

MAGMATIC CASSITERITE AND CRYOLITE MINERALIZATION IN ALBITE GRANITE, PITINGA, BRAZIL

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Summary

Tin, rare metals (Zr, Nb, Ta, Y, REE) and cryolite mineralization at the Pitinga Mine is associated with a late albite granite phase of the Madeira pluton. The albite granite is a subcircular body with a strongly altered border facies.

The fine- to coarse-grained, greyish porphyritic albite granite contains phenocrysts of quartz and Na-amphibole. The matrix is composed of albite, K-feldspar, quartz and accessory minerals including lepidolite, biotite, Na-amphibole, cryolite, zircon, cassiterite, pyrochlore, columbite-tantalite, thorite, xenotime, magnetite, hematite, pyrite, ilmenite, rutile, galena, sphalerite and metamict minerals.

Vermicular to rounded cryolite inclusions in quartz phenocrysts form consecutive circular to hexagonal discontinuous trails (snowball texture), and indicate rapid contemporaneous growth of quartz and cryolite.

Cassiterite occurs as subhedral to euhedral crystals and as small, anhedral inclusions in quartz, mica, Na-amphibole and columbite-tantalite.

Geochemically, the nucleus of the albite granite is a magnetite series, A-type, peralkaline ($A/CNK = 0.836$) phase enriched in Na_2O (6.3 wt.%) and F (6.3 wt.%) with high Fe_2O_3/FeO (2.893).

The petrographic and geochemical features and the oxidised character of the albite granite indicate that cryolite and cassiterite occur as magmatic phases which crystallised in a highly chemically specialised system. However, the albite granite is not related to the earlier granites by magmatic fractionation, and the origin of the extreme chemical specialisation has not been established.

Introduction

Several authors have emphasised the importance of fractional crystallisation (Lehmann 1990; Haapala & Rämö 1992) or magmatic differentiation (Rämö & Haapala 1995) in producing residual magmas enriched in Sn, Rb, F, Be, etc.. Others have considered that the redox state of the melt strongly influences Sn enrichment (Ishihara 1977; Blevin & Chappell 1992).

According to some authors (Kovalenko 1978; Pollard 1989, 1995), peraluminous albite granites are commonly associated with Be, Li, Ta, Sn and W mineralization, while peralkaline albite granites are mainly associated with Zr, Nb, Y, Th, U and REE mineralization.

Economic cryolite mineralization was previously known only at Ivigtut in Greenland, and was considered to result either from late-stage, residual fluid circulation, or interaction between residual magmatic and F-rich hydrothermal fluids (Blaxland 1976). The occurrence of accessory cryolite in the Younger Nigerian Granites was interpreted by Bowden and Kinnaird (1984) to reflect extensive recrystallization due to pervasive, F-rich, late-stage hydrothermal fluid circulation.

The peralkaline albite granite at the Pitinga Mine is a world class example of an unusual, disseminated, granite-hosted deposit which has Sn, Zr, Nb, Ta, Y, REE and cryolite mineralization in addition to Li, F, Na, Rb, U and Th enrichment. In this contribution, the petrographic and geochemical characteristics of the albite granite are used to elucidate the origin of the mineralization, particularly tin and cryolite.

Geological Setting

The Pitinga mine is located in the northern part of the Amazonian Craton. During 14 years of alluvial and eluvial operation it has produced 181,153 tonnes of tin, which is approximately 12% of western world tin production.

At the Pitinga mine, acid volcanic and pyroclastic rocks of the Paleoproterozoic Iricoumé Group with a U/Pb age of 1962±42–33 Ma (Schobbenhaus *et al.* 1994) have been intruded by the multiphase Água Boa and Madeira granites in successive stages of magma injection.

The ca. 350 km² NE-SW oval-shaped Água Boa Granite comprises: an early facies of medium- to coarse-grained inequigranular rapakivi granite; a medium- to coarse-grained biotite granite with a fine-grained, marginal porphyritic phase; and a final elongate and narrow body of fine-grained porphyritic topaz granite in the central part of the batholith. Mineralization includes cassiterite-topaz-mica-quartz greisen and cassiterite-bearing sodic episyenite styles.

The ca. 60 km² NE-SW elongate Madeira Granite, which is separated from the Água Boa Granite by a 1 km wide corridor of volcanic rocks, is composed of: an early fine- to coarse-grained, equigranular to porphyritic rapakivi granite; fine- to medium-grained, equigranular and locally porphyritic biotite granite; and a final fine- to coarse-grained porphyritic albite granite which occurs as a ca. 2.5 km² subcircular body in the central-southern part of the pluton. The albite granite is composed of a nucleus facies surrounded by a ring-shaped autometasomatically altered border facies. The contact with the rapakivi and biotite granites generally occurs through the marginal border facies and dips outwards at 25° to 45°. The albite granite contains disseminated cryolite – zircon – cassiterite – pyrochlore – columbite-tantalite – xenotime mineralization. In addition, the albite granite contains two massive cryolite bodies that occur approximately 150 m below the roof of the granite.

Petrographic Features

The fine- to coarse-grained porphyritic albite granite displays a transitional contact between the nucleus and border facies which is characterised by the replacement of cryolite by hydrated fluorides and then by fluorite, alteration of amphibole and micas to hematite, destabilization of pyrochlore, and hematization of the feldspars (Costi *et al.* 1995).

The albite granite nucleus is inequigranular and porphyritic, with a fine-grained groundmass and rounded phenocrysts mainly of quartz (up to 3 mm) and subordinate dark blue to creamy amphibole, and zoned perthitic K-feldspar. The groundmass is composed predominantly of albite and K-feldspar.

The quartz phenocrysts show successively arranged trails of inclusions of small crystals of albite and/or cryolite (Photo 1) forming a snowball texture, as described in other rare-metal granites (Pollard 1989). Quartz phenocrysts also contain inclusions of pale blue mica, dark blue amphibole and cassiterite. Amphibole phenocrysts comprise subhedral single crystals with outer dendritic intergrowths of slightly different composition and rounded aggregates of euhedral to subhedral crystals joined in a radial or parallel form. Zoned perthitic K-feldspar phenocrysts are subhedral and display small albite inclusions near their

margins. Generally, the phenocrysts comprise about 31% of the rock with 30% quartz, 1% amphibole and a very small amount of K-feldspar.



Photo 1: Quartz phenocryst from the albite granite with cryolite inclusions (black) in circular to hexagonal ordered sequence. Field of view approximately 5.0 mm

The groundmass is commonly fine-grained and composed of albite (30%), K-feldspar (30%) and quartz (1.5%). Medium- to fine-grained mica (2%) occurs in the groundmass, and comprises three different types: green zinwaldite is associated with amphibole and opaques; pale-blue lepidolite occurs filling spaces associated with zircon, cryolite and opaques; and dark cream to brown biotite replaces amphibole and occurs within cryolite cleavages and surrounding opaques. Amphibole (2%) in the groundmass is dark blue (riebeckite/arfvedsonite), subhedral to anhedral and medium- to fine-grained. Cryolite (3.5%) is medium-grained, anhedral with 60-120° cleavages.

The main accessory minerals (1 to 3% - see below) are medium-grained, commonly subhedral to euhedral, suggesting that their crystallization occurred earlier than the formation of the matrix. Opaques and iron oxide minerals are medium- and fine-grained and range from euhedral to anhedral, suggesting an extended period of crystallization.

Alteration features in the albite granite include: 1) amphibole is partially altered to white mica (fengite), biotite and hematite; 2) cryolite is partly altered to biotite; 3) green mica is partly altered to opaques and iron oxides; 4) opaques are replaced by biotite; and 5) K-feldspar is partially albitised; and 6) hematite alters albite and K-feldspar.

Petrographically, the texture of the albite granite border facies is very similar to that in the nucleus facies. However, the groundmass is either fine-grained hypidiomorphic to allotriomorphic or medium-grained panidiomorphic to hypidiomorphic. The medium-grained matrix portions resemble infill space and display growth of euhedral crystals of albite and K-feldspar from the wall to the core. This core is filled by fluorite, acicular opaques (hematite), yellow to greenish mica (sericite), chlorite and euhedral, zoned medium- to coarse-grained zircon. The accessory minerals are commonly medium-grained, subhedral to euhedral. Hematization is intense and widespread, and has imparted a reddish colour to the border facies.

The quartz phenocrysts contain irregularly distributed pods of matrix inclusions and fractures filled by matrix. Veins of the same composition as the matrix (quartz, albite, acicular hematite, yellow greenish mica and fluorite) also cross cut the quartz

phenocrysts. Rare K-feldspar phenocrysts are generally subhedral to anhedral, tabular, perthitic or strongly replaced by albite. The phenocrysts comprise about 26 % of the rock with 26% of quartz and traces of K-feldspar.

The groundmass is commonly fine- to medium-grained and composed of albite (32%), K-feldspar (32%) and quartz (3%). Mica (2.5%) comprises at least three different types: green to brown (biotite and chlorite) and yellow-greenish to pale cream (sericite), and occurs either as part of the groundmass or as an alteration, mainly of opaques. Amphibole and cryolite are absent. Fluorite (0.5%) is commonly anhedral and occurs as a component of the groundmass. Accessory minerals range from 1.5 to 7% (average of 4%), with zircon ranging from 0.5 to 3% and opaques from 1 to 5%. Other accessory minerals are commonly subhedral, medium-grained. Carbonates and white mica are commonly present and associated with opaques and micas. Locally the albite granite border facies is cut by mica-quartz veins (greisens).

Accessory Minerals

Accessory minerals in the albite granite decreasing order of estimated abundance, include: cryolite and its alteration products (thomsenolite and pachnolite), zircon and a metamictic variety (malacon), columbite-tantalite and derivations containing Pb, U and Th and minor Zn, minerals of the pyrochlore group, Fe-oxide (magnetite and hematite), cassiterite, thorite to uranothorite and probably thorianite, rutile to Nb-rutile, ilmenite, xenotime, U-oxide (uraninite) and sulphides, mainly pyrite and sphalerite. Other minerals of common occurrence include: Si-Fe-mineral with minor Zn, Ce-mineral (oxide or fluocarbonate), U-silicate (uranosilite?), U-Pb-mineral (oxide?) and Pb-mineral (oxide or sulphide?). Generally, the main accessory minerals are coarse-grained. Allanite, titanite and apatite were not observed.

Cryolite (10 µm - 5 mm) is commonly subhedral to anhedral, and occurs either as rounded to vermicular inclusions in quartz phenocrysts forming circular to hexagonal discontinuous trails (snowball texture) or in the matrix, indicating rapid contemporaneous growth with the quartz phenocrysts and continuous growth during later formation of the matrix. Cryolite is associated with all accessory minerals and may be surrounded by Fe-oxide, probably hematite. Alteration products of cryolite which contain Ca and H₂O (thomsenolite and/or pachnolite), are also observed.

Cassiterite (5 µm - 5 mm) commonly occurs as subhedral crystals and as tiny anhedral inclusions within quartz, mica, Na-amphibole and columbite. Cassiterite may be zoned due to varying amounts of Ta and Fe. Cassiterite is intergrown with Fe-oxides, columbite and rutile to Nb-rutile and contains inclusions of a U-Pb-mineral (Photo 2).

The extraordinary abundance and composition of accessory minerals in the albite granite phase of the Madeira Granite appears to represent an end-product of major magmatic differentiation, in which F, alkalis and oxygen fugacity were important agents affecting the solubilities of zircon, rutile, columbite, pyrochlore group minerals, cassiterite and probably thorite and xenotime.

Geochemical features

In diagrams combining major and trace elements, most of the Pitinga granites shows different evolutionary trends (Fig. 1), suggesting that they are not directly related by fractionation of a single parent magma. The albite granite constitutes a separate group that shows no correlation with the other Pitinga granites.

The nucleus facies commonly forms a cluster without an internal fractionation trend, while the border facies has a wide compositional range that reflects its strongly altered character (Fig. 1).

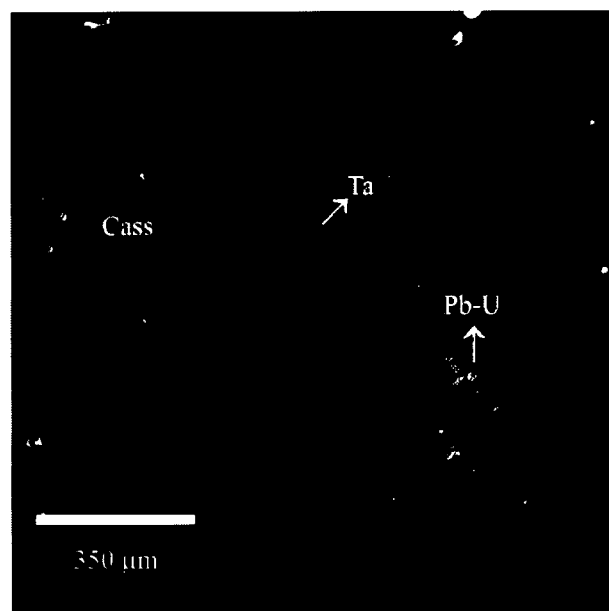


Photo 2: Weakly zoned Ta-bearing cassiterite with inclusions of a Pb-U-mineral

In the Madeira Granite, both the rapakivi ($A/CNK=0.928$) and biotite (0.965) facies are metaluminous, while the albite granite nucleus facies is peralkaline (0.78 - 0.86) and the border facies is mainly peraluminous (0.92 - 2.14).

The major geochemical characteristics of the A-type nucleus facies include low TiO_2 , Al_2O_3 , K_2O , CaO and P_2O_5 and high Na_2O (5.81-6.98 wt.%), Fe_2O_3 (2.28-2.71 wt.%), F (4.00-9.20 wt.%), Rb (4199-5010 ppm), Sn, Zn, Ga, Nb, Ta, Zr, Hf, Th, U, Pb and HREE compared with the other facies.

Magnetic susceptibility measurements, mineralogy and Fe_2O_3/FeO ratio (2.893) indicate high oxygen fugacity conditions for the crystallisation of the albite granite nucleus facies (magnetite-series).

The REE pattern of the albite granite nucleus facies displays a steeply positive slope, with the high zircon content and crystallization of pyrochlore, columbite-tantalite, thorite, xenotime and other REE-bearing phases, responsible for the HREE enrichment.

Conclusions

In the albite granite nucleus facies the snowball textures, composed of quartz phenocrysts and laths of albite and/or vermicular to rounded cryolite, are interpreted to reflect rapid, contemporaneous growth of quartz and albite and/or cryolite. Following initial growth of quartz phenocrysts, saturation in albite and cryolite resulted in their incorporation in the margins of the growing quartz crystals (gross hexagonal shape of inclusion trails). Albite and cryolite continued to crystallise during formation of the matrix. The snowball textures and slightly dendritic intergrowths probably reflect changes in the degree of undercooling, with subsequent re-equilibration of the system and final rapid growth of the groundmass.

Subhedral to euhedral, medium-grained cassiterite, is commonly associated with columbite, zircon and rutile, and also occurs as an inclusion in quartz phenocrysts. These textural features suggest that cassiterite is a magmatic phase, and crystallised before formation of the matrix of the albite granite.

The presence of columbite, rutile to Nb-rutile and their typical association with cassiterite are important indicators of the specialized nature of the melt that formed the albite granite.

The redox state of the albite granite would have been higher than the NNO buffer since crystallization of magmatic cassiterite is a good mineralogical indicator of highly oxidised conditions (Pichavant *et al.* 1996).

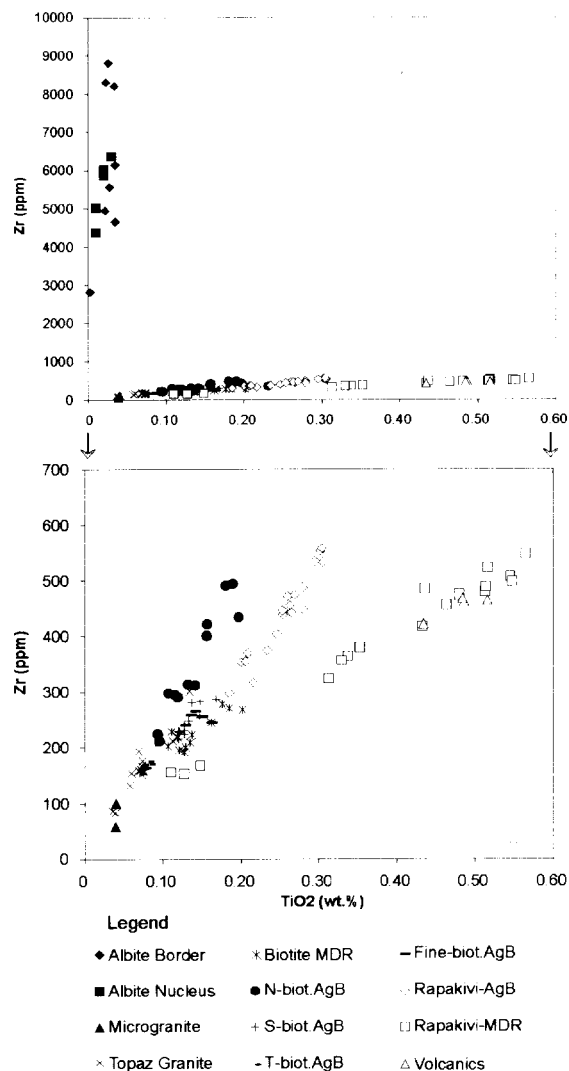


Figure 1: Variation diagrams indicating the evolution of the Água Boa (AgB) and Madeira (MDR) Granites. (N = north-; S = south-; and T = topaz-biotite)

The petrographic and geochemical features of the Pitinga rapakivi granites suggest an evolution associated with partial melting of different sources (rapakivi, biotite and albite granites) with likely later fractionation to form the topaz granite and microgranite.

The lack of any chemical or mineralogical relationship between the albite granite and the other facies of the Madeira Granite, suggests that the albite granite originated from a different granitic melt and, hence, a different source.

Zircon solubility in magmas is dependent mainly on melt composition and temperature. The Zr enrichment of the albite granite suggests that the melt which formed this facies was strongly enriched in alkalis to maintain a solubility of around 6000 ppm Zr. The high solubility of Zr in peralkaline melts is due to complexing of dissolved Zr^{4+} with free alkalis not associated with Al in the melt (Watson & Harrison 1983).

In the peralkaline albite granite, F contents range up to 9.2 wt.%, suggesting that the melt would have persisted to temperatures below 600°C, leading to the crystallization of magmatic albite.

Cryolite stability in SiO_2 -volatile-rich environments with low Ca and high alkali/alumina ratios is consistent with experimental work summarised by Bailey (1980). Above 10-12 wt.% F in the granite- H_2O -HF system at 1000 kg/cm², the granite melt and the coexisting supercritical hydrous solution coalesce into a supercritical hydrous fluoride melt (Glyuk & Anfilogov 1973, cited in Bailey, 1980).

Experimental study of interaction between granite and NaF (Anfilogov *et al.* 1973) shows that with 4.4 to 6 wt.% NaF in the charge, the melt separates into immiscible silicate and fluoride melts. Under natural conditions, the two liquids may separate in the magma chamber due to differences in their densities. Fluoride melts could also extract ore components which form complexes with F from the silicate melt.

The F- and Na-rich peralkaline albite granite contains two massive cryolite bodies approximately 150 m below the roof of the granite. These cryolite bodies may reflect the formation of immiscible fluoride melts during crystallization of the albite granite.

Considering the oxidised character of the albite granite, tin enrichment may reflect: 1) promotion of high Sn solubility due to the F- and alkali-rich (peralkaline) character of the magma, 2) strong depletion in Ti, Ca and Fe, thereby preventing tin depletion by substitution of Sn^{4+} for Fe^{3+} and Ti^{4+} in minerals such as titanite, or 3) the redox state was initially lower, allow enrichment of Sn^{2+} by fractionation, with subsequent oxidation of the magma during crystallisation.

The only possible precursor to the albite granite that is known in the district is the peralkaline Europa Granite, which is located ca. 15 km NW of the albite granite. There are only a few chemical analyses available from the Europa Granite, and these indicate a peralkaline character and possible association with Nb mineralization.

If the albite granite is not related to the Europa Granite, the other possibility for its origin is through derivation from a very specific source. Partial melting of a specialized, metaluminous syenogranite source could produce a magma with the geochemical characteristics of the albite granite. The pressure, temperature and water activity conditions likely for the tonalitic source(s) of the other Pitinga granites could also apply to a specialized syenogranitic source. The residual assemblage would be composed of Ca-plagioclase and Fe-Mg minerals, resulting in enrichment in alkalis over alumina in the melt. F, Rb and HFS elements, which would have been saturated in the source, would have partitioned entirely to the melt phase.

The textural features of the albite granite border facies suggest its origin as a carapace of the nucleus facies, with primary miarolitic cavities infilled by quartz and late sericite, hematite and fluorite alteration.

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