

Li-Mineralization at Tres Arroyos (Alburquerque, Badajoz) as a result of the mineralogical and geochemical evolution of the Alburquerque batholith

La mineralización de Li de Tres Arroyos (Alburquerque, Badajoz), como resultado de la evolución mineralógica y geoquímica del batolito de Alburquerque

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ABSTRACT

La mineralización de Tres Arroyos está formada por un haz de pegmatitas litíferas situado en el límite SW del batolito de Alburquerque. Los diques pegmatíticos aparecen en transición petrológica y geoquímica con el batolito, constituido por granitos de dos micas y diversas facies leucograníticas marginales. Geoquímicamente, los grupos litológicos establecidos corresponden a granitos calcoalcalinos, peralumínicos, fértiles, con elevados contenidos en P y F. La evolución geoquímica observada se caracteriza por un fraccionamiento extremo, con concentración de elementos incompatibles (Li, Rb, Cs, Ga, Sn, Nb, Ta) en las fracciones magmáticas residuales y una evolución compleja en cuanto a los contenidos en Tierras Raras.

Key words: Li-pegmatites, fertile granite, geochemical fractionation.

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Introduction: geological setting

The Tres Arroyos Li-mineralization is located at the SW margin of the Alburquerque batholith in the Central-Iberian Zone of the Hercynian Massif, close to its southern limit to the Ossa-Morena Zone (Fig. 1). The mineralization consists of a N120-140°E trending pegmatite dyke-swarm striking parallel to the batholith contact. Both the dyke-swarm and the batholith are considered to be late events in the Hercynian Orogeny ($K/Ar 287 \pm 10$ Ma., Penha y Arribas, 1974; $Rb/Sr 286 \pm 3.6$ Ma., Roberts *et al.*, 1991). The Hercynian Orogeny was characterized in the area by a long-lived left-lateral transpressive regime, with greater strike-slip shear-component towards the Ossa-Morena Zone and prevalent folding and thrusting to the N (Sanderson *et al.*, 1991). The Alburquerque batholith represents the northern margin of this transpressive zone and intrude into a releasing bend within the shear zone (Sanderson *et al.*, *op. cit.*).

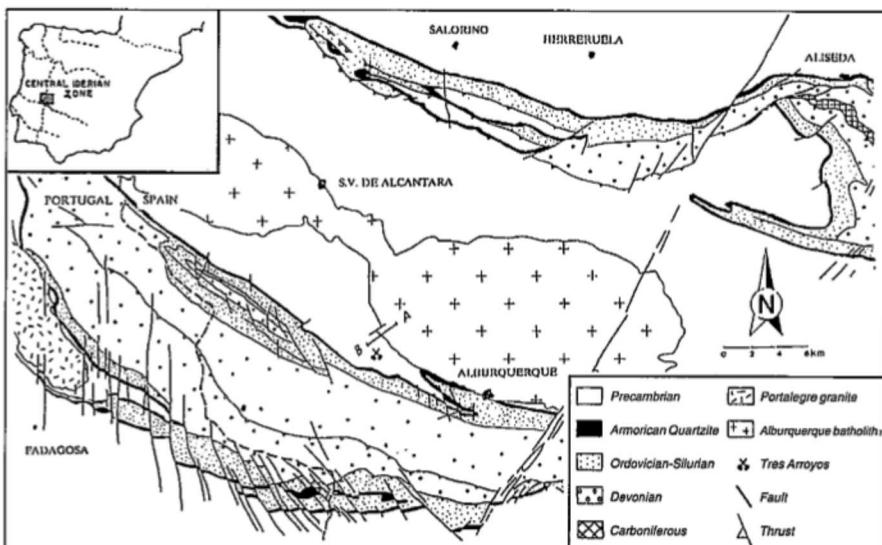
Host-rocks are part of a low-grade metasedimentary sequence comprising phyllites, slates, schists and minor quartzites and metagreywackes

belonging to the so-called "Complejo Esquisto - Grauváquico" (Schists-Greywacke Complex, presumably Precambrian in age). The series show lower greenschists facies due to regional metamorphism and in the vicinity of the batholith are affected by contact

metamorphism leading to the formation of cordierite porphyroblasts. Pegmatic dykes intrude at high-angle with respect to the main hercynian cleavage and contribute to the development of a small-scale crenulation cleavage parallel to the dykes contacts.

Fig. 1.— Regional geology and location map.

Fig. 1.— Esquema geológico de situación.



The Alburquerque granite is a peraluminous batholith with associated U-, P-, Sn-, and Li-mineralization, and in the area provides a good example of a complete and gradual mineralogical and geochemical transition between granite and Li-pegmatites.

Petrography

From NE to SW five main granite facies have been distinguished (Fig. 2):

1. The Central Granite Facies (CGF), which consists of a porphyritic two-mica granite with microcline megacrysts. Groundmass is a coarse-grained assemblage of quartz-K feldspar-plagioclase-biotite-muscovite with minor garnet. Accessory minerals include andalusite, cordierite, apatite, zircon, ilmenite and phosphates.

2. The Marginal Granite Facies (MGF), a finer-grained, generally aplitic, assemblage of albite - quartz - K

feldspar - muscovite - tourmaline with minor biotite. Accessory minerals comprise andalusite, apatite, zircon and monazite.

3. The Layered Aplite-Pegmatite Sequence (LAP), which represents a transition from the MGF and occurs as a N130-140°E trending sheet dipping slightly towards NE, intruding the Precambrian Schists of the Complejo Esquisto-Grauváquico. It is characterized by a layered sequence of aplitic and

| | CGF (3) | | MGF (3) | | LAP (3) | | LED (2) | | LIP (11) | |
|--------------------------------|---------|-------|---------|--------|---------|--------|---------|-------|----------|--------|
| Element | Avg | SD | Avg | SD | Avg | SD | Avg | SD | Avg | SD |
| (%) | | | | | | | | | | |
| SiO ₂ | 72.18 | 0.21 | 72.85 | 0.38 | 71.07 | 0.28 | 69.52 | 0.41 | 68.95 | 1.39 |
| Al ₂ O ₃ | 13.93 | 0.32 | 14.47 | 0.08 | 15.67 | 0.58 | 16.81 | 0.10 | 17.56 | 0.90 |
| Na ₂ O | 3.49 | 0.08 | 3.67 | 0.13 | 4.81 | 0.38 | 5.37 | 0.52 | 5.94 | 1.11 |
| K ₂ O | 4.97 | 0.19 | 4.17 | 0.21 | 3.02 | 0.48 | 2.18 | 0.28 | 1.89 | 0.62 |
| CaO | 0.57 | 0.06 | 0.29 | 0.07 | 0.18 | 0.04 | 0.56 | 0.18 | 0.37 | 0.33 |
| MgO | 0.31 | 0.04 | 0.06 | 0.00 | 0.04 | 0.01 | 0.05 | 0.01 | 0.09 | 0.06 |
| Fe ₂ O ₃ | 1.82 | 0.21 | 1.01 | 0.17 | 0.80 | 0.25 | 0.41 | 0.15 | 0.90 | 0.59 |
| P ₂ O ₅ | 0.36 | 0.03 | 0.61 | 0.12 | 1.15 | 0.36 | 1.36 | 0.29 | 0.79 | 0.55 |
| F | 0.08 | 0.06 | 0.30 | 0.15 | 0.51 | 0.12 | 0.61 | 0.15 | 0.37 | 0.39 |
| ASI | 1.12 | 0.01 | 1.27 | 0.01 | 1.31 | 0.06 | 1.29 | 0.11 | 1.35 | 0.14 |
| A/CNK | 1.14 | 0.02 | 1.30 | 0.01 | 1.36 | 0.06 | 1.38 | 0.01 | 1.42 | 0.15 |
| Mol Na/K | 0.95 | 0.03 | 1.20 | 0.10 | 2.24 | 0.52 | 3.44 | 0.53 | 4.84 | 2.12 |
| (ppm) | | | | | | | | | | |
| Li | 307 | 21.55 | 354 | 31.79 | 566 | 136.06 | 1121 | 468.0 | 743 | 903.58 |
| Rb | 345 | 32.56 | 574 | 102.36 | 938 | 103.71 | 1069 | 1.05 | 933 | 621.27 |
| Cs | 23 | 7.35 | 40 | 7.13 | 98 | 52.63 | 39 | 4.50 | 31 | 31.75 |
| Ga | 23 | 0.47 | 32 | 1.62 | 35 | 5.98 | 43 | 4.50 | 49 | 6.36 |
| Sn | 21 | 4.07 | 40 | 3.66 | 66 | 14.45 | 464 | 317.6 | 409 | 395.93 |
| Nb | 17 | 1.7 | 20 | 3.35 | 38 | 4.23 | 72 | 15.75 | 76 | 15.39 |
| Ta | 4 | 2.05 | 8 | 2.16 | 21 | 3.68 | 87 | 37.50 | 93 | 40.52 |
| Sr | 30 | 3.56 | 24 | 8.51 | 11 | 6.07 | 301 | 50.90 | 232 | 199.30 |
| Ba | 178 | 25.43 | 23 | 2.81 | 18 | 6.39 | 48 | 15.35 | 62 | 33.41 |
| Zr | 112 | 22.46 | 26 | 1.96 | 25 | 7.73 | 24 | 6.50 | 40 | 19.23 |
| K/Rb | 118.5 | 14.11 | 36.70 | 5.81 | 44.30 | 12.00 | 16.56 | 2.11 | 19.01 | 4.65 |
| K/Cs | 2006 | 724 | 895 | 222 | 337 | 190 | 470 | 111 | 652 | 199 |
| K/Ba | 230.3 | 27.8 | 1519 | 166.3 | 1433 | 245.5 | 390.7 | 77.8 | 354.3 | 290.1 |
| Mg/Li | 6.63 | 1.28 | 1.05 | 0.17 | 0.52 | 0.17 | 0.38 | 0.21 | 1.52 | 1.50 |
| Rb/Cs | 16.54 | 4.62 | 24.08 | 2.07 | 7.04 | 2.26 | 28.00 | 3.15 | 34.22 | 8.93 |
| Rb/Sr | 11.81 | 2.70 | 47.17 | 20.79 | 102.1 | 96.90 | 3.66 | 0.62 | 7.87 | 7.61 |
| Ba/Rb | 0.53 | 0.12 | 0.02 | 0.00 | 0.03 | 0.02 | 0.05 | 0.01 | 0.10 | 0.08 |
| Al/Ga | 3163 | 113 | 2367 | 108 | 2468 | 462 | 2088 | 231 | 1919 | 229 |
| Zr/Y | 9.17 | 1.64 | 6.62 | 1.43 | 20.12 | 6.88 | 34.60 | 0.60 | 20.57 | 15.50 |
| Zr/Sn | 5.79 | 2.13 | 0.65 | 0.11 | 0.37 | 0.05 | 0.12 | 0.09 | 0.49 | 0.62 |
| Nb/Ta | 4.69 | 1.59 | 2.5 | 0.20 | 1.92 | 0.55 | 0.92 | 0.22 | 0.92 | 0.30 |

Table 1.- Summarized data for major and trace elements contents and geochemical coefficients for the Tres Arroyos facies. ASI calculated as mol Al₂O₃/Σmol (CaO+Li₂O+Na₂O+K₂O+Rb₂O) as suggested by London (1992) for Li-rich granites. (): number of analyses; AVG: average; SD: Standard deviation.

Tabla 1.- Resumen de los contenidos en elementos mayores, trazas y coeficientes geoquímicos de las facies de Tres Arroyos. ISA calculado como mol Al₂O₃/Σmol (CaO+Li₂O+Na₂O+K₂O+Rb₂O) como ha sido sugerido por London (1992) para granitos ricos en Li. (): número de análisis; AVG: media; SD: Desviación estándar.

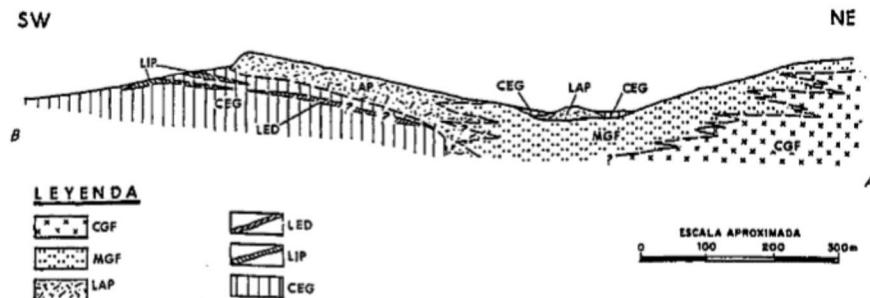


Fig. 2.— Idealized geological cross-section (A-B) of the Tres Arroyos area. Facies labels correspond to those described in text. CEG: Schist-Greywacke Complex.

Fig. 2.— Sección geológica idealizada (A-B) del sector de Tres Arroyos. Las abreviaturas corresponden a las descritas en el texto. CEG: Complejo Esquisto-Grauváquico.

pegmatic levels, usually parallel to the strike and dip of the sheet. While aplites are mineralogically similar to MGF (with abundant topaz), the pegmatic levels are made up of K-feldspar-quartz-albite-muscovite and tourmaline, forming occasionally miarolitic cavities.

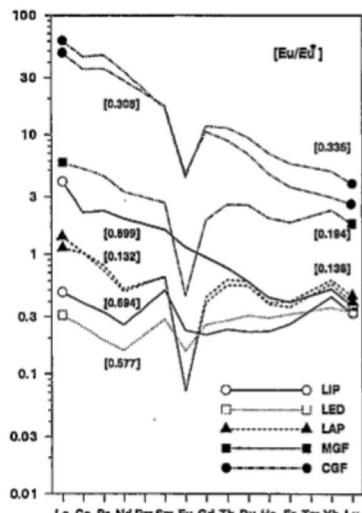
4. The Leucocratic Dyke (LED), which is observed in the northern part of the area. This is a N148°E/38°SW trending dyke composed by K-feldspar and albite phenocrysts in a aplitic groundmass of plagioclase-quartz-muscovite-topaz-amblygonite.

5. The Lithium Pegmatites (LIP) are subhorizontal zoned dykes, in which several mineral assemblages can be distinguished:

Fig. 3.— Chondrite-normalized REE values of Tres Arroyos Facies.

Fig. 3.— Valores de Tierras Raras normalizados respecto a la condrita de las facies de Tres Arroyos.

REE/CHON.



—Cleavelandite-quartz-topaz unit, up to 10 cm thick, discontinuous and observed in the upper contact of the dykes.

—Quartz-K feldspar-Plagioclase unit, variable in grain size and usually being the contacts with the host-rocks.

—Albite - lepidolite - quartz layered unit, characterized by a banded texture of alternating aplitic and pegmatic bands of the same composition in the inner parts of the dykes. Topaz and amblygonite are abundant.

—Quartz unit, in contact with the quartz-K feldspar-plagioclase unit or filling late fractures.

Geochemistry

In order to characterize the geochemical features and evolutionary trends of the different facies, major and trace elements and REE's were analyzed in all the rock groups. Data are summarized in Table 1.

All the facies show high Al₂O₃ contents, moderate to high contents of Na₂O+K₂O, SiO₂, P₂O₅ and F, and low Fe₂O₃, CaO and MgO values, forming a calc-alkaline association plotting in the I and II fields of the AB diagram (Debon & Le Fort, 1983). They are also markedly peraluminic, as shown by values of ASI and A/CNK > 1.

An evolutionary trend is observed from CGF to LIP consisting in an increase of Al₂O₃, ASI and A/CNK values. SiO₂ values show a slight increase in MGF, followed by an steady decrease from the layered sequence to the Li-pegmatites. Moreover, the rocks become progressively more sodic, as shown by the increasing values of Mol Na/K, which is consistent with the

presence of albite as predominant feldspar in the outer facies. Finally, trends for P₂O₅ and F are irregular, increasing from CGF to LAP and LED respectively, and decreasing in the Li-pegmatites. However, considerable scattering of data occur in the pegmatites for these elements as a result of their internal compositional heterogeneity: samples including the layered albite-lepidolite-quartz-(topaz-amblygonite) unit show high concentrations of P₂O₅ and F.

Regarding the trace elements, the facies generally show high concentrations of Li, Rb, Cs, Ga, Nb, Ta and Sn, and low for Ba and Zr. From CGF to LIP, an increase in the concentration of incompatible elements (Li, Rb, Ga, Nb, Ta, Sn) is observed. For the compatible elements Ba, Zr and Sr, an initial decreasing trend is followed by an increase in their concentration in the extragranitic dykes.

REE's contents are highly variable, with a significant decrease of Σ REE in the outermost facies. From the central granite CGF to the leucocratic dyke LED, there is a continuous decrease in Σ REE and (Ce/Yb)n values (Fig. 3). The Eu/Eu* ratio shows a similar evolution, with a slight increase in LED. However, this trend is reversed in the Li-pegmatites that present higher REE's contents and (Ce/Yb)n values, together with a clear reduction of the Eu anomaly.

Discussion

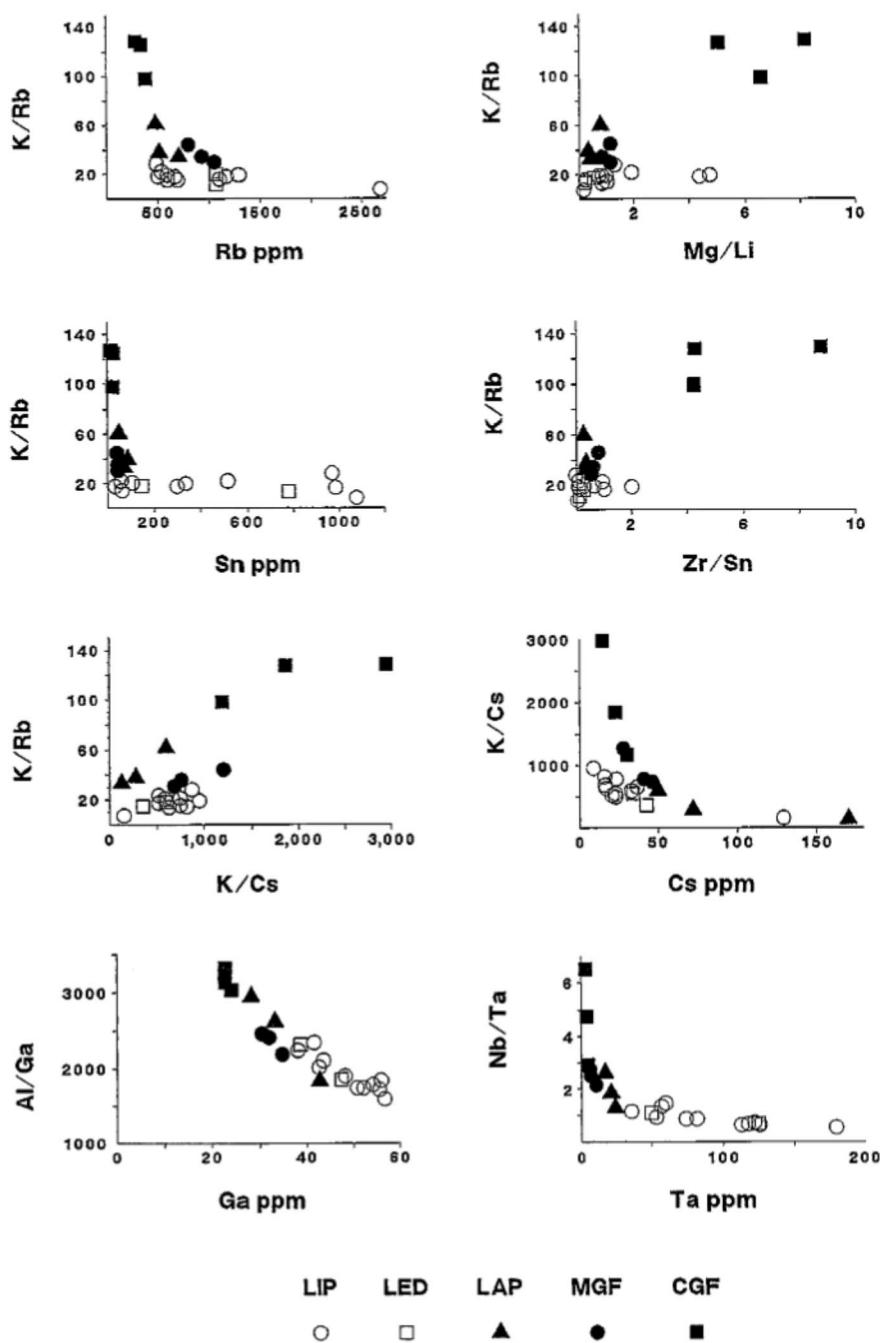
The facies observed at Tres Arroyos show a gradual transition from the centre (CGF) to the margin (LIP) of the Alburquerque batholith. This is characterized by a) a change in the type of mica phase in the sense biotite (CGF) - muscovite (MGF, LAP, LED) - lepidolite (LIP); b) progressive substitution of K-feldspar by albite as the dominant feldspar phase; c) a change in the type of accessory peraluminous minerals (from andalusite-cordierite in CGF to topaz-amblygonite in LED and LIP); d) the existence of rare-elements phases together with a progressive development of pegmatic fabrics in the external facies (LAP, LED and LIP). Both the nature and sequence of facies are similar with those described as typical of fertile granites (Cerny & Meintzer, 1988).

The geochemical data for major and trace elements also support the idea of considering the facies of Tres Arroyos as typical of a fertile granite (*sensu* Cerny & Meintzer, op. cit.). The transition from CGF to LIP shows an increase of the peraluminous and sodic character of the magma (ASI and mol Na/K ratios), together with a decrease of the SiO₂ contents. Trace elements

data show an increase in the concentrations of incompatible elements in the magma (particularly the rare-elements). Finally, the comparison between major and trace elements behaviour shows an extreme geochemical fractionation from CGF to LIP (Fig. 4), characterized by decreasing K/Rb, Al/Ga and Mg/Li ratios, among others.

Fig. 4.— Variation diagrams K/Rb vs. Rb, Mg/Li, Sn, Zr/Sn; K/Cs vs. Cs; Al/Ga vs. Ga and Nb/Ta vs. Ta, indicating geochemical fractionation from CGF to LIP.

Fig. 4.— Diagramas de variación K/Rb frente a Rb, Mg/Li, Sn, Zr/Sn; K/Cs frente a Cs; Al/Ga frente a Ga y Nb/Ta, indicando un fraccionamiento geoquímico de CGF a LIP.



Both the petrological and the geochemical evolution from the central facies to the Li-pegmatites are considered to be the result of differentiation of a fertile magma through a fractional crystallization process (Gallego, 1992). The changes observed in the magmatic evolution probably stem from the changes in the magma properties (composition of eutectic minimum, solidus and liquidus temperatures and viscosity, among others) derived from its high F-and particularly P-contents. Regarding the latter, the study of phosphorous content of magma through P concentration in alkali feldspars (London, 1992), shows that the different magma batches at Tres Arroyos were phosphorous-rich (Gallego, op. cit.). The consequences of such concentrations can explain the changes observed in ASI and mol Na/K values and the rare-elements concentration from CGF to LIP (D. London and M. Gallego, in preparation).

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