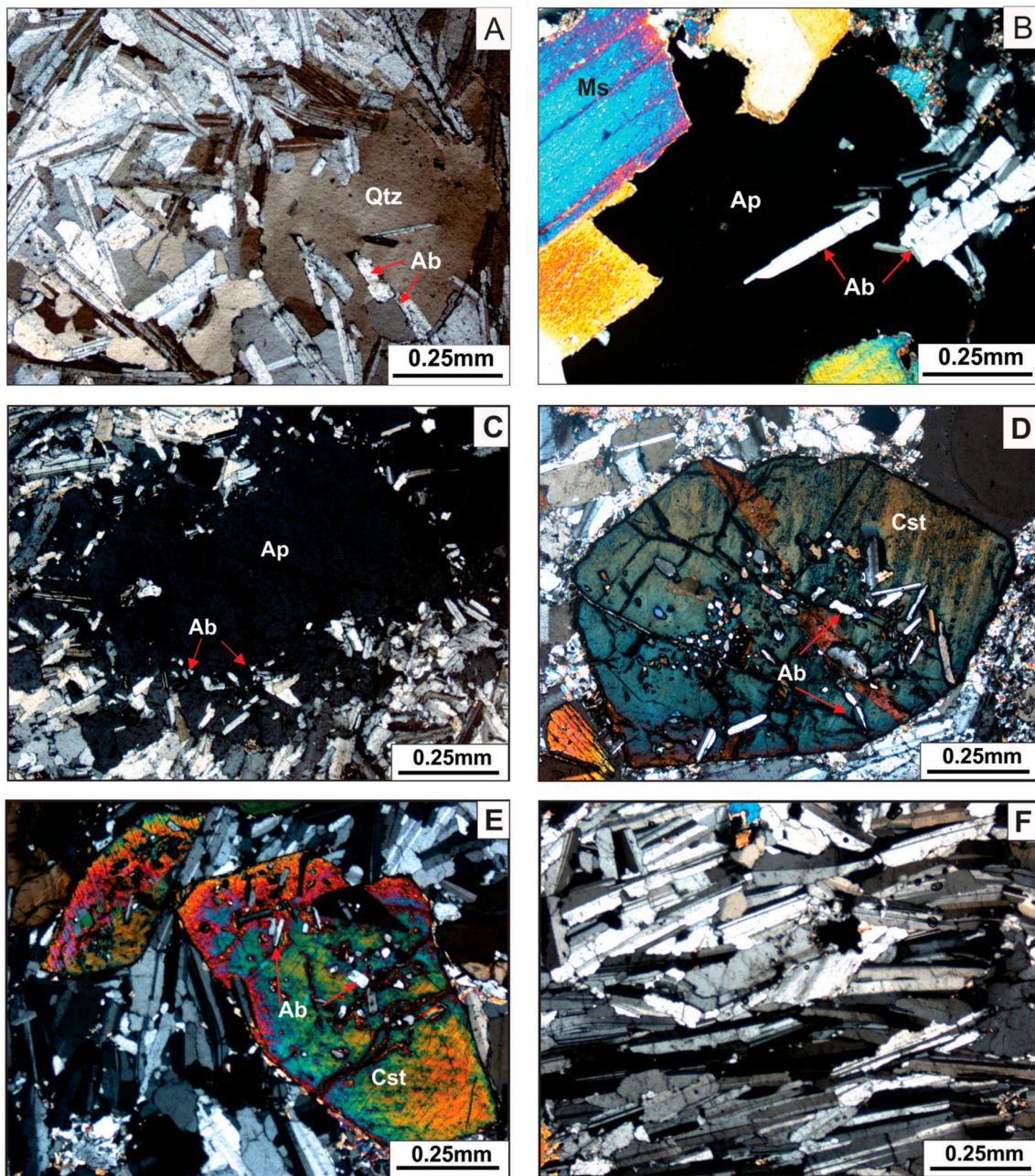


brown to yellowish brown. Type-2 albite inclusions are common, often forming snowball texture (Figure 3C,D). There are also inclusions of quartz and, more rarely, of muscovite.



**Figure 2.** Photographs of representative rocks and features of the study area. (A) Coexisting garnet and biotite in muscovite-biotite monzogranite with garnet; (B) garnet phenocryst containing quartz inclusion in muscovite-biotite monzogranite with garnet; (C) textural aspect of the graphite-chlorite schist in reflected light, showing graphite lamellae; (D) altered orthoclase from biotite-muscovite monzogranite; (E) magmatic muscovite from biotite-muscovite tonalite; and (F) sharp contact between albite and monzogranite. Kfs: K-feldspar; Grt: garnet; Qtz: quartz; Gr: graphite.





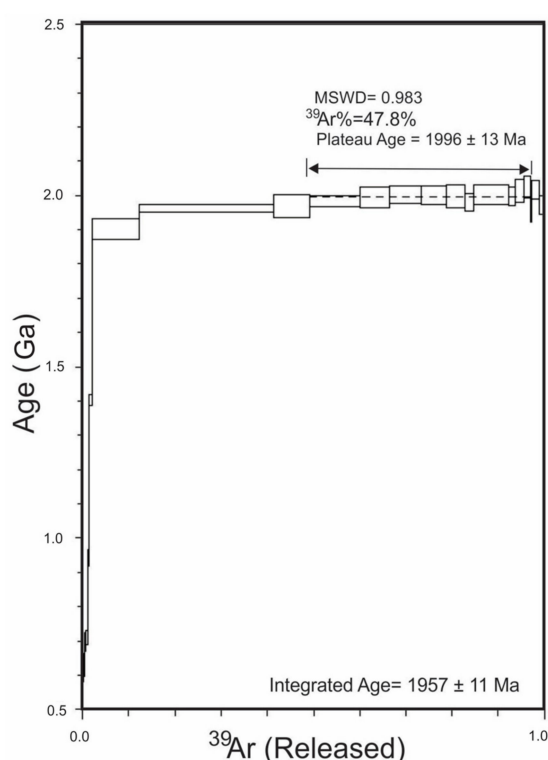
**Figure 3.** Representative photomicrographs showing textural features of albitites from the Boa Vista and Pelotas artisanal mines. (A) Quartz crystals with albite lath inclusions; (B) interstitial apatite with albite inclusions in reentrant contact with magmatic muscovite; (C) magmatic apatite crystal containing albite inclusions interpreted to be along apatite growth zones; (D) cassiterite with albite lath inclusions in the core, forming snowball texture; (E) cassiterite with albite lath inclusions and contact relationship with albite from the rock matrix; and (F) alignment of albite laths. Ab: albite; Ap: apatite; Cst: cassiterite; Ms: muscovite; Qtz: quartz.

## 4. Results

### 4.1. $^{40}\text{Ar}/^{39}\text{Ar}$ Age

$^{40}\text{Ar}/^{39}\text{Ar}$  data were obtained for magmatic muscovite of the albitite from Boa Vista Artisanal Mine. In order to estimate age of the crystallization, 23 increment temperature steps were run.

The obtained age spectrum show a staircase pattern. The first step accounts only for 3.5% of  $^{39}\text{Ar}$  released and yields an age of  $618.0 \pm 36.2$  Ma. The high temperature steps yield a plateau-like pattern, which accounts for 47.8% of  $^{39}\text{Ar}$ , with the mean age of  $1996.6 \pm 13.0$  Ma (MSWD = 0.983), near the integrated age of  $1957.18 \pm 11.15$  Ma (Figure 4). Typical criteria to define the plateau age are: (1) the plateau region of age spectrum with at least 70% of total  $^{39}\text{Ar}$  released; (2) at least three steps on the plateau; and (3) the individual ages of these steps must agree with each other within analytical error (e.g., Corsini et al. [32]). The dated sample do not fit two these criteria by the amount of  $^{39}\text{Ar}$  released. Thus, we interpret the age of  $1996.6 \pm 13.0$  Ma as approaching the muscovite crystallization age, but not necessarily reflecting the true crystallization age of albite due to partial resetting at the regional metamorphism during the Brasiliano (Pan-African) event. The lowest age of  $618.0 \pm 36.2$  Ma may directly correspond to this metamorphism. Obviously, the crystallization of the albitite is equal, or older, than the mean age of the plateau-like steps ( $\sim 2.0$  Ga) and may be younger, or equal, to the age of Paleoproterozoic Aurumina granites ( $\sim 2.12$ – $2.17$  Ga).



**Figure 4.** Results of  $^{40}\text{Ar}/^{39}\text{Ar}$  obtained in primary muscovite from the Boa Vista albitite, showing the plateau age, interpreted as approaching the muscovite crystallization age.

#### 4.2. Litho geochemistry

The chemical representative compositions of the studied rocks are shown in Table 1 and Figures 5 and 6. For comparison, an analysis of a tourmaline-albite granite (TAG) described by Cuadros et al. [14] near the region of the studied albitites was added to Figure 5. According to the Alumina Saturation Index ( $\text{ASI} = \text{Al}_2\text{O}_3 / (\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}) - \text{molar}$ ; [33]), albite granites, monzogranites and tonalites are classified as peraluminous rocks ( $\text{ASI} = 1.1$  to  $1.8$ ), while albitites are classified as metaluminous to peraluminous ( $\text{ASI} = 0.8$  to  $1.3$ ; Figure 5A). Albitites with lower  $\text{SiO}_2$  content show ASI varying from 0.8 to 0.95, and albitites with higher  $\text{SiO}_2$  content present ASI ranging from 1.1 to 1.25. These higher ASI values can be explained by the increased amount of muscovite in some samples. Albitite samples richer in muscovite and quartz and poorer in albite and apatite presents higher  $\text{K}_2\text{O}$  and  $\text{SiO}_2$  and less  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ , and  $\text{P}_2\text{O}_5$  contents (Table 1).

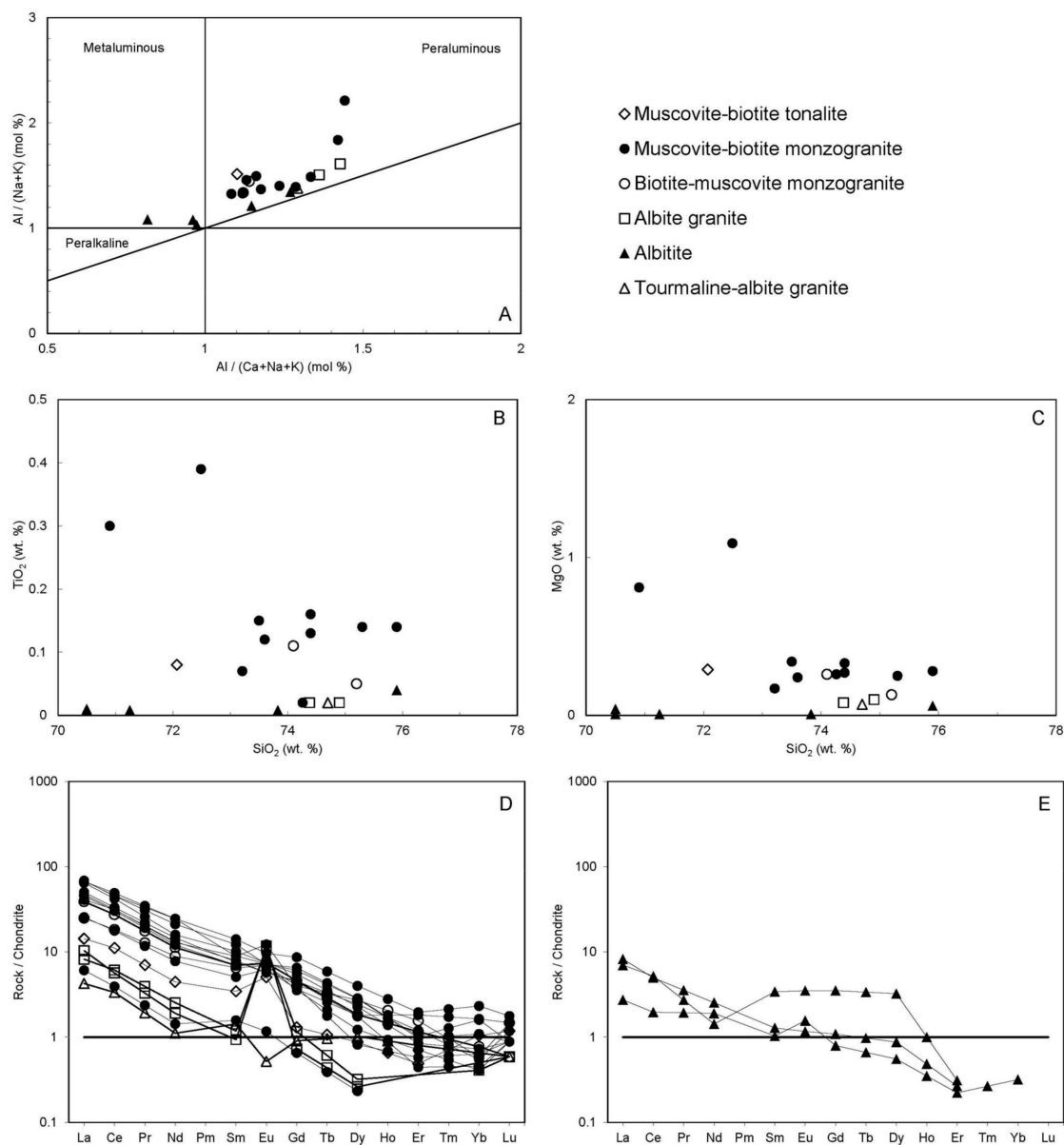
**Table 1.** Representative whole-rock chemical analysis of the studied rocks (wt %).

Rock	Albitite			Tonalite			Schist			Monzogranite					
%															
SiO <sub>2</sub>	70.5	71.25	75.9	70.5	74.38	74.9	49.83	75.3	73.6	74.4	75.9	73.5	70.9	75.2	74.1
TiO <sub>2</sub>	<0.01	<0.01	0.04	0.01	0.02	0.02	0.8	0.14	0.12	0.13	0.14	0.15	0.3	0.05	0.11
Al <sub>2</sub> O <sub>3</sub>	17.1	16.83	14.3	15	16.25	15.5	23.58	14.3	14.5	14.3	13.5	14.6	14.4	14.1	14.4
Fe <sub>2</sub> O <sub>3</sub>	0.1	0.15	0.27	0.22	0.36	0.35	9.19	0.79	1.15	1.21	1.09	1.51	2.45	0.62	1.22
MnO	0.01	0.06	0.01	0.05	<0.01	<0.01	0.27	<0.01	<0.01	0.01	<0.01	0.02	0.02	<0.01	0.01
MgO	<0.01	<0.01	0.06	0.04	0.08	0.1	2.21	0.25	0.24	0.27	0.28	0.34	0.81	0.13	0.26
CaO	1.07	0.53	0.36	2.46	0.71	0.6	2.35	0.46	1.35	1.56	0.89	1.54	1.13	1.12	1.47
Na <sub>2</sub> O	9.59	9.86	6.6	8.08	4.79	5.12	2.49	3.76	4.29	3.95	4.03	3.68	3.23	3.66	3.89
K <sub>2</sub> O	0.06	0.1	0.88	0.54	2.04	1.73	4.55	3.78	3.58	3.06	2.98	3.43	5.09	4.18	3.29
P <sub>2</sub> O <sub>5</sub>	0.78	0.43	0.26	1.82	0.07	0.06	0.11	0.07	0.06	0.88	0.09	0.1	0.3	0.09	0.07
LOI	0.7	0.6	0.9	0.8	1.2	1.5	4.3	1.1	0.9	1.0	1.0	1.0	1.1	0.7	1.0
TOTAL	99.9	99.83	99.5	99.6	99.85	99.9	99.72	99.9	99.9	99.9	99.9	99.9	99.8	99.9	99.9
ppb															
Au	<0.5	0.5	<0.5	0.6	1.1	0.8	0.7	<0.5	<0.5	<0.5	1.3	<0.5	0.8	1	1.3
ppm															
Be	31	148	4	4	4	<1	14	4	11	15	4	8	8	<1	8
Rb	1.5	2.5	282	33.4	63.8	57.1	219	157	101	96	115	124	142	114	107
Cs	0.2	2.8	84.6	1.9	10.4	9.5	28.7	9.3	6.4	6.8	9.9	6.8	13.4	2.9	7.7
Ba	3	7	49	31	602	526	701	311	352	259	353	352	1022	394	321
Sr	115	75.3	33.4	139	289.7	265	378.6	78.6	187	152	183	169	145	152	198
Ga	15.7	13.4	15.4	14	13.3	111	28.7	15.7	15.3	17	13	16.8	17	14.9	14.1
V	21	27	21	23	32	33	146	41	36	27	30	31	57	46	46
Sn	8	398	3218	2851	11	11	4	5	2	1	3	5	4	2	1
W	<0.5	<0.5	2	0.9	1.5	1.4	4.1	0.6	<0.5	<0.5	<0.5	<0.5	0.7	<0.5	<0.5
Ta	1.7	18.7	24.2	111	0.1	<0.1	0.9	0.5	0.2	0.2	0.2	0.8	0.6	0.2	0.3
Nb	1.3	12.9	12	72.2	0.6	0.7	11.9	3.8	3.1	3.3	2.2	4.6	5	1.7	3.1
Th	0.5	<0.2	0.9	0.2	2.8	0.4	17.5	8	6.3	7.4	10.5	5.5	6.1	2.8	5.2
U	2.8	0.8	1.5	6.2	<0.1	0.2	4.3	2.4	4	6.3	3.9	5.5	4.4	2.1	2.3
Zr	15.5	21.5	36.3	16.1	1.2	5.5	189.1	70.7	68.6	82.1	114	76.7	90.6	32	58.4
Hf	1.4	2.9	3.3	2.6	<0.1	<0.1	4.6	2.1	2.1	1.9	3.4	2	2.3	1.1	1.4
Y	2	0.1	1.6	4	0.4	0.9	34.9	2.1	2.2	4	3.7	3.4	6.9	3.8	3.1
Sc	<1	<1	<1	<1	<1	<1	23	1	1	2	2	2	3	1	1
La	0.9	0.2	2.7	2.3	3.4	2.7	57.9	16.5	14.9	15.5	22.5	13.4	22	8.2	12.8
Ce	1.7	0.2	4.3	4.5	4.9	5.3	117.7	28.7	26.2	27.1	39	27.2	42.4	15.8	23.7
Pr	0.16	<0.02	0.44	0.46	0.52	0.52	12.96	2.79	2.38	2.51	3.91	2.68	4.36	1.55	2.31
Nd	1.2	<0.3	1.6	0.9	1.2	1.6	46.4	9.2	7.6	8.3	13.3	8.1	15.4	5.6	7.1
Sm	0.21	<0.05	0.26	0.69	0.19	0.24	9.03	1.55	1.42	1.6	2.48	1.81	2.85	1.32	1.41
Eu	0.12	<0.02	0.09	0.27	0.9	0.87	1.72	0.44	0.54	0.44	0.55	0.56	0.74	0.53	0.57
Gd	0.22	<0.05	0.3	0.97	0.2	0.32	7.43	1.23	0.98	1.25	1.8	1.67	2.39	1.1	1.27
Tb	0.06	<0.01	0.05	0.28	0.03	0.03	1.11	0.14	0.14	0.18	0.23	0.21	0.33	0.18	0.16
Dy	0.19	<0.05	0.3	1.11	0.09	0.11	7.08	0.6	0.42	0.83	0.98	0.97	1.37	0.93	0.63
Ho	<0.02	<0.02	0.05	0.09	0.03	0.02	1.37	0.08	0.08	0.21	0.13	0.13	0.28	0.18	0.16
Er	0.05	<0.03	0.06	0.07	<0.03	<0.03	4.09	0.1	0.16	0.27	0.23	0.22	0.44	0.35	0.26
Tm	0.02	<0.01	<0.01	0.01	<0.01	<0.01	0.61	0.01	0.03	0.03	0.03	0.03	0.08	0.05	0.03
Yb	0.07	<0.05	<0.05	<0.05	<0.05	0.09	3.96	0.1	0.09	0.12	0.35	0.24	0.51	0.13	0.17
Lu	<0.01	<0.01	<0.01	<0.01	0.02	0.02	0.59	0.03	0.03	0.04	0.03	0.03	0.06	0.05	0.02
Ni	0.1	0.5	<0.1	<0.1	0.2	0.3	42.1	<0.1	0.6	0.9	0.9	0.6	6.8	<0.1	0.6
Cr	<20	<20	<20	<20	<20	<20	116.3	<20	<20	<20	27.4	<20	20.5	<20	<20
Co	<0.2	<0.2	0.4	0.3	0.7	0.5	21.6	1.1	1.4	1.8	2	2.3	5	1.1	1.4
Cu	1.3	1.7	0.5	1.2	1.2	1.4	73.2	1.7	2.7	0.9	1.9	1.3	9.2	1.4	1.7
Cd	<0.1	<0.1	0.1	2.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	10	3	4	14	<1	<1	97	6	19	20	18	18	63	3	13
Pb	4	0.6	3.8	8.5	22.7	25.8	5.5	6.6	9.6	6.3	11.8	29.9	37.8	6.6	5.1
Mo	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	0.7	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	<0.1	<0.1
Ag	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.1	<0.1	<0.1
As	<0.5	<0.5	<0.5	<0.5	0.6	<0.5	3	<0.5	<0.5	<0.5	1.3	0.6	1.4	<0.5	<0.5
Sb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.01	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bi	<0.1	<0.1	<0.1	<0.1	1.9	0.8	0.1	<0.1	<0.1	0.1	0.1	0.3	0.3	<0.1	<0.1
Se	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0	<0.5
Hg	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tl	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	0.2	<0.1	0.2	0.1	0.2	0.1	0.4	<0.1	0.2

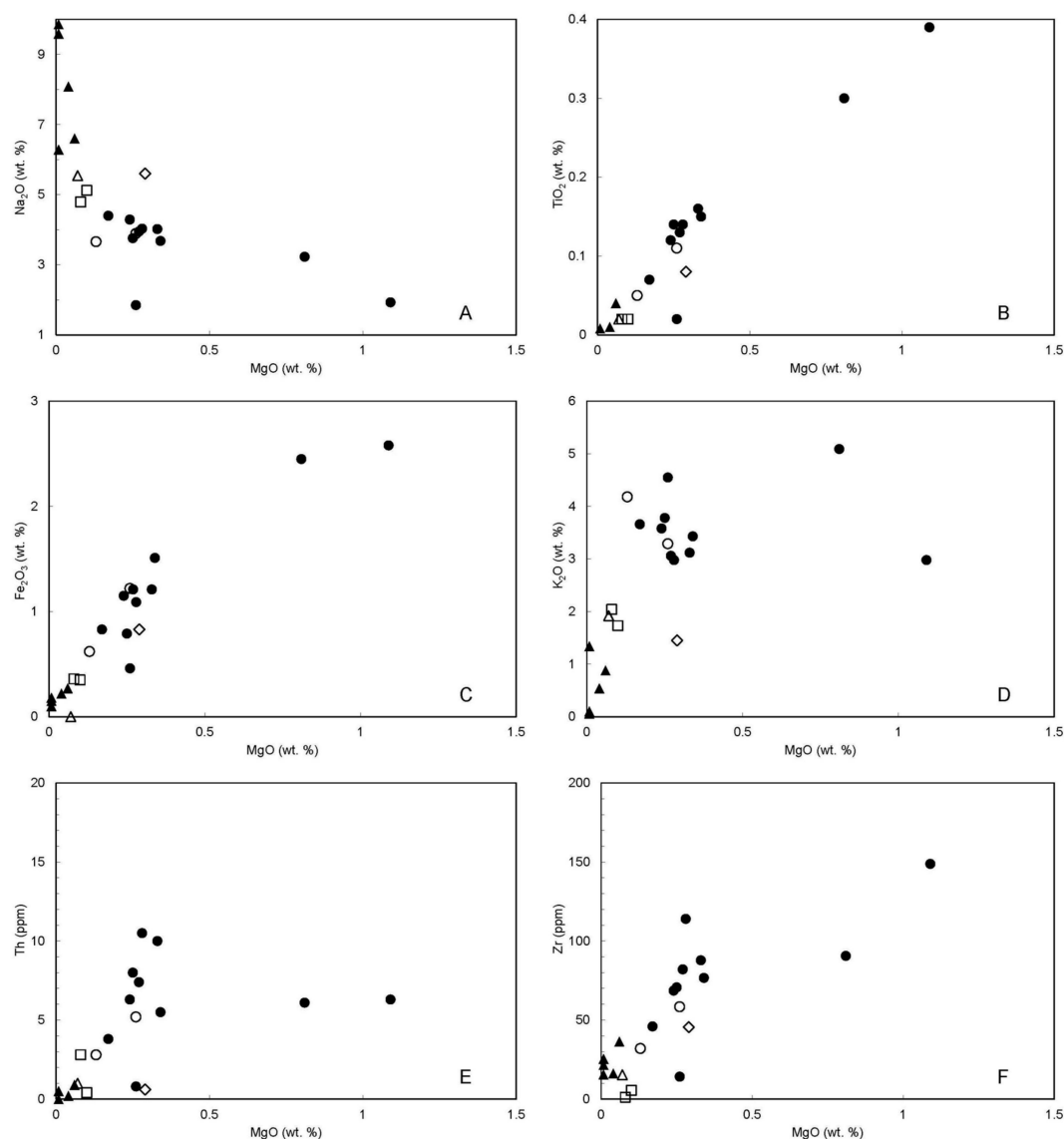
Albitites display high contents of Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, Sn, Ta, and Nb (Ta > Nb), and low contents of K<sub>2</sub>O, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, Ba, Sr, Zr, Th, and Rb. Compared with albitites, albite granites have higher contents of K<sub>2</sub>O, Ba, and Sr and lower contents of Na<sub>2</sub>O, CaO, P<sub>2</sub>O<sub>5</sub>, Sn, Ta, Nb, and Zr. Compared with albitites and albite granites, monzogranites are enriched in TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, K<sub>2</sub>O,



Th, Rb, and Zr; depleted in  $\text{Na}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Al}_2\text{O}_3$ , Sn, Nb and Ta ( $\text{Nb} > \text{Ta}$ ); and they have intermediate contents of Sr and Ba. The analysed tonalite have intermediate levels of  $\text{Fe}_2\text{O}_3$ , MgO,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$  ( $\text{Na}_2\text{O} > \text{K}_2\text{O}$ ), and CaO; high contents of  $\text{Al}_2\text{O}_3$ , Ba, and Sr; and low contents of  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ , Zr, Rb, Sn, Nb, Ta ( $\text{Nb} > \text{Ta}$ ), and Th (Figure 6). The content of U in all the analysed rocks is low ( $<7$  ppm; Table 1).  $\text{MgO}/\text{TiO}_2$  average ratios are 3.6 and 2.2 for tonalites and monzogranites, respectively (Table 1; Figures 5B,C and 6).



**Figure 5.** Representative diagrams of compositional characteristics of granites and albitites. (A) Classification based on Shand index in Maniar and Piccoli diagram [33], showing the peraluminous character of tonalite, monzogranites and albite granites, and the metaluminous to peraluminous character of albitites from the Pelotas and the Boa Vista artisanal mines; (B)  $\text{TiO}_2 \times \text{SiO}_2$  diagram; (C)  $\text{MgO} \times \text{SiO}_2$  diagram; (D) REE patterns of tonalite, monzogranites and albite granites normalized to chondrite, using Nakamura [34] values; and (E) REE patterns of albitites normalized to chondrite using Nakamura [34] values. Tourmaline-albite granite (TAG) sample from Cuadros et al. [14] was added to the diagrams.

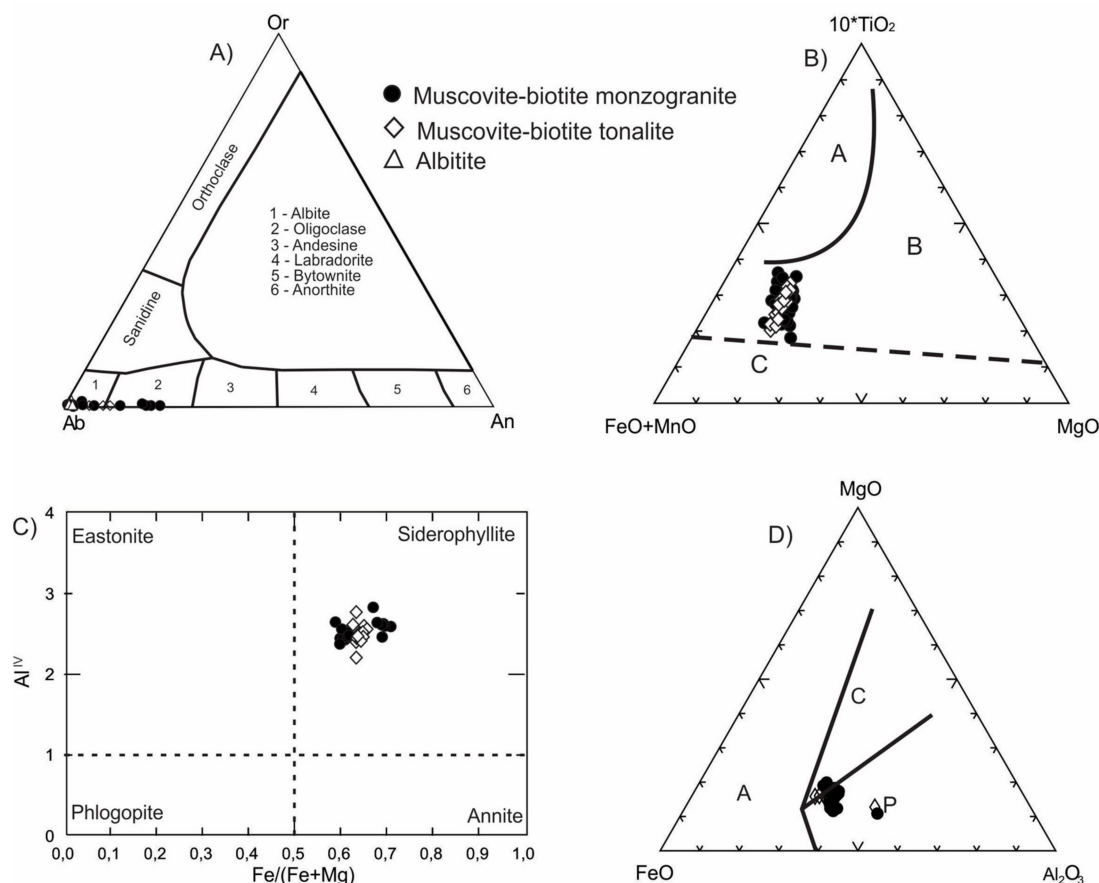


**Figure 6.** Variation diagrams for monzogranite, tonalite and albitite samples from the Pelotas and the Boa Vista artisanal mines. (A) MgO  $\times$  Na<sub>2</sub>O diagram; (B) MgO  $\times$  TiO<sub>2</sub> diagram; (C) MgO  $\times$  Fe<sub>2</sub>O<sub>3</sub> diagram; (D) MgO  $\times$  K<sub>2</sub>O diagram; (E) MgO  $\times$  Th diagram (F) MgO  $\times$  Zr diagram. Legend as in Figure 5.

The values of rare earth elements ( $\Sigma$ REE) are low in all felsic rocks, in contrast to the schists values. They range from 0.4 to 11.6 ppm in albitites, from 11.5 to 11.6 ppm in albite granites, from 35–93 ppm in monzogranites, and reach 20.3 ppm in the tonalite (Table 1). The REE patterns normalized to the Nakamura [34] chondrite values for monzogranites (Figure 5D) are enriched in light rare earth elements (LREE) and depleted in heavy rare earth elements (HREE). Eu anomalies range from slightly positive to negative ( $0.99 < \text{Eu}/\text{Eu}^* < 1.44$ ). The patterns are slightly to strongly fractionated ( $\text{La}_n/\text{Yb}_n = 15.6$  to 110.7). For albite granites, the REE patterns are enriched in LREE as opposed to HREE, whose concentrations are below or near the detection limit of the analytical method (Table 1). They have a pronounced positive Eu anomaly ( $\text{Eu}/\text{Eu}^* = 2$ –14), and their REE patterns are strongly fractionated ( $\text{La}_n/\text{Yb}_n$  ranges from 20 to 106; Figure 5D). Albitites do not follow the same REE pattern (Figure 5E). There is a slight enrichment in LREE compared to HREE ( $\text{La}_n/\text{Yb}_n$  ranges from 2.6 to 30). The Eu anomalies are absent or very discrete, and slightly positive ( $\text{Eu}/\text{Eu}^* = 1$  to 1.7).

### 4.3. Mineral Chemistry

Plagioclase chemical composition in the analysed rocks varies from albite to albite-oligoclase (Figure 7A). Albite ( $Ab_{90-99}An_{10-0.6}Or_{0.4}$ ) occurs in albitites and muscovite-biotite tonalite facies. It contains  $Na_2O$  values between 12% and 13 wt % in albitites and between 10.5% to 11.9% in the muscovite-biotite tonalite facies.  $CaO$  contents are between 0.1% and 0.6 wt %, and 0.5% and 2.8% in albitites and tonalites, respectively.



**Figure 7.** Chemical composition diagrams of plagioclase and biotite of tonalite, monzogranite, and albitite. (A) Classification diagram of the analysed plagioclase; (B)  $(FeO + MnO) - (10 \cdot TiO_2) - MgO$  diagram of Nachit et al. [35], showing the compositional variations of the analysed biotite (A = field of primary magmatic biotite; B = field of magmatic reequilibrated biotite; C = field of secondary biotite); (C)  $Al^{IV}$  vs.  $Fe/(Fe + Mg)$  diagram, proposed by Deer et al. [36]; and (D) the relationship between  $MgO-Al_2O_3$ ,  $FeO_{(t)}-Al_2O_3$ ,  $MgO-FeO_{(t)}$ , and  $MgO-FeO_{(t)}-Al_2O_3$  for the biotite from monzogranites and tonalites in the diagram proposed by Abdel-Rahman [37] (A = alkali granites; C = calc-alkaline granites; P = peraluminous granites).

Albite from albitites has a more sodic composition, with  $Ab = 96-99\%$ . The albite molecule in albite of muscovite-biotite tonalite has  $Ab = 90-97\%$ , revealing little less sodic compared to albitites.

The muscovite-biotite monzogranite has plagioclase with albite-oligoclase composition ( $Ab_{77-99}An_{22-1}Or_1$ ; Figure 7A). It presents  $Na_2O$  values between 9.2% and 12.3% and  $CaO$  values between 0.1 and 4.8%. In grains where there is a compositional variation, the core is more calcic than the rim.

According to the triangular diagram  $10 \cdot TiO_2$  vs.  $FeO + MnO$  vs.  $MgO$  [35], the different biotite types are positioned in the reequilibrated magmatic biotite field (Figure 7B). The  $TiO_2$  content is between 0.8 and 1.7%,  $MgO$  content generally ranges from 6 to 9.5%, while the values of  $Al_2O_3$ , from 17



to 19% (Table 2). The biotite of monzogranite and tonalite is classified as siderophyllite in the Mg/(Mg + Fe) vs. Al<sup>IV</sup> diagram proposed by Deer et al. [36]; Figure 7C). The Fe/(Fe + Mg) ratio is between 0.58 to 0.71 apfu, and the content of Al<sup>IV</sup> varies from 2.1 to 3.3 apfu. The average chemical formula can be defined as: (K<sub>1.82</sub>,Na<sub>0.02</sub>,Ca<sub>0.01</sub>)<sub>1.85</sub> (Fe<sub>3.06</sub>,Mg<sub>1.75</sub>,Al<sup>VI</sup><sub>0.69</sub>,Ti<sub>0.14</sub>,Mn<sub>0.03</sub>)<sub>5.71</sub> Si<sub>5.44</sub>Al<sup>IV</sup><sub>2.56</sub>O<sub>20</sub>(OH<sub>3.7</sub>F<sub>0.3</sub>)<sub>4</sub>.

**Table 2.** Representative analyses of muscovite, biotite, and cassiterite from the studied rocks (wt %).

	Muscovite				Biotite				Cassiterite				
	Albitite		Tonalite		Tonalite		Monzogranite		Boa Vista Albitite		Pelotas Albitite		
	S	P	S	P	S	P	S	P	N	B	N	B	
SiO <sub>2</sub>	47.70	48.40	48.77	47.36	36.04	35.61	35.84	36.05	SiO <sub>2</sub>	0.03	0.00	0.00	0.10
TiO <sub>2</sub>	0.02	0.07	0.15	0.28	1.10	1.20	1.41	0.96	Al <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.02
Al <sub>2</sub> O <sub>3</sub>	33.79	33.67	33.60	34.67	17.65	17.47	17.91	17.76	FeO	0.10	0.25	0.12	0.24
FeO	0.93	0.86	2.50	1.85	23.04	23.45	22.92	22.51	MnO	0.02	0.03	0.00	0.03
MnO	0.06	0.02	1.19	0.12	0.29	0.10	0.15	0.25	WO <sub>3</sub>	0.00	0.00	0.00	0.00
MgO	0.02	0.11	0.05	1.06	7.48	8.11	8.08	8.08	As <sub>2</sub> O <sub>5</sub>	0.00	0.00	0.00	0.00
CaO	0.06	0.00	0.04	0.00	0.02	0.07	0.30	0.05	Ta <sub>2</sub> O <sub>5</sub>	0.45	0.96	0.48	0.73
Na <sub>2</sub> O	0.88	0.68	0.27	0.30	0.05	0.08	0.04	0.21	Sb <sub>2</sub> O <sub>5</sub>	0.38	0.46	0.35	0.36
K <sub>2</sub> O	10.56	10.23	10.67	10.60	9.65	9.56	9.28	9.47	SO <sub>3</sub>	0.00	0.01	0.00	0.00
SrO	0.11	0.00	0.00	0.05	0.03	0.00	0.02	0.00	Bi <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.00
BaO	0.02	0.00	0.06	0.00	0.26	0.00	0.01	0.00	Nb <sub>2</sub> O <sub>5</sub>	0.11	0.38	0.22	0.66
F	0.00	0.00	0.38	0.32	0.62	0.27	0.30	0.29	In <sub>2</sub> O <sub>3</sub>	0.17	0.13	0.12	0.17
Cl	0.00	0.00	0.01	0.00	0.03	0.03	0.03	0.04	SnO <sub>2</sub>	99.32	98.30	99.31	97.74
H <sub>2</sub> O*	4.46	4.49	4.38	4.39	3.61	3.77	3.79	3.78	UO <sub>2</sub>	0.00	0.02	0.00	0.00
Total	98.61	98.58	101.90	100.86	99.66	99.65	99.98	99.40	CuO	0.00	0.01	0.02	0.00
FORMULE ON THE BASIS OF 22O									ZnO	0.00	0.00	0.00	0.01
Si	6.409	6.470	6.406	6.249	5.524	5.466	5.453	5.510	TOTAL	100.57	100.55	100.63	100.05
Al <sup>IV</sup>	1.591	1.530	1.594	1.751	2.476	2.534	2.547	2.490	FORMULE ON THE BASIS OF 2O				
Site T	8	8	8	8	8	8	8	8	Si	0.001	0.000	0.000	0.002
Al <sup>VI</sup>	3.760	3.775	3.609	3.640	0.712	0.628	0.666	0.710	Al	0.000	0.000	0.000	0.000
Ti	0.002	0.007	0.015	0.028	0.126	0.138	0.162	0.110	Fe	0.002	0.005	0.003	0.005
Fe	0.105	0.096	0.274	0.204	2.953	3.011	2.916	2.878	Mn	0.001	0.001	0.000	0.001
Mn	0.003	0.003	0.132	0.014	0.038	0.013	0.019	0.032	W	0.000	0.000	0.000	0.000
Mg	0.007	0.021	0.011	0.208	1.708	1.857	1.832	1.840	As	0.000	0.000	0.000	0.000
Site M	3.876	3.907	4.040	4.094	5.538	5.647	5.594	5.570	Ta	0.003	0.007	0.003	0.005
Ca	0.008	0.001	0.006	0.000	0.003	0.012	0.049	0.007	Sb	0.003	0.004	0.003	0.003
Na	0.229	0.176	0.068	0.076	0.016	0.024	0.013	0.063	Nb	0.001	0.004	0.003	0.008
K	1.810	1.744	1.788	1.784	1.886	1.872	1.802	1.847	In	0.002	0.001	0.001	0.002
Sr	0.009	0.000	0.000	0.004	0.003	0.000	0.001	0.000	Sn	0.987	0.977	0.986	0.973
Ba	0.001	0.000	0.003	0.000	0.015	0.000	0.001	0.000	U	0.000	0.000	0.000	0.000
Site I	2.057	1.921	1.866	1.864	1.926	1.911	1.867	1.924	Cu	0.000	0.000	0.000	0.000
OH*	4.000	4.000	3.842	3.866	3.691	3.862	3.851	3.853	Zn	0.000	0.000	0.000	0.000
F	0.000	0.000	0.157	0.134	0.301	0.130	0.142	0.138	TOTAL	1.000	0.999	1.000	1.000
Cl	0.000	0.000	0.001	0.000	0.009	0.008	0.006	0.009					
Site A	4	4	4	4	4	4	4	4					
TOTAL	31.867	31.656	31.812	31.915	35.905	35.940	35.823	35.964					

\* Calculated values; S = Secondary mineral; P = Primary mineral; N = Nucleus; B = Border.

In tectonic discrimination diagrams proposed by Abdel-Rahman [37], the biotite analyses of monzogranite and tonalite are located predominantly in the biotite field of peraluminous granitic suites (Figure 7D).

Muscovite with textural characteristics of primary muscovite has variation in the chemical composition between biotite-muscovite tonalite and albitite (Table 2). The muscovite from biotite-muscovite tonalite has the following composition: SiO<sub>2</sub> = 45.43–49.50%, Al<sub>2</sub>O<sub>3</sub> = 32.58–38.75%, FeO (t) = 0.54–3.70%, TiO<sub>2</sub> = 0.0–1.15%, MgO = 0.04–1.07%, MnO = 0.0–1.8%, K<sub>2</sub>O = 10.11–11.24%, Na<sub>2</sub>O = 0.20–0.69%, and CaO = 0.0–0.08%. The muscovite from albitites has the following content: SiO<sub>2</sub> = 45.26–48.40%, Al<sub>2</sub>O<sub>3</sub> = 26.28–33.99%, FeO (t) = 0.20–3.40%, TiO<sub>2</sub> = 0.0–0.07%, MgO = 0.0–0.93%, MnO = 0.0–0.15%, K<sub>2</sub>O = 9.20–10.89%, Na<sub>2</sub>O = 0.26–0.96%, and CaO = 0.0–0.17%. It has mostly no fluorine and chlorine.

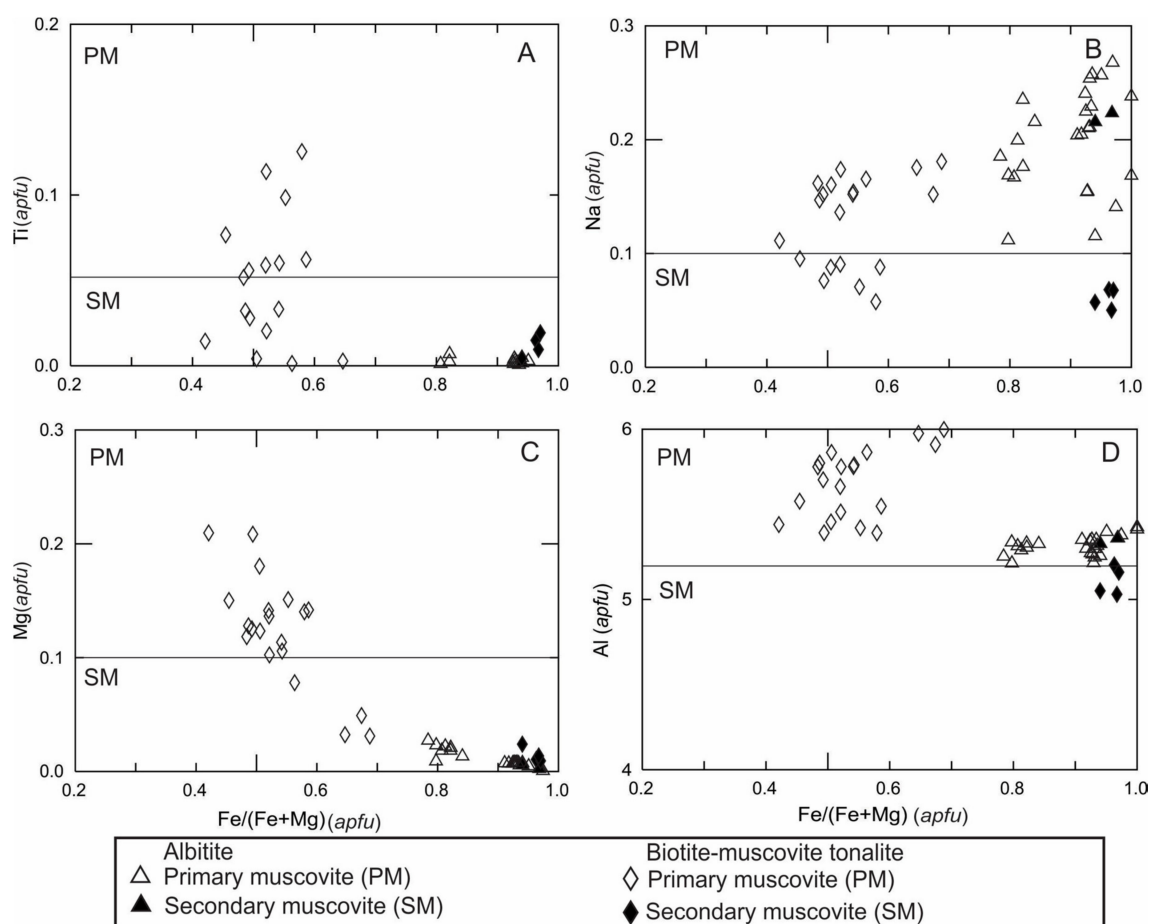
Primary muscovite of tonalite differs from the secondary one for having higher Al, Mg, and Na contents and lower Fe and Si contents (Table 2; Figure 8). In relation to Ti concentrations, usually used to distinguish primary (high Ti) from secondary (low Ti) muscovite [38,39], analyses of magmatic muscovite of tonalite displayed different contents of titanium, apparently contradicting the textural

interpretation. On the other hand, the muscovite petrographically interpreted as secondary always has low  $\text{TiO}_2$  (0.0–0.02 apfu) contents (Figure 8A). With the exception of Ti content, the chemical composition of primary muscovite of tonalite follows the conclusions of Miller et al. [38], according to whom crystals that have the textural aspect of primary muscovite have typically higher Ti, Na, and Al contents and lower Si and Mg contents compared with secondary muscovite.

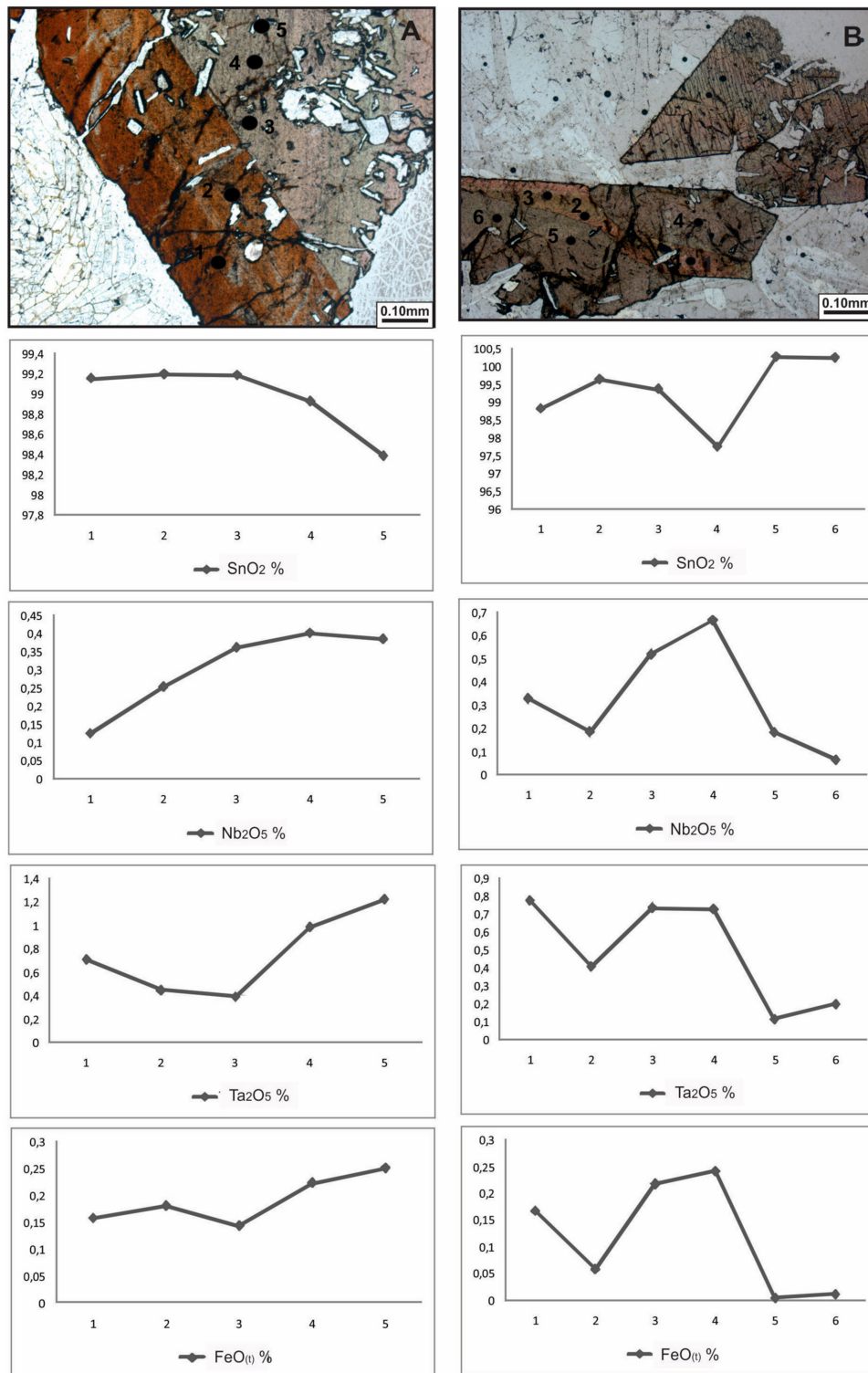
All analyses of muscovite of albitites had almost zero Ti contents, and low Mg and Fe contents. In contrast, both the primary and the secondary muscovite of albitite have high Na, Al and Si contents (Table 2; Figure 8).

The results made it possible to conclude that the combination of textural and compositional characteristics should be used to distinguish primary from secondary muscovite. Similar conclusions were obtained by Zane and Rizzo [40] and Tao et al. [41]. The chemical composition of the studied rocks is interpreted to have acted as a control factor on the composition of primary muscovite, especially in  $\text{Na}_2\text{O}$  and  $\text{TiO}_2$  contents.

Cassiterite with textural characteristics of primary mineral from albitites of the Boa Vista and Pelotas artisanal mines were analysed. In general, the reddish-brown portions have higher  $\text{SnO}_2$  contents and lower  $\text{FeO}$ ,  $\text{Ta}_2\text{O}_5$ , and  $\text{Nb}_2\text{O}_5$  contents ( $\text{Ta} > \text{Nb}$ ) for both areas. The opposite occurs in bands with light brown pleochroism (Figure 9). In cassiterite from Boa Vista, this pattern is more evident than in cassiterite from the Pelotas mine. In crystals without zonation, the nucleus is generally richer in Sn and poorer in Ta, Nb, and Fe in comparison with the border (Table 2).

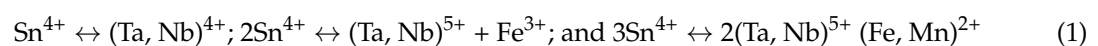


**Figure 8.** Geochemical discrimination diagram for the primary and secondary muscovite. (A) Ti vs.  $\text{Fe}/(\text{Fe} + \text{Mg})$  diagram; (B) Na vs.  $\text{Fe}/(\text{Fe} + \text{Mg})$  diagram; (C) Mg vs.  $\text{Fe}/(\text{Fe} + \text{Mg})$  diagram; and (D) Al (t) vs.  $\text{Fe}/(\text{Fe} + \text{Mg})$  diagram, based on Miller et al. [38]. apfu = atoms per formula unit.



**Figure 9.** Compositional variation in different cassiterite crystals. (A) Cassiterite from albitites in Boa Vista Artisanal Mine; and (B) cassiterite from albitites in the Pelotas Artisanal Mine.

The compositional variation is due to the substitution of Sn for Ta, Nb and Fe in the cassiterite structure. Some possible substitution equations are [42]:





Similar results were obtained by Costi et al. [43] in magmatic cassiterite of within-plate granites in the Pitinga Province, which has a high Nb<sub>2</sub>O<sub>5</sub> (0.063 to 0.6%) and Ta<sub>2</sub>O<sub>5</sub> (0.1 to 1.3%) contents. However, cassiterite from hydrothermal origin showed lower Nb<sub>2</sub>O<sub>5</sub> (0.0–0.1%) and Ta<sub>2</sub>O<sub>5</sub> (0.0–0.1%) contents. Higher Ta<sub>2</sub>O<sub>5</sub> values in relation to Nb<sub>2</sub>O<sub>5</sub> were also identified in other magmatic cassiterites from peraluminous granites of the Aurumina suite, while the opposite (Nb > Ta) occurs in hydrothermal cassiterite from within-plate granites of the Goiás Tin Province [44].

#### 4.4. Oxygen Isotopes

Analyses of oxygen isotopes were performed in pairs of albite and cassiterite interpreted petrographically as to be in paragenesis. The obtained values were  $\delta^{18}\text{O}_{\text{VSMOW}} = 6.7$  to  $9.3\text{‰}$  and  $\delta^{18}\text{O}_{\text{VSMOW}} = 5.3$  to  $6.6\text{‰}$ , respectively (Table 3).

**Table 3.** Oxygen isotope values ( $\delta^{18}\text{O}_{\text{VSMOW}}$ ) of albite and cassiterite from Pelotas and Boa Vista albitite samples, and calculated isotopic equilibrium temperature and isotopic composition of fluid.

Deposit	Mineral (V-SMOW)		Isotopic Equilibrium Temperature (°C) <sup>a</sup>	Isotopic Composition of the Fluid (‰)
	Albite (‰)	Cassiterite (‰)		
Pelotas	9.3	5.3	653 °C	9.35
Pelotas	6.7	6.6	1163–1319 °C	9.17
Boa Vista	7.7		-	9.40 <sup>b</sup>
Boa Vista	7.8	6.0	943 °C	9.39
Boa Vista	7.9	6.5	1016 °C	9.72

<sup>a</sup> Temperature calculated considering the analytical error ( $\pm 0.3\text{‰}$ ); <sup>b</sup> Composition estimated using the isotopic equilibrium temperature average for the Boa Vista artisanal mine.

The calculated temperature of isotopic equilibrium of the albite-cassiterite pair from albitites varied from 653 to 1319 °C. The highest temperature, however, was achieved for albite and cassiterite with relative isotopic fractionation ( $\Delta_{xy}$ ) of 0.1‰. Since the difference in the minerals' isotopic composition is smaller than the analytical error (0.3‰), the temperature of isotopic equilibrium estimated for this pair must be considered with caution. Considering the margin of analytical error, the temperature obtained for this pair is 1163 to 1319 °C (Table 3).

The isotopic composition of albitite fluids from the two artisanal mines is very close regardless of the difference in the temperature of isotopic equilibrium: it varies from 9.17‰ to 9.72‰ (Table 3).

Data of the isotopic fluid composition obtained for albitites are consistent with water of magmatic origin. According to Taylor Jr. [45], they show  $\delta^{18}\text{O}$  between 5.5‰ and 10.0‰. Despite the wide range of values for the isotopic equilibrium temperature, the results are consistent with petrological data and with the interpretation of albitite crystallization in magmatic conditions and at high temperature.

The calculated values of the isotopic fluid composition and isotopic equilibrium temperature are different from those obtained for greisens mineralized in tin described in the region: 3.4–3.9‰ and 285–370 °C for Li-muscovite greisen, and 4.8–7.9‰ and 520–660 °C for zinnwaldite greisen and quartz-topaz rock [5].

As Kalamarides [46] stated, the plutonic rocks generally crystallize in several stages and experience changes of  $\delta^{18}\text{O}$  in the subsolidus phase until they reach the isotopic closure temperature. Consequently, the isotopic equilibrium temperatures obtained for these rocks commonly lie below 800 °C. In contrast, the  $\delta^{18}\text{O}$  values of volcanic rocks and their minerals tend to represent the final product of igneous processes that generated them, as crystallization occurs instantaneously. Considering the obtained data and the mode of occurrence of the studied albitites, it is reasonable to suggest elevated isotopic closure temperature and the existence of subsolidus reequilibrium.

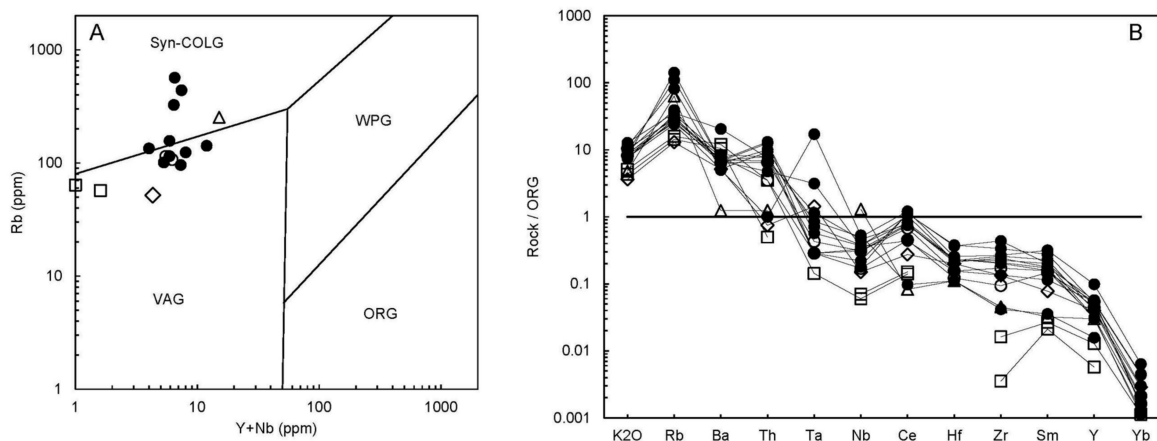
## 5. Discussion

### 5.1. Tectonic Setting and Regional Geological Context

Field, petrographic, and chemical characteristics obtained from the studied monzogranites and tonalites are consistent with the interpretation that these are peraluminous granites, generated in a syn-collisional environment. Diagnostic primary minerals of peraluminous granites are identified in tonalites and granites, such as muscovite and garnet.

Chemical compositions of biotite from tonalite and monzogranite, where  $\text{TiO}_2$  varies from 0.8% to 1.7%,  $\text{MgO}$  from 4.9% to 11.6%, and  $\text{Al}_2\text{O}_3$  from 15.9% to 22.5%, are similar to biotite from peraluminous granitic suites [35,37].

In the Rb vs. (Y + Nb) and Rb vs. (Ta + Yb) diagrams elaborated by Pearce et al. [47], samples of monzogranites from the Pelotas Artisanal Mine are located near the boundary between volcanic arc granites (VAG) and syn-collisional (syn-COLG) granites. The plot of tonalite and some monzogranite samples in the field of VAG is in agreement with the interpretation of Cuadros et al. [14] that these rocks are derived from hybrid magmas (Figure 10A).



**Figure 10.** Tonalite, monzogranite, and albite granite samples in Pearce et al. [47] diagrams. (A) Rb – (Y + Nb) discriminant diagram; (B) ocean ridge granite (ORG) normalized geochemical patterns for representative analyses. syn-COLG: syn-collision granites; VAG: volcanic arc granites; WPG: within-plate granites. Legend as in Figure 5.

In the multi-element diagram normalized to ocean ridges granite (ORG), with values of Pearce et al. [47], positive anomalies of Rb, Th, Ce, and Sm are observed in monzogranite and albite granite samples (Figure 10B). Pearce et al. [47] attributed the enrichment of Rb and Th with respect to Nb and Ta, and Ce and Sm in regard to their adjacent elements, to crustal involvement. The pattern is described by the authors as crust-dominated. Patterns show that the studied monzogranites and albite granites are similar to those presented by Pearce et al. [47] for syn-COLG granites of Tibet.

The Sn-mineralized albitites are in contact with peraluminous granites and schists, attributed to the Aurumina granite suite and the Ticunzal Formation, respectively [12,16]. The  $^{40}\text{Ar}/^{39}\text{Ar}$  age obtained for muscovite from albitite of Boa Vista Artisanal Mine ( $1996.55 \pm 13$  Ma) is interpreted as approaching the crystallization age, which suggests that the albitites were formed during the Paleoproterozoic. They probably comprise, together with tourmaline-bearing pegmatites and granites, the younger phases of the Aurumina Suite peraluminous magmatism, whose granites are considered to have crystallized between 2.12 and 2.17 Ga (zircon U-Pb) [14,22]. These Ar-Ar data are similar to the results obtained by Sparrenberger and Tassinari [17] in peraluminous pegmatites situated at about 40 km north of the studied area. According to the authors, coarse-grained muscovite from pegmatites yielded K-Ar ages of  $2129 \pm 26$  Ma and  $2006 \pm 24$  Ma. After the albitites' formation, the  $^{40}\text{Ar}/^{39}\text{Ar}$  data

registered an event at  $1901.2 \pm 30$  Ma, which caused the release of 47% of  $^{39}\text{Ar}$ . It is suggested that this release of  $^{39}\text{Ar}$  could be related to the first crust perturbations due to the continental rifting experienced by the region in the Paleoproterozoic. In this geotectonic setting, the intrusion of within-plate granites occurred about 1.8 Ga [48,49]. Another heating event was recorded at  $618.0 \pm 36.2$  Ma by  $^{40}\text{Ar}/^{39}\text{Ar}$  data, interpreted as related to the Brasiliano tectono-metamorphic event (Pan-African) described in the region and registered as incipient deformation in the studied rocks.

### 5.2. Genesis and Evolution of Albitites and Associated Granitic Rocks

Albitites in the Pelotas and the Boa Vista artisanal mines have textures interpreted as magmatic, such as snowball texture in quartz, apatite and cassiterite. Albite inclusions have crystallized during its host mineral growth. Albite also has flow texture, with alignment of equigranular albite laths in the matrix (Figure 3). Field relationships suggest that, at least in the Pelotas Artisanal Mine, the studied albitite occurs as dikes or lenses 1 to 2.5 m thick. They occur in sharp contact with peraluminous monzogranites and tonalites, assigned to the peraluminous Aurumina Granitic Suite (2.15–2.0 Ga) by Botelho et al. [16], and with schists of the Ticunzal Formation, which was intruded by the Aurumina Suite. Magmatic albitite, regarded as the end stage of magmatic crystallization, has also been reported in other regions of the world [7,8,50].

The obtained data allow interpretation of the snowball texture in the studied rocks following the authors who consider those textural relationships as a characteristic of evolved granites that crystallized from a residual melt. These granites occur in the apical part of subvolcanic granite complexes and are commonly associated with rare-metal mineralization [51].

The oxygen isotope data showed that the isotopic fluid composition in equilibrium with albitite, from 8.68 to 9.72, is consistent with magmatic signature without influence of meteoric water. This reinforces the interpretation of magmatic origin for the Sn-mineralized albitite of the two studied areas. The estimated albitite isotopic equilibrium temperatures are also consistent with direct crystallization from highly specialized magma rich in  $\text{Na}_2\text{O}$ , P, and B, and depleted in fluorine, with subsolidus reequilibrium.

The studied albitites are probably related to tourmaline-albite granites and tourmaline pegmatites recently described by Cuadros et al. [14] in the region and considered as the most evolved rocks of the Aurumina Suite. In the Boa Vista and Pelotas area we find only tourmaline-bearing pegmatites and tourmaline-free albite granites. We interpret the albitite as primary in origin. One possibility is its formation by the accumulation of albite crystals, which separated from an evolved granitic liquid that gave rise to the tourmaline-albite granite and associated pegmatitic facies. The albite granite would represent a residual liquid. The albitite is similar to the Sn-Ta-bearing albitite described in Slovakia by Breiter et al. [52]. However, at least considering the actual level of investigation in the area, a granite cupola does not occur. The albitite and pegmatite occur as isolated bodies into the granite-tonalite terrain. The albitite is composed of more than 90% albite instead of the compositional variation in Slovakia. The observed flow textures and the pockets of massive albite allow suggest an accumulation of albite laths by separation of the liquid. These interpretations are reinforced by the oxygen isotope data and the flow textures described above.

### 5.3. Tin Transport and Concentration

Crystallization and economic concentration of cassiterite have been reported as a product of direct crystallization from evolved granitic magma or, more commonly, as the result of hydrothermal alteration. In the latter case, tin was leached from granite and/or country rocks and crystallized as cassiterite.

Cassiterite in the studied artisanal mines is interpreted as having been formed by crystallization from an evolved tin-rich granitic magma. When cassiterite occurs as a magmatic mineral, tin must be incompatible with the whole history of melt crystallization. According to Linnen [53], tin must be partitioned into silicate liquid, or the vapor fraction should be sufficiently low so that the tin



concentration in the liquid will continue to increase with fractionation. Magmatic cassiterite can be crystallized in highly evolved systems because, in granitic intrusions with low chlorine content, tin is partitioned into the granitic melt [53]. The results of Linnen et al. [54] and Bhalla et al. [55] showed that Al plays an important role in tin solubility in evolved granitic magmas. SnO<sub>2</sub> solubility in peraluminous magmas will also depend on oxygen fugacity and temperature. Oxygen fugacity increase and temperature decrease tend to reduce tin solubility [31,54–56]. Linnen et al. [55] uses the strong oxygen fugacity dependence of tin solubilities to explain the existence of some magmatic tin deposits. The presence of volatiles in magma is also an important factor in Sn concentration: B, F, Cl, and P contents are generally concentrated in the final stages of evolved magmas and contribute to tin solubility [55,57,58].

The studied granitic rocks have features typical of LCT [59], peraluminous and syn-orogenic systems. Albitites have primary apatite due to high contents of phosphorous. The less-evolved system in the region contains high boron, expressed as magmatic tourmaline. Granitic rocks do not possess cassiterite on their mineral assemblages and have low Sn, Ta, and Nb contents (Table 1). The existing data suggested that tin remained in solution in the peraluminous granitic magma until it precipitated in albitites. Probably, Sn transport occurred in low oxygen fugacity conditions, in P-rich peraluminous magma. Tantalum and niobium precipitation occurred along with Sn and tantalite was recovered together with cassiterite in some artisanal mines

## 6. Conclusions

The main conclusions of this research are:

1. The studied albitites have a snowball texture in quartz, apatite, and cassiterite and flow texture, with alignment of albite laths in the matrix, interpreted as magmatic texture. These rocks are interpreted as magmatic and occur as dikes or lenses in monzogranite, peraluminous tonalite, and graphite schist.
2. Albitites have high Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, Sn, Ta, and Nb (Ta > Nb) contents and represent cumulates separated from evolved Na-rich peraluminous magmas related to the Aurumina suite tourmaline-bearing rocks. The albite granite represents a residual liquid from the late stages of magmatism.
3. Biotite from monzogranite and tonalite have compositions similar to those from peraluminous granitic suites. Tin in cassiterite is replaced by Fe, Ta, and Nb, with Ta > Nb contents. The chemical composition of the studied rocks acted as a control factor on the composition of primary muscovite, especially in Na<sub>2</sub>O and TiO<sub>2</sub> contents. Primary muscovite from tonalite has higher Al, Mg, and Na, and lower Fe and Si contents than secondary ones. While secondary muscovite always has low TiO<sub>2</sub> (0.0–0.07%) contents, magmatic muscovite of tonalite has variable Ti contents. Both primary and secondary muscovite from albitites and albite granites have virtually no Ti and are high in Na, Al, and Si.
4. The isotopic fluid composition in equilibrium with albitites varies from 8.68‰ to 9.72‰ and is consistent with the interpretation of magmatic origin. Although the calculated isotopic equilibrium temperatures are elevated for the evolved peraluminous granite system in place, they also demonstrate the absence of hydrothermal influence on albitite crystallization.
5. <sup>40</sup>Ar/<sup>39</sup>Ar data in muscovite suggest that albitites crystallized around 1996 ± 13 Ma and they can be correlated to the final stages of the Aurumina Suite (2.12–2.17 Ga). Argon loss in 618.0 ± 36.2 Ma is interpreted as related to the Brasiliano (Pan-African) tectono-metamorphic event.
6. In addition to containing hydrothermal tin mineralization hosted in greisens and within-plate granite magmatism, of approximately 1.7 Ga, the Goiás Tin Province has magmatic tin economic concentrations hosted in igneous albitite of about 2.0 Ga. These results, therefore, extend the possibilities of a tin source in the Goiás Tin Province. They have implications for the province's

economic potential and also help understand solubility and tin concentration in peraluminous granitic systems highly evolved and very rich in sodium.

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