P-T Conditions of Subsolidus Modifications on Rare Metal Enriched Pegmatites. An Example from Central Portugal

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Abstract. In order to contribute to study the role of hydrothermal fluids on granite pegmatites enriched in rare metals, petrographic and fluid inclusion studies were carried in beryl, quartz, and lithiophilite from the pegmatitic structures from Companheiro (C) and Mesquitela (M), Central Portugal. The fluid evolution follow a trend from higher to lower pressure and temperature conditions, with the formation of the beryl corresponding to a pneumatolytic pegmatitic stage and quartz and lithiophilite corresponding to a hydrothermal stage, where the aqueous fluids formed subsequently to the CH_4 and N_2 fluids.

Keywords. Fluid inclusions, quartz, beryl, lithiophilite

1 Introduction

A central question about the meaning of evolved pegmatite systems is whether their distinctive chemical signature is magmatic or due to a subsolidus modification through addition from a superimposed or derivative fluid phase or a mixture of both.

The study on evolved Li rich pegmatites from the Variscan belt of Portugal indicate that some pegmatites reached their specialized status at the magmatic stage but in others mineralization is of secondary, metasomatic origin (Charoy and Noronha 1999).

In order to contribute to the study of granitic pegmatites from Central Portugal and in particular the role of hydrothermal fluids on its genesis, petrographic and fluid inclusion studies were carried in beryl, hyaline quartz, and lithiophilite from pegmatitic structures of Central Portugal.

2 Geology

Geologically, the studied pegmatites, which present great typological diversity belong to the important " Iberian Massif Pegmatite Field " (IMPF), located in a segment of the European Variscan chain, the Central Iberian Zone (CIZ) (Fig. 1).

The CIZ, that corresponds to an autochthonous terrane, is marked by the existence of an important granite batholith (Beiras Batholith) consisting of different sinorogenic granite massifs that are grouped into different main series intrusive in metasedimentary formations of a pre-ordovician sequence mainly composed of metapelites and metagreywakes the "Complex Schist greywacke" (CXG) (Azevedo and Aguado 2013).

The IMPF from central Portugal arises in an area of over 100 km^2, and results of spatial overlap of several vein structures, preferably hosted by granitic rocks of various types and only rarely installed in the metasedimentary formations (Farinha-Ramos 2010).
The IMPF is mainly composed of granitic pegmatites, deserving particular attention to the LCT type with lithiniferous minerals such as lepidolite, amblygonite/montebrasite and lithiophilite.

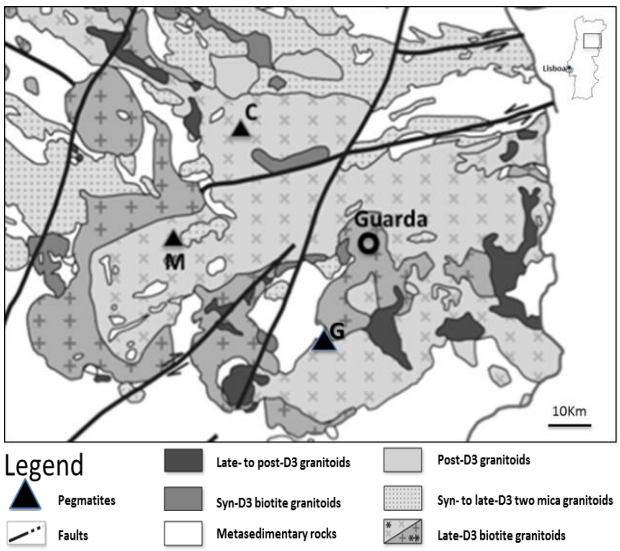

Figure 1. Location of the pegmatites, adapted from "Mapa Geológico de Portugal 1: 500 000, Serviços Geológicos de Portugal, 1992". C: Companheiro; M: Mesquitela; G: Gonçalo.

The studied pegmatites, Mesquitela and Companheiro, are located in the Central of Portugal in the West part of the IMPF. They are primarily composed by quartz and potassium feldspar and subordinated albite and muscovite. Beryl and lithiophilite are the main accessory minerals. Petrographic study reveals a succession of different overprinting stages: the earlier, corresponding to the pegmatitic texture, is essentially characterized by quartz, muscovite, albite, and K-feldspar. The later, characterized by presence of beryl, albite, quartz and Li-Mn phosphates. Cassiterite, as well as scarce sulphides (arsenopyrite, pyrite, chalcopyrite, sphalerite and molybdenite), can be present.

In quartz richer areas, the Companheiro pegmatite exhibits alternations of milky and clear quartz parallel to a latter N30ºE fracturing system.

Considering the mineralogy and the relationship with orogenic granites, the studied pegmatites belong to the group of orogenic pegmatites, so formed in a collision scenario, and LCT type once they have lithium (Cerny 1991). According to the classification of Cérny and Ercit (2005) they can be classified as REL class; REL-Li subclass, beryl type; subtype - beryl- phosphate with geochemical signature - Be, P (Li, F, ± Sn, B) and

therefore presenting as typical minerals beryl and lithiophilite**.**

3 Methodology

Petrographic and mineralogical studies using XRD, SEM, MEB, XRF analysis were performed in order to characterize potassium feldspar and the main phosphate phase.

Fluid inclusion studies were performed using a Chaixmeca and a Linkam stages and a Horiba Jobin-Yvon LabRaman spectrometer interfaced to Olympus microscopes. Raman spectra were obtained using the 632.8 nm emission line of HeNe laser (20mW).

4 Results

K feldspar, the most important mineral, occurs, usually, as white feldspar (WF); however reddish feldspar (RF) is also present. The microscopic study of both, revealed the presence of a perthitic orthoclase exhibiting a late albitization. However, RF presents a troubled aspect not affecting the late albite plates. The chemical analysis showed that RF has higher values of total Fe and LOI (0.26 and 1.01 %, respectively) than WF (0.04 and 0.5 %). For K_2O and Na_2O there are smaller differences (11.43 % and 3.06% for WF as 12.38% and 2.42% for RF). RF and WF show 1230 and 2320 ppm of Rb. RF and WF have also anomalous contents in U (24 and 34 ppm), Sn (17 and 24 ppm) and W (12 ppm in RF).

Petrography on transmitted light of the studied phosphate showed a colourless to pale yellow mineral very rich on fluid inclusions and with birefringence on grey colour. This phase is crossed by a brown mineral with higher birefringence (Fig. 2). SEM-EDS analyses revealed a different composition compatible with a late phosphate phase, having more complex composition than the primary one (Fe, Mn, Mg, Ca, K, Cl).

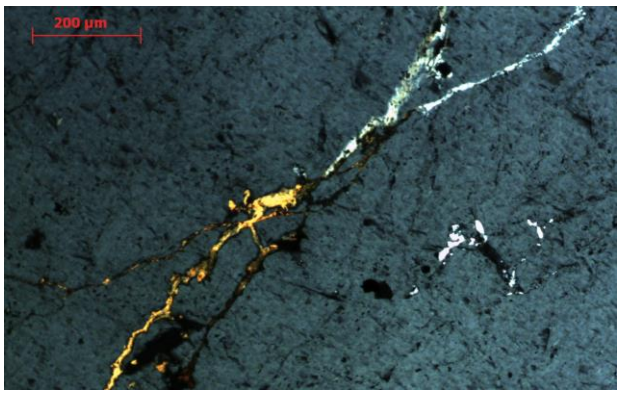

Figure 2. Lithiophilite cutted by a latter phosphate (X nicols).

XRD analysis of primary phosphate showed a spectrum with peaks of lithiophilite and triphylite. XRF analysis revealed scarcity of Rb (<3 ppm), Pb (8 ppm); Sr (20 ppm) and Ba (30 ppm) and a higher content on Zn (1311 ppm).

The results confirm precedent studies that consider the colour of RF related with Fe content and the most important phosphate corresponding to a member of the triphylite-lithiophilite series (Jesus 1934, Bertelli et al. 1982).

Microthermometric and Raman microspectrometric studies performed in the studied minerals reveal the existence of primary, pseudosecondary and secondary fluid inclusions.

The beryl shows primary and pseudosecundary two-phase fluid inclusions containing low salinity H_2O-NaCl aqueous fluids (<5 wt% eq. NaCl) revealing trapping conditions of 350ºC and 300-500 MPa.

The quartz studies revealed the existence of three-phase primary fluid inclusions and two-phase pseudo-secondary fluid inclusions. The primary fluid inclusions contain aqueous carbonic H_2O-CO_2-(CH_4-N_2-NaCl) fluids and were trapped during quartz crystallization at minimum temperatures and pressures of 330ºC and 190-240 MPa.

The lithiophilite reveal the presence of aqueous fluids with CH_4 and N_2 in primary two-phase fluid inclusions and were trapped at temperature conditions between 330 and 500 ºC and pressures between 150 and 300 MPa; similar to the P-T conditions of the aqueous-carbonic fluids studied in hyaline quartz. Finally, the secondary fluid inclusions present in lithiophilite contain aqueous fluids trapped at temperature between 250 and 400 ºC and pressures between 100 and 250 MPa.

4 Discussion

The origin of pegmatites continues to be debated and there is little doubt that hydrothermal metasomatism occurs namely in rare element pegmatites (Linnnen et al. 2012).

Disequilibrium is dominant all along the late stages of pegmatite crystallization and will be highly enhanced during subsolidus reworking (Charoy and Noronha 1989) and the pegmatites usually display aspects of both igneous and hydrothermal systems (London and Kontak 2012).

Previous petrographic and fluid inclusion studies of lepidolite bearing granitic pegmatites of Gonçalo on East side of IMPF (Fig. 1) already demonstrate the importance of homogeneous aqueous fluids with temperatures lower than 300°C for the expression of the main Li mineralizing episode expressed by lepidolite (Ramos and Noronha 1995).

5 Conclusions

The contents on Fe, U, Sn and W revealed by the K feldspars, namely the RF, suggest a latter enrichment in those elements which can be attributed to metasomatic alteration.

Fluid inclusion studies in beryl, revealed the importance of low-salinity aqueous fluids on mineral deposition at trapping conditions of 350ºC and 300-500 MPa. The aqueous fluids with CH_4 and N_2, contained in the lithiophilite were trapped at temperature conditions between 330 and 500ºC and pressures between 150 and 300 MPa; similar to the P-T conditions of the aqueous-carbonic fluids studied in hyaline quartz from Companheiro pegmatite. Finally, the later aqueous fluids present in lithiophilite were trapped at temperature between 250 and 400ºC and pressures between 100 and 250 MPa.

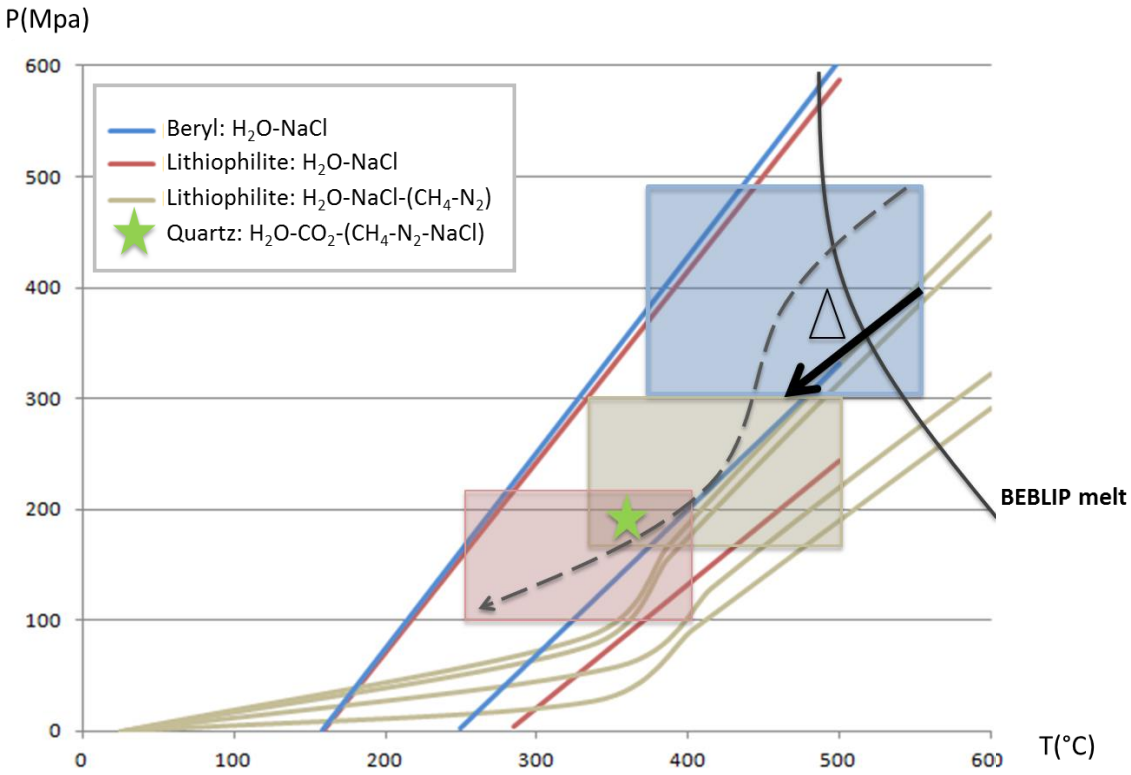

Figure 3. P-T-X evolution of the fluids presented in the studied pegmatites. (Δ) – Triple point And-Sil-Ky.

The PT evolution of the fluids contained within the studied minerals seems to follow a trend from higher to lower pressure and temperature conditions, with the formation of the beryl and the conditions defined for the deposition of lithiophilite, corresponding to a hydrothermal stage, where the aqueous fluids formed subsequently to the CH_4 and N_2 fluids.

The fluids present in these pegmatitic structures together with the trapping conditions found are similar to those described for late orogenic Variscan hydrothermal systems in Central Iberian Zone (Noronha et al. 2012) and confirm the important role of hydrothermal fluids also in the pegmatites history, especially in those specialised in lithium.

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