EXTREME FRACTIONATION IN A GRANITE-PEGMATITE SYSTEM
DOCUMENTED BY QUARTZ CHEMISTRY: THE CASE STUDY OF
TRES ARROYOS (CENTRAL IBERIAN ZONE, SPAIN)

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ABSTRACT

The Tres Arroyos granite-pegmatite system is located in the SW margin of the Nisa-Alburquerque Variscan batholith. Two granitic facies (monzogranite and marginal leucogranite), and three types of aplite-pegmatite dykes (barren, intermediate and highly evolved Li-rich), have been distinguished in the area, with a zoned distribution from the granite southwards. Trace elements in quartz from the five facies have been analyzed by LA-ICP-MS in order to obtain information about the petrogenetic links among the different lithologies of this system, as well as to better understand the regional and individual fractionation processes that led to the distinct rocks. Aluminium, Ti, Li and Ge show continuous trends from the monzogranite, through the marginal granitic facies, the barren and intermediate aplite-pegmatites, up to the most evolved Li-rich dykes.
Titanium and Ge contents, respectively, decrease and increase gradually with fractionation. In contrast, Al and Li show a more complex trend, with an initial descending trend to the marginal granitic facies, and then showing the highest Al and Li contents in the quartz from the most fractionated Li-rich aplite-pegmatites. This suggests the influence of different competing factors controlling the incorporation of these trace elements in quartz, such as the chemical composition of the melt, the P and T conditions and the rate of crystallization. Based on the good correlation between Al and Li, the substitution $\text{Si}^{4+} \leftrightarrow \text{Al}^{3+} + \text{Li}^+$ seems to be the dominant mechanism of Li incorporation into quartz. The negligible amount of other trace elements suggests that the remaining Al was mainly compensated with $\text{H}^+$ ions, via the $\text{Si}^{4+} \leftrightarrow \text{Al}^{3+} + \text{H}^+$ substitution.

A continuous fractionation trend from the monzogranite up to the most fractionated aplite-pegmatites is inferred from geochemical modelling by applying the Rayleigh equation for fractional crystallization. Fractionation rates over 50% are needed to obtain the marginal granite and the barren aplite-pegmatites compositions, and over 99% for the most evolved dykes. No pattern in the chemical variation of the trace elements in quartz from different layers in the layered aplite-pegmatites has been found, suggesting the lack of internal fractionation processes, most probably due to the rapid crystallization of the pegmatitic melt, intruded into a colder country rock.

**Keywords:** quartz, trace elements, LA-ICP-MS, aplite-pegmatites, granites, Tres Arroyos, Central Iberian Zone

1. Introduction
Quartz is a rock-forming mineral in silica-saturated igneous rocks including granitic pegmatites. Because of its abundance and the technical development of micro-analytical methods, the trace element content of quartz has been utilized in the last two decades for gaining information about the parental signature and the fractionation degree of the melt from which the quartz crystallized. However, trace element studies of igneous quartz are not very abundant (Schrön et al., 1988; Larsen et al., 2004; Müller et al., 2008, 2015; Jacamon and Larsen, 2009; Breiter and Müller, 2009; Beurlen et al., 2011; Breiter et al., 2013; Drivenes et al., 2016) in comparison to other minerals such as feldspar, micas or tourmaline (Černý and Burt 1984; Foord et al., 1995; Larsen, 2002; Roda et al., 2007; Vieira et al. 2011, Marchal et al., 2014), due to the very low concentrations of trace elements in quartz and the related analytical challenges.

Quartz has a strong atomic bond between Si-O allowing only some elements to enter the lattice in small concentrations (Rusk, 2012). Lithium, H, Be, B, Mn, Ge, Rb, Sr, Na, Al, P, K, Ca, Ti, and Fe are the most common trace elements in natural quartz (e.g., Larsen et al., 2004; Götze et al., 2004; Rusk et al., 2008; Müller and Koch-Müller, 2009; Müller et al., 2010; Rusk, 2012). Each element either enter crystal lattice, or is in the interstices. Common substitutional impurities are, Al³⁺, Ti⁴⁺ or Ge⁴⁺, and interstitial impurities are K⁺, Na⁺ or Li⁺ (Rusk, 2012). ICP-MS analyses of dissolute quartz were already done on quartz since the late 1980’s, early 1990’s (Schrön et al., 1988). However, techniques to analyse very low concentrations of trace elements in quartz in situ (within individual crystals) were not available until the beginning of the 21st century. The last two decades laser ablation combined with inductively coupled plasma mass spectrometry (LA-ICP-MS) is applied for performing analysis of quartz µgg⁻¹ to ngg⁻¹ range.
In this study quartz from the late-Variscan granite-pegmatite system from the Tres Arroyos area (Alburquerque, Badajoz), in SW Spain, is investigated. There, besides different granitic facies belonging to the Alburquerque batholith, a number of aplite-pegmatite bodies occur, with different degrees of evolution, some of them enriched in Li-F. Quartz from granites and aplite-pegmatites has been analysed by LA-ICP-MS, combined with the scanning electron microscope cathodoluminescence (SEM-CL), in order to establish the petrogenetic links among the different lithologies constituting the Tres Arroyos granite-pegmatite system. Geochemical modelling applying Rayleigh equations for fractional crystallization has been used for interpretation of the results obtained by LA-ICP-MS of quartz. In addition, the results of the trace element study were applied to reconstruct the internal chemical evolution of some pegmatite bodies. There are previous studies on the variations in the trace elements contents in igneous quartz from granitic rocks with different fractionation degrees (e.g., Breiter and Müller, 2009; Jacamon an Larsen, 2009; Breiter et al., 2012; 2013; Müller et al., 2003; 2005; Drivenes et al., 2016); and also on the trace elements in quartz from pegmatitic rocks of different types (e.g., Larsen et al., 2004; Müller et al., 2008; Beurlen et al., 2011; Müller et al, 2015). Despite Jacamon and Larsen (2009) already described the gradual change of chemistry in a layered granitic pluton that fractionated from ortopyroxene and clinopyroxene-bearing granite, over hornblende and biotite-granite, to aplogranitic layers, pegmatites, aplites, and finally hydrothermal veins, this is the first time where a study of the chemical quartz variations for a complete fractionation trend from granitic to highly evolved Li-rich pegmatitic facies is presented.

2. Geological setting and rock description
The Late-Variscan Tres Arroyos granite-pegmatite system is located to the south of the Central-Iberian-Zone of the Variscan Massif, near to the limit with the Ossa Morena Zone. The Tres Arroyos area occurs to the SW of the easternmost part of the Nisa-Alburquerque (NA) batholith (Fig. 1). This batholith intruded into a Precambrian low-grade metasedimentary sequence, including phyllites, slates, schists, quartzites and metagreywackes belonging to the metamorphic Schist-Greywacke Complex (SGC). Cordierite is the only contact metamorphic mineral developed together with a high temperature biotite as a result of the granite thermal input (González-Menéndez et al., 2010). The main facies of the NA batholith corresponds to a peraluminous monzogranite, with minor two-mica leucogranitic facies (González-Menéndez, 1998). Quartz, K-feldspar, plagioclase, biotite and muscovite are the main minerals, with andalusite and cordierite, apatite and tourmaline as minor phases (Table 1). The monzogranite shows a porphyritic texture, although locally it may be equigranular. In the Tres Arroyos area the batholith exhibits a marginal facies (Gallego-Garrido, 1992) characterized by a finer grain size, a higher abundance of tourmaline and certain enrichment in F, Li and Fe in the muscovite. The emplacement conditions for the monzogranite was ≤ 2.5 kbars (González-Menéndez et al., 2010) and the emplacement age of 307-309 Ma (U-Pb, Solá et al., 2009). Regarding the Variscan deformation, this granite is considered to be late- to post-tectonic.

Besides these granitic rocks, in the Tres Arroyos area three different kinds of aplite-pegmatite bodies are observed, all of them intruded into metasediments of the SGC: barren, intermediate, and evolved aplite-pegmatites (Table 1, Fig. 1). The barren bodies are layered aplite-pegmatites that outcrop near the NA batholith (Fig. 1), which show a N135E direction, dipping towards NE (Gallego-Garrido, 1992). Locally it is not easy to distinguish in the field the marginal granitic facies from these barren aplite-pegmatites.
due to the bad quality of the outcrops and to the similarities in hand-sample, but 15 bodies belonging to this type may be recognized in the field. The main mineralogical differences between the two lithologies are the lack of biotite and the occurrence of Fe-Mn phosphates in the aplite-pegmatites. Moreover, the meteoric alteration of the phosphates gives frequently a characteristic greenish color to some of these dykes. Micas from barren aplite-pegmatites are usually richer in F, Li and Fe than the muscovite from the marginal granitic facies, belonging to the muscovite- zinnwaldite series. The grain size changes from 0.1 to 3 cm. Some of the dykes show just aplitic facies, whereas in other cases aplitic and pegmatitic layers are present.

The intermediate bodies correspond to sub-horizontal, discordant, leucocratic aplite-pegmatite dykes, with up to 8 meters of thickness. In the field 7 intermediate dykes have been localized. These bodies are mainly composed of albite and quartz, with K-feldspar and micas as minor minerals, and topaz, Li-Al-phosphates and Nb-Ta-Sn-oxides as accessory phases. Some of these bodies display a rhythmical layering, where albite-rich layers alternate with quartz-rich ones (Fig. 2a).

Evolved lithium-rich aplite-pegmatites constitute the third category. According to previous studies and the present work, there are around a dozen of Li-F-rich aplite-pegmatite bodies in the studied area. They show an important enrichment in Li and F, reflected in their mineral association that includes Li-rich micas, topaz and montebrasite. As the other aplite-pegmatite types, some of these Li-rich dykes show different layering patterns, with layers rich in Li-micas alternating with quartz + albite rich ones (Fig. 2b).

3. Sampling and analytical methods
Thirteen representative samples of quartz were selected for textural and geochemical characterization, from the five different facies distinguished in the Tres Arroyos area. The quartz samples were prepared as surface-polished, 300-μm thick sections mounted on standard glass slides.

Scanning electron microscope cathodoluminescence (SEM-CL) images of quartz were obtained from the thick sections coated with carbon using the LEO 1450VP analytical SEM with an attached CENTAURUS BS BIALKALI type cathodoluminescence (CL) detector. The applied acceleration voltage and current at the sample surface were 20 kV and ~3 nA, respectively. The BIALKALI tube has a CL response range from 300 (violet) to 650 nm (red). It peaks in the violet spectrum range around 400 nm. The CL images were collected from one scan of 43s photo speed and a processing resolution of 1024 × 768 pixels and 256 grey levels. SEM-CL was applied to quartz in order to reveal intra-crystal, micro-scale (<1 mm) growth zonation and alteration structures and different quartz generations. Grey-scale contrasts visualized by SEM-CL are caused by the heterogeneous distribution of lattice defects (e.g., oxygen and silicon vacancies, broken bonds) and trace elements in the quartz lattice (e.g., Sprunt, 1981; Ramseyer et al., 1988; Perny et al., 1992; Stevens Kalceff et al., 2000; Götze et al., 2001; 2004; 2005). Although the physical background of the quartz CL is not fully understood, the structures revealed by CL give information about crystallization, deformation and fluid-driven overprint.

Concentrations of Li, Be, B, Mn, Ge, Rb, Sr, Na, Al, P, K, Ca, Ti, and Fe in quartz were determined with the laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) technique. One of the advantages of this method is that the quartz crystals are analyzed in situ, meaning distinct parts of a crystal can be chosen for analyses. Nevertheless, micro fluid and mineral inclusions have to be avoided to make
sure that the obtained trace element concentrations represent lattice-bound and interstitial elements. 58 quartz analyses were undertaken on a double-focusing sector field inductively coupled plasma mass spectrometer, HR-SF-ICP-MS, model ELEMENT XR from Thermo Scientific, which is linked to an excimer laser probe New Wave UP193FX ESI. The 193-nm laser had a repetition rate of 20 Hz, a spot size of 50 μm, and energy fluence about 5 to 6 J·cm⁻² on the sample surface. A continuous raster ablation on an area of approximately 150 × 400 μm was applied.

The approximate depth of ablation was between 10 and 50 μm. An Hitachi CCD video camera, type KP-D20BU, attached to the laser system, was used to observe the laser ablation process and to avoid the analyses of micro mineral and fluid inclusions. Occasionally, however, individual fluid inclusions were hit, where it was not possible to find crystal domains entirely free of fluid inclusions. These analyses are recognizable from concentration spikes for Na, K, and/or Ca.

The carrier gas for transport of the ablated material to the ICP-MS was He mixed with Ar. The isotope ²⁹Si was used as the internal standard applying the stoichiometric concentration of Si in SiO₂. External multistandard calibration was performed using NIST SRM 610, 612, and 614 and NIST SRM 1830 soda-lime float glass (0.1% m/m Al₂O₃), the certified reference material BAM No. 1 amorphous SiO₂ glass from the Federal Institute for Material Research and Testing in Germany, and the Qz-Tu synthetic pure quartz monocrystal provided by Andreas Kronz from the Geowissenschaftliches Zentrum Göttingen (GZG), Germany. Certified, recommended, and proposed values for these reference materials were taken from Jochum et al. (2011) and from the certificates of analysis where available. For the calculation of P concentrations, the procedure of Müller et al. (2008) was applied.
Each measurement comprised 15 scans of each isotope, with the measurement time varying from 0.15 s/scan for K in medium mass resolution mode to 0.024 s/scan of, Li in low mass resolution mode. An Ar blank was run before each reference material and sample measurement to determine the background signal. The background was subtracted from the instrumental response of the reference material/sample before normalization against the internal standard in order to avoid effects of instrumental drift. This was carried out to avoid memory effects between samples. A weighted least squares regression model, including several measurements of the six reference materials, was used to define the calibration curve for each element. Ten sequential measurements on the BAM No.1 SiO₂ quartz glass were used to estimate the limits of detection (LOD) which were based on 3 × standard deviation (3σ) of the 10 measurements. LODs are listed in Table 2.

14 representative bulk samples of aplite-pegmatites were analyzed for trace elements, including Ba as compatible and Li, Rb and Cs as incompatible elements. These data were obtained by X-ray fluorescence (XRF) and ICP-MS at the Activation Laboratories Ltd. (Actlabs, Canada).

4. Results

4.1. Micro-textures in cathodoluminescence images of quartz

Quartz occurs in plutonic rocks as fine-grained crystals, homogeneously distributed. Under the microscope it appears as anhedral, granular grains, most commonly exhibiting undulose extinction. In the aplite-pegmatite dykes, quartz occurs also as anhedral crystals with a much more variable grain size, from medium-sized grains (up
to 3 cm) in the pegmatitic layers to finer grains (200-1000 µm) in the aplitic ones. Quartz is the only phase in some layers, whereas in others it coexists with feldspars, micas and, less commonly, phosphates. Quartz also appears as small inclusions (<2 mm) in schorl.

In general, quartz crystals from the Tres Arroyos area appear very homogeneous in SEM-CL images (Fig. 3a). Only one sample from a simply layered unit of an intermediate pegmatite shows a weakly-contrasted growth zoning (Fig. 3b). The general lack of primary growth zoning and the very low CL contrasts may indicate that trace elements are homogeneously distributed within the quartz crystals. Also the abundance of secondary microstructures is relatively low in the Tres Arroyos quartz, comparing with quartz associated with pegmatites from other localities (e.g., Larsen et al., 2004; Müller et al., 2008; Drivenes et al., 2016). Only a few thin (<5 µm), intra and transgranular healed cracks, connecting non-luminescent domains, were observed in some quartz crystals from layered intermediate (Fig. 3c) and Li-rich (Fig. 3d) dykes.

4.2. Trace elements in quartz from aplitic-pegmatites and granites

For LA-ICP-Ms analyses, relative coarse, clear crystals (>1 mm) were chosen due to the applied laser raster technique (150 × 400 µm). In the layered pegmatites the choice of quartz crystals was more difficult, in particular in the aplitic layers, due to the small grain size. There sometimes it was not always possible to avoid the contamination of the analyses by fluid inclusions. In those cases the Na, K, Ca, P and Fe values may be anomalously high and, thus, the determined concentrations may not correspond to the concentration of lattice-bound trace elements. For example, the presence of NaCl-bearing fluid inclusions in quartz is indicated by concentration pikes of Na (up to 240
μgg⁻¹) compared to the average lattice-bound content of 1-5 μgg⁻¹. In order to exclude all the point analyses that could be contaminated by fluid inclusions, only Na values <10 μgg⁻¹ have been taken into account. On the other hand, micro apatite inclusions may be also identified in some analyses from intermediate aplite-pegmatites and lithium rich dykes owing to P high values (up to 30 μgg⁻¹). The rest of analyses commonly show P contents under 10 μgg⁻¹.

Data obtained by LA-ICP-MS are given in Table 3. In Fig. 4 representative trace element binary plots are provided, illustrating variations in the trace element contents of quartz from different granites and pegmatites. Besides Al and Ti, which are generally the most common trace elements in igneous quartz, Li contents are relatively high in most of the analyzed quartz crystals from Tres Arroyos.

Concentrations of Al are in the range 132-854 μgg⁻¹ (Fig. 4a, b), with a continuous but not rectilinear variation from the less to the most fractionated lithologies (Table 3, Fig. 4a and b). The monzogranite shows intermediate values (258-540 μgg⁻¹), whereas the marginal granitic facies and the barren aplite-pegmatites show lower Al contents (165-263 μgg⁻¹ and 160-297 μgg⁻¹, respectively). There is an increase in the intermediate bodies (132-653 μgg⁻¹); and finally, the highest values are found in the quartz from the Li-rich aplite-pegmatites (324-854 μgg⁻¹) (Table 3, Fig. 4a, b). In contrast, there is a continuous decrease in the Ti contents from the monzogranite to the Li-bearing dykes; through the intermediate lithologies, with values in the ranges 50-134 μgg⁻¹ for the monzogranitic facies, 5-30 μgg⁻¹ for the marginal granite, 5-15 μgg⁻¹ for the barren aplite-pegmatites, 1-5 μgg⁻¹ for the intermediate aplite-pegmatites, and <2 μgg⁻¹ for the Li-rich dykes (Fig. 4a, c). The contents of Li in the quartz from the five different facies vary between 14-134 μgg⁻¹ (Fig. 4b). As expected, the highest values are found in the Li-rich dykes (45-134 μgg⁻¹). Nevertheless, the other values are also
quite high, in the range 35-71 μgg⁻¹ for the monzogranite, 36-43 μgg⁻¹ for the marginal granite, 31-47 μgg⁻¹ for the barren dykes, and 14-80 μgg⁻¹ for the intermediate aplite-pegmatites. Aluminium and Li show a significant positive correlation (Fig. 4b), which is due to the incorporation of both elements via the substitution Si⁴⁺ ⇔ Al³⁺ + Li⁺, where Al replaces Si in the tetrahedral site, whereas the small Li ions occur in interstitial lattice position (Dennen, 1966). Germanium values are in the range of 0.99-6.35 μgg⁻¹. The lowest values are related to the monzogranite facies, not exceeding 2 μgg⁻¹. Taking into account the average values, there is a Ge enrichment from the monzogranite, through the marginal granite, barren and intermediate dykes, up to the lithium aplite-pegmatites, with values >1.5 μgg⁻¹ for the marginal granite and the three types of aplite-pegmatites, which are values typical of pegmatite quartz (Götze et al., 2004) (Table 3, Fig. 4c). Boron values vary over a wide range in each type of bodies, with the lowest values associated with the monzogranite (1-2 μgg⁻¹), and the highest with the Li-rich dykes (2-7 μgg⁻¹) (Table 3, Fig. 4d). The Be contents are generally low (<1 μgg⁻¹), in the range 0.01-0.52 μgg⁻¹, achieving the highest values also in the Li-rich dykes. Iron values for the quartz from the monzogranite change from 5 to 49 μgg⁻¹, which are in the range of the S type granites. These are considerably high when compared to the contents in the I type granites (Breiter et al., 2013). In contrast, the marginal granitic facies and the different aplite-pegmatite dykes exhibit low Fe (<1 μgg⁻¹) (Table 3).

The Al/Ti and Ge/Ti ratios in quartz, good indicators of the degree of fractionation of the parental melt (e.g., Jacamon and Larsen, 2009; Breiter et al., 2012, 2013; Drivenes et al., 2016), show a clear positive correlation, with the lowest values belonging to the monzogranite and the highest to the Li-rich dykes (Fig. 4d).
In order to check if there is a correlation between the trace elements contents in quartz and the bulk composition of its hosting rock, the values of Al, Ti, Li and Ge in quartz (mean values for every sample), versus the contents of those elements in the bulk rock have been plotted (Fig. 5). Titanium is the only element with a clear positive correlation among the quartz and the bulk rock contents. Aluminium and Li show the highest contents in the most fractionated and most peraluminous Li-rich aplite-pegmatites, whereas the lowest values of Ge in both, quartz and whole rock, belong to the monzogranite samples. A correlation between the quartz contents and the bulk rock composition is not evidenced for these elements in the rest of the facies. The Al/Ti vs Ge/Ti values for the whole rock data have been also plotted in order to compare to the trend of these values in quartz, obtaining a similar result, with a relatively good positive correlation between the two sets of data, and a gradual increase from the monzogranite to the Li-rich aplite-pegmatites (Fig. 5e).

Some of the investigated aplite-pegmatite bodies show a layered structure, whereby coarse-grained comb-textured layers alternate with aplitic layers. Quartz from different layers has been analyzed to examine if there are differences in the trace element content of quartz in order to better understand the internal evolution of the dykes. Quartz analyses are summarized in Table 4. The Al and Li contents are in general lower in the aplitic layers than in the pegmatitic ones, whereas the Ti and P concentration in quartz seems to be independent from the facies. Some samples have slightly higher Ge contents in the coarse quartz crystals. During crystallization no variation in the contents of trace elements is noticed from the contacts inward the dykes.

4.3. Bulk rock trace element modelling
Different models have been proposed to explain the origin of highly evolved pegmatitic melts, mainly including fractional crystallization of granitic magmas (e.g., London 2008; Vieira 2010), partial melting of metasediments (e.g., Norton, 1973; Stewart, 1978; Sokolov, 1982; Shmakin, 1983; Simmons et al., 1995; Simmons and Webber, 2008; Novak et al., 2013; Shaw et al., 2016; Simmons et al., in press) and a combination of these two mechanisms (Jolliff et al., 1992; Roda-Robles, 1993).

Fractional crystallization is the most accepted mechanism to understand the “exotic” composition of some pegmatites, starting from a granitic composition.

A geochemical modelling has been made in order to evaluate the petrogenetic relationships between the Nisa-Alburquerque granite and the aplite-pegmatites from Tres Arroyos. This modelling is developed starting from the whole-rock data on Ba, Rb and Li of the Nisa-Alburquerque monzogranitic facies, by applying the Rayleigh equation for fractional crystallization (Neumann, 1954):

\[
\frac{C_1}{C_0} = F^{(D-1)}
\]

where \(C_1\) is the concentration (ppm) of trace elements in the melt at different degrees of fractionation, \(C_0\) is the concentration (ppm) of the elements in the parental melt (the Nisa-Alburquerque granite); F is the fractionation degree and D represents the partition coefficients between the melt and the forming minerals of the granite, taking into account their modal proportions. The distribution of trace elements between solid and melt in high-silica systems is imprecise, and therefore it is not always easy to select the partition coefficients. In addition, there is often an important variation in the results depending on the chosen Kd. For this work, some of the partition coefficients employed in trace element modelling (fractional crystallization) (Table 5) have been used previously by Jolliff et al. (1992) in their study of the petrogenetic relationships between pegmatites and granites in the Black Hills (Dakota, USA); and by Roda-
Robles, 1993 and Vieira, 2010, to determine the relationships between granites and aplite-pegmatites from the Fregeneda-Almendra field, located to the north of the Tres Arroyos area, and also belonging to the Central Iberian Zone. Partition coefficients for biotite have been compiled by Icenhower and London (1995) (Table 5).

The concentrations in Ba, Rb and Li of melts formed by different degrees of fractional crystallization of a parent magma with the composition of the Nisa-Alburquerque granite are plotted in Fig. 6. As Ba behaves as a compatible element in this system, its concentration decreases in the residual melt with fractionation, whereas Rb and Li, incompatible with most of the granite forming minerals, show an important increase in the melts as fractional crystallization proceeds. A plot of the results of the modelling together with the data of bulk-composition for the different lithologies may be seen in Fig 6.

5. Discussion

5.1. Geochemical evolution of quartz from Tres Arroyos

Quartz crystallized during all the stages of magmatic/pegmatitic evolution of the Tres Arroyos area, appearing in all the facies in this system. This makes quartz especially suitable to evaluate the fractionation mechanisms and crystallization processes that led to the different types of aplite-pegmatites occurring there, as it has been done in a considerable number of cases with the chemistry of other rock-forming minerals such as micas and/or K-feldspar (e.g., Roda et al., 1995; Foord et al., 1995; Roda-Robles et al., 2006; Vieira et al., 2011; Martins et al., 2012).
The chemical composition of quartz from primitive granites is usually quite homogeneous, in contrast to the quartz associated with highly fractionated granites and pegmatites that use to contain several populations of quartz with different trace element contents (Larsen et al., 2004; Breiter and Müller, 2009; Müller et al., 2010). However, despite of the highly fractionated nature of some of the magmatic facies occurring in Tres Arroyos, according to the textural study under the microscope and to the SEM-CL images (Fig. 3), all the quartz crystals in each facies crystallized primarily from magmatic or pegmatitic melts, and nearly no subsolidus or hydrothermal overprints affected this mineral.

Overall, quartz associated with the different magmatic facies from the Tres Arroyos granite-pegmatite system is relatively rich in trace elements (mainly those behaving incommensurately in the quartz structure, such as Al, Li, Ge, B and P), as it is the case of other fractionated granites and pegmatites (e.g., Jacamon and Larsen, 2009; Breiter and Müller, 2009; Müller et al., 2010; Beurlen et al., 2011; Drivenes et al., 2016) compared with chemically more primitive granites and pegmatites, which commonly show much lower contents in those elements (e.g., Larsen et al., 2004; Müller et al., 2008). Quartz from the monzogranitic facies contains high Al values, lower values in the barren and intermediate aplite-pegmatites, and the highest values are related to the Li-rich aplite-pegmatites (Fig. 5a, b). Therefore, there is not a continuous increasing trend in the Al content in quartz from the monzogranite, through the intermediate facies, up to the most fractionated Li-rich aplite-pegmatites. When plotted Al versus Ti, which behaves as a compatible element in quartz and, hence, decreases with decreasing temperature (Wark and Watson, 2006), a “C”-shape trend is observed, with a positive Al-Ti correlation for the highest Ti contents and a negative or no correlation for the lowest Ti values (Figs. 4a and 7). A quite similar trend has been already shown by Müller et al. (2002), Breiter
and Müller (2009) and Breiter et al. (2013) for the highly peraluminous P-rich granite suite of Podlesí, in the Saxothuringian Zone of the Bohemian Massif (Fig. 10), which is a Variscan granitic system with many similarities to that of the Tres Arroyos area (Roda-Robles et al., under review). Also in the Variscan Rozvadov S-type pluton from the Bohemian Massif (Breiter et al., 2013) and in the Land’s End granite in the Variscan Cornubian Batholith (Drivenes et al., 2016), positive Ti-Al correlations for the highest Ti contents in quartz are observed. Evidence for a single fractionation path starting from the Nisa-Alburquerque monzogranite is supported by the: (i) field relationships, (ii) results of the geochemical modelling (Fig. 6), (iii) continuous decrease in the Ti contents (Figs. 4a, c; 5d), and (iv) continuous increase of the Ge/Ti and Al/Ti ratios in quartz, the marginal granitic facies, the barren and intermediate aplite-pegmatites, and the Li-rich aplite-pegmatites (Fig. 4d, e). However, the Al content in quartz shows a more complex trend, which could be related to different factors. Some authors have proposed that an increase in the aluminium saturation index of the melt could increase the Al contents in quartz (Jacamon and Larsen, 2009). Nevertheless, the peraluminosity of the monzogranite in Tres Arroyos (and the Al content) is lower than that of the marginal granitic facies and of the barren and intermediate aplite-pegmatites, whereas its Al content in quartz is higher (Fig. 5). Only in the case of the most fractionated aplite-pegmatites (Li-rich dykes), the highest peraluminosity corresponds to the highest Al content in quartz. The depolymerization of alumina-silica complexes caused by high H$_2$O (Mysen 1987; Müller et al., 2000; Larsen et al., 2004; Breiter and Müller, 2009; Drivenes et al., 2016) or F (London, 1992; Breiter et al., 2013) contents in the parental magmas has been also suggested as a cause of an increase in the Al content in quartz. In the case of Tres Arroyos, according to bulk-rock chemical data, the amount of F was higher in the marginal granite and in the barren and intermediate aplite-pegmatites than
in the monzogranite; i.e., the higher F concentration in the melt is not reflected in a higher Al content in quartz in those cases. Regarding the H$_2$O content of the melts, a priori the water activity in residual late fractionates of granitic melts is supposed to be higher than that of the parental magma. However, micas, the main OH-bearing mineral in the barren and intermediate aplite-pegmatites from Tres Arroyos, are fairly scarce in these rocks. Taking into account that the aplite-pegmatite dykes are supposed to have crystallized in open fractures at relatively low pressures, we consider it feasible that the crystallization of the pegmatitic melts in a relatively shallow, open system, allowed the exsolution of a water-rich fluid phase that separated from the melt, lowering its water content and, hence, preventing the incorporation of Al in the quartz (Larsen and Jacamon, 2009). This did not happen during the crystallization of the monzogranite, where micas are abundant and crystallization mainly proceeded under closed system conditions and over 4 wt.% H$_2$O in the melt (González-Menéndez, 1998). Nevertheless the scenario for the crystallization of the barren and intermediate aplite-pegmatites, with an undercooled melt due to the sudden loss of H$_2$O and volatiles, crystallizing at shallow emplacement levels, has been proposed to be suitable for a high growth rate in quartz that would result in disequilibrium growth that may allow the uptake of Al and other impurities into the quartz lattice (Pankrath, 1988; Merino et al., 1989). In this sense, experimental data have shown that growth rate affects Ti and Al contents in quartz (Huang and Audétat, 2012). Moreover, differences in the crystal structure of alpha and beta quartz have been experimentally demonstrated to influence the capability of quartz to incorporate Al and Li, favoured in the high-quartz (Frigo et al., 2016). In such case, comparisons between beta quartz, the most likely primary quartz crystallized in the monzogranitic facies (T of crystallization: 583°C-652°C by applying the Ti-in biotite geothermometer (Henry, 2005); 567-666°C by applying the TitaniQ
geothermometer (Thomas et al., 2010), assuming the system is saturated in ilmenite and the Ti activity is in the range 0.5-1 (Ghent and Stout, 1984); final T of crystallization close to 650°C according to the mineral paragenesis (González-Menéndez, 1998)); and alpha quartz, presumably the primary silica polymorph crystallized in the marginal granite (T of crystallization: 514-578°C by applying the Ti-in biotite geothermometer (Henry, 2005)). All these facts suggest that, most probably, Al content in quartz depends on different competing factors, which makes it much more difficult to understand its variations during crystallization and fractionation.

After Al, Ti is the most abundant trace element in quartz associated with the monzogranite (Fig. 4a, c, Table 3). There is an important decrease from this to the quartz occurring in the marginal granitic facies; whereas Ti decreases gradually from this facies, through the barren and intermediate aplite-pegmatites; with the lowest values in the quartz from the Li-rich aplite-pegmatites (Fig. 4a, c, Table 3). Titanium has been used as an indicator of temperature: high Ti contents are related to deep magma reservoirs (Schrön et al., 1988), whereas a decreasing Ti concentration is correlated to a lower crystallization temperature (Wark and Watson, 2006). Even if the lack of Ti saturation in the studied aplite-pegmatites (no rutile in equilibrium with quartz has been observed) prevents the use of the Ti-in quartz geothermometer (Huang and Audétat, 2012), there is a clear descending trend in the Ti content in quartz during fractionation in the Tres Arroyos granite-pegmatite system. Overall there is a good positive correlation between the Ti content in quartz and the Ti concentration in the hosting rock (Fig. 5). The marked decrease in Ti in the quartz from the monzogranite to that from the marginal granitic facies may indicate a change in the conditions of crystallization, with the transition from a granitic to a pegmatitic regime; or well, it could respond to the crystallization of ilmenite in the monzogranite, much more
abundant than in the marginal granitic facies, which could buffer the Ti content in the
residual melt.

The studied quartz is significantly enriched in Li compared to previous quartz studies
owing to the fact that the Tres Arroyos suite is a Li enriched system. Thus, quartz from
the monzogranite facies from Tres Arroyos is slightly enriched in this element when
compared to other European granites, such as the granites from the Bohemian Massif,
with the exception of the Nedjeck pluton (Breiter et al., 2013; Breiter and Müller,
2009); whereas similar Li-contents are described for the Land’s End Pluton in Cornwall
(Drivenes et al., 2016). As it happens with the trend for the Al contents in quartz, the Li
concentration is lower in the marginal granitic facies and in the barren and intermediate
aplite-pegmatites, than in the monzogranite, with a final increase in the quartz from the
Li-rich aplite-pegmatites (Fig. 4b, Table 3). Therefore, Li contents are strongly
correlated with Al contents in quartz, with Li/Al atomic proportions close to 0.65 (Fig.
4b). The good correlation between Al and Li accounts for the substitution $\text{Si}^{4+} \Leftrightarrow \text{Al}^{3+} + \text{Li}^+$, where every atom of interstitial $\text{Li}^+$ is counterbalancing one $\text{Al}^{3+}$ atom replacing
one $\text{Si}^{4+}$ in the quartz structure. The introduction of other cations, such as $\text{K}^+$, $\text{Na}^+$ and
$\text{P}^{5+}$ besides $\text{Li}^+$, and of $\text{Fe}^{3+}$ and $\text{B}^{3+}$ besides $\text{Al}^{3+}$, could have also operated in the quartz
in some extent. Nevertheless, taking into account the general low concentrations of
those elements in most of the analyzed quartz, the amount of Al that was not balanced
by Li was most likely charge compensated by $\text{H}^+$, as proposed by Müller and Koch-
Müller, (2009), Breiter et al. (2013), and, Baron et al. (2015). As it happens with Al, in
general there is no correlation between Li contents in the quartz and in the bulk rock
(Fig. 5), as it was described for some pegmatites from the Bohemian Massif by Breiter
et al. (2014). Lithium contents in quartz have been related to the peraluminosity of the
melt (Jacamon and Larsen, 2009), as well as to the fractionation degree and coexisting
Li-bearing minerals (Breiter et al., 2013, 2014). However, none of these reasons seems easy to apply in this case, as discussed above for Al. Taking into account the good Al/Li correlation, we consider that the Li proportion in the quartz is most likely conditioned by the Al incorporation into quartz lattices, at least for low and intermediate Li concentrations in the bulk rock.

Germanium is another trace element of quartz that reflects the degree of melt differentiation. According to Jacamon and Larsen, (2009), the Ge/Ti ratio in quartz usually increases with fractionation. Such is the case in the Tres Arroyos system, where Ge concentration increases from the monzogranite, through the barren aplite-pegmatites, up to the most fractionated dykes (Table 3, Fig. 4c). When compared to the Ge content in quartz and in the whole rock, there is certain correlation, mainly for the poorest (monzogranite) and richest (Li-rich aplite-pegmatites) ones (Fig. 5).

The remaining trace elements (B, Fe, K, P, Na) show low contents for most of the analyzed samples. The most abundant of those is K, mainly in quartz associated with the monzogranite and the Li-rich pegmatites; showing a similar correlation with Al as Li (Si ⇔ Al$^{3+}$ + K$^+$. Phosphorus occurs also in appreciable amounts, in the ranges 1-5, 2-3, 0-8, 1-9, 0-8 for the monzogranite, marginal granite, barren, intermediate and Li-rich aplite-pegmatites respectively. No correlation has been observed between Al and P, which means that a supposed incorporation of P via the berlinite substitution (2Si$^{4+}$ ⇔ Al$^{3+}$ + P$^{5+}$) was not significant (Maschmeyer and Lehmann, 1983). Boron may also appear in measurable concentrations, with an overall gradual increase with fractionation from monzogranite to the Li-rich aplite-pegmatites (Table 3, Fig. 4e). Tourmaline is the only B-bearing mineral occurring in these rocks, and occurs in the marginal granitic facies and barren pegmatites. The B content in quartz from these lithologies does not seem to be significantly affected by the crystallization of tourmaline, as it fits in the
increasing trend from monzogranite toward more fractionated facies. The addition of
K\(^+\), Na\(^+\) and P\(^{5+}\) to Li\(^+\), and of Fe\(^{3+}\) and B\(^{3+}\) to Al\(^{3+}\), in the plot of Al versus Li (Fig. 4b),
increases just slightly the degree of correlation, diminishing insignificantly the deviation
from the 1:1 atomic proportion vector (Fig. 4f). This indicates that the substitutions
Si \(\leftrightarrow\) Al\(^{3+}\) + K\(^+\), Si \(\leftrightarrow\) Al\(^{3+}\) + Na\(^+\) and the same ones with B\(^{3+}\) or Fe\(^{3+}\) instead of Al\(^{3+}\),
could have operated in the quartz but in a very limited way. The extremely low Fe and
Mn contents in the quartz from the aplite-pegmatites (< 1 µgg\(^{-1}\)) could indicate that the
impact of meteoric fluids during quartz primary crystallization was negligible, opposite
to that observed in the stockscheider of Podlesí (Bohemian Massif) (Breiter and Müller,
2009), with significant mineral, chemical and textural similarities to those of the aplite-
pegmatites from Tres Arroyos (Roda-Robles et al., under review).

5.2. Fractionation trends and internal evolution of the aplite-pegmatite dykes

Taking Ti as a compatible element to get inside the quartz structure, and Al and Ge
as incompatible ones, the Al/Ti and Ge/Ti ratios have been also used to illustrate the
fractionation trends of different plutons (Breiter et al., 2012; 2013; Jacamon and Larsen
2009; Drivenes et al., 2016). As stated above, in the quartz from Tres Arroyos the two
ratios increase with fractionation, with a strong positive correlation among them (Fig.
4d, e), also observed for the whole rock data (Fig. 5). According to these data, the
monzogranite is the less fractionated lithology. The marginal granitic facies and the
barren aplite-pegmatites show a higher evolution degree, followed by the intermediate
aplite-pegmatites. Finally, the highest fractionation level is attained by the Li-rich
aplite-pegmatites.
A quite similar trend is also obtained by the geochemical modelling applying Rayleigh equations to the Li, Rb and Ba bulk contents of the Alburquerque monzogranite, and comparing the results to the bulk contents of the rest of lithologies in the Tres Arroyos system (Fig. 6). According to the data, the different lithologies may be explained by a single crystallization path that well could start from a composition similar to that of the Nisa-Alburquerque monzogranitic facies. At fractionation degrees of ≈ 50% the marginal granitic facies could crystallize; whereas extreme degrees of fractionation (≈ 99%) would be necessary to obtain the concentrations in Ba, Li and Rb observed in the lepidolite-rich aplite-pegmatites. Intermediate degrees of fractionation are needed for the barren and intermediate aplite-pegmatites (Fig. 6). Deviations from the ideal fractionation trends are observed for some of the samples, mainly those from the albite-richest bodies (Fig. 6). Such deviations may be attributed to different reasons: firstly, it could be related to the representativeness of the analyzed samples, as the strong heterogeneity of these rocks makes it often difficult to obtain a sample representative of the whole-rock composition; secondly, the mineral association of the albite-richest rocks is not probably the most suitable to make a modelling for the Ba, Li and Rb, as these elements are usually hosted in micas and K-feldspar, whereas albite shows much lower values; and, thirdly, in some of these dykes metasomatic processes, mainly including albitization, seem to be locally important, which would most probably change the primary Ba, Rb and Li concentrations in those aplite-pegmatites.

Accordingly, fractional crystallization was an important mechanism that well could explain the chemical and mineral variations observed for the different facies occurring in the Tres Arroyos granite-pegmatite system and the extreme Li-F-enrichment in the most evolved aplite-pegmatites. Crystal fractionation is often also reflected inside single pegmatitic bodies all over the world, where an internal zoning is developed during
crystallization, usually from the borders inward with the most fractionated facies occurring in the core margin and core zone, witnessing the internal evolution of the melt (e.g., London, 2008; Roda-Robles et al., 2012b; Roda-Robles et al., 2015). Such is not the case of the aplite-pegmatites from Tres Arroyos, which do not present internal zoning nor quartz cores. However, the presence of comb textured feldspars and quartz crystals, growing perpendicularly to the pegmatite contacts and increasing in width in the direction of the core of the bodies; as well as the frequent occurrence of layering disposed parallel to the margins of the dykes, indicate that crystallization in the Tres Arroyos aplite-pegmatite dykes also proceeded mainly from the borders inward. Studies on the variation of the trace elements contents in quartz during the crystallization of single pegmatites are scarce: e.g. strong variations have been observed in some LCT pegmatites from the Borborema Pegmatite Province (Beuren et al., 2011); similar evolutionary trends from fractioned granites to LCT pegmatites are described in the Bohemian Massif, (Breiter et al., 2014); noticeable variations are also described for the NYF pegmatites in Evje-Iveland (Müller et al., 2015). In contrast, almost no variation is found in quartz chemistry across the internally zoned abyssal pegmatites from Froland (Müller et al., 2015). In order to check a possible internal fractionation in the aplite-pegmatites from Tres Arroyos, quartz from different layers was analyzed. According to the obtained data, no variation in the contents of trace elements is noticed from the contacts inwards the dykes. This, together with the lack of internal zoning inside the aplite-pegmatites, where, for example, in the Li-rich dykes the Li-rich micas crystallize across the whole aplite-pegmatite body, indicate that during the crystallization of the aplite-pegmatites, fractionation of the melts was negligible. The distribution of the most fractionated aplite-pegmatites occurring farthest from the monzogranite (Fig. 1) suggests a previous vertical chemical zonation of the melt within the source pluton, as it
has been indicated for the Fregeneda-Almendra field, occurring to the north of Tres Arroyos, also in the CIZ, and in some Li-rich leucogranitic cupolas occurring in the region (Roda-Robles et al., 2012a; Roda-Robles et al., 2016, Roda-Robles et al., under review). Such compositional zoning in the melt would have developed in the magma chamber before the granitic system opened and the melt intruded the fractures where it finally crystallized. The greater enrichment in Li, F, and probably also H₂O at the top of the magma chamber would notably reduce the viscosity of the most fractionated melts (Dingwell et al., 1996), and would also lower the liquidus temperature, enhancing its mobility. That most fractionated portion of melt in the upper part of the magma chamber would escape first and move further. The aplite-pegmatite dykes from Tres Arroyos are relatively thin, with thicknesses under 7 m. The temperature of the hosting metasediments at epizonal emplacement levels (350-400°C) was presumably significantly lower than that of the intruded melt (over 500°C according to the presence of monoclinic feldspar in all the aplite-pegmatite dykes), which would cause an important undercooling of the melt and the increase of its solidus temperature, reinforced by the likely exsolution of a fluid phase from the pegmatitic melt, mainly due to the drop of pressure. Pegmatites crystallizing in similar scenarios have been modelled by Webber et al. (1999) in order to calculate their crystallization time, obtaining very short periods, in the order of days to weeks. Therefore, all these evidences suggest that once intruded into the fractures, melts should crystallize very quickly, preventing the internal fractionation of the aplite-pegmatite. It has also been suggested that low Rb contents in quartz, as it is the case, correspond to rapid crystallization at low pressures, after melt emplacement (Breiter et al., 2013). Therefore, the lack of variation in the trace element contents in quartz from different layers reflects the lack of internal zoning inside individual dykes, probably due to the rapid crystallization of the melt.
6. Conclusions

Taking into account the textural and chemical variations observed in the studied quartz, together with the geochemical modelling on whole-rock data, the following conclusions can be summarized:

1) Quartz from the highly evolved Tres Arroyos granite-pegmatite system crystallized primarily from magmatic or pegmatitic melts, with no evident subsolidus or hydrothermal overprint.

2) Aluminium, Li, Ti, and Ge are the main trace elements in the studied quartz, with different concentrations depending on the facies: the highest Al, Li and Ge, and the lowest Ti being associated with the quartz from the most fractionated aplite-pegmatites (Li-rich), and the highest Ti values with the monzogranite.

3) Continuous trends for the main trace elements are observed for the quartz from the monzogranite, through the marginal granitic facies, the barren and intermediate aplite-pegmatites, up to the most evolved Li-rich dykes. Titanium contents decrease in that sense, i.e. with descending temperature; whereas the inflexion observed in the Al and Li values suggests the influence of different competing factors (e.g., chemical composition and content in water of the melt, P and T conditions, rate of crystallization, quartz structure).

4) The good correlation between Al and Li, suggests that the main substitution mechanism for the inclusion of these two elements in the quartz was: Si$^{4+} \leftrightarrow$
Al$^{3+}$ + Li$^+$. The important deviation of the Li/Al rate below the 1:1 atomic proportion vector, suggests that the remaining Al was equilibrated by H$^+$ ions.

5) A continuous fractionation trend from the monzogranite up to the most fractionated pegmatites is evidenced from the trace element contents in quartz and from the geochemical modelling (Rayleigh fractional crystallization): the granitic melt should fractionate over 50% to obtain the composition of the marginal granitic facies and the barren aplite-pegmatites, and over $\approx$ 99% for the most fractionated Li-rich dykes.

6) The negligible and erratic variations of the trace elements contents of quartz in the different layers inside the aplite-pegmatites suggest the lack of internal fractionation inside the dykes, probably as a consequence of a rapid crystallization from highly undercooled melts, in contact with a colder hosting-rock.

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**Figure caption**

Fig. 1: Schematic geological map of the Central Iberian Zone (CIZ) and detailed map from the Tres Arroyos pegmatitic field (modified from Gallego-Garrido 1992). Locations of studied samples: 1) Barren aplite-pegmatites; 2) Intermediate aplite-pegmatites; 3) Layered intermediate aplite-pegmatites; 4) Li-rich aplite-pegmatites

Fig. 2: (a) Sample from an intermediate aplite-pegmatite showing a simple pattern layering, with alternating albite-rich layers with quartz-rich layers (b) hand sample from
a Li-rich dyke exhibiting a complex layering (for location of the samples see Figure 1).

Fig. 3: SEM-CL images from: (a) homogeneous quartz from the monzogranitic facies showing little cracks; (b) quartz from intermediate aplite-pegmatite with a weakly-contrasted growth zoning; (c) and (d) quartz from an intermediate and a Li-rich dyke respectively, with intra and transgranular healed cracks (for location of the samples see Figure 1).

Fig. 4: Plot of the trace elements contents in quartz: (a) Al vs Ti; (b) Al vs Li, the arrows indicate Li/Al atomic ratios 1:1 and 1:2; (c) Ti vs Ge; (d) Al/Ti vs Ge/Ti; (e) Ge/Ti vs B; (f) molar values of $\Sigma$Al + B + Fe vs $\Sigma$ Li + K + Na + P, the arrows indicate (Li+K+Na+P)/(Al+B+Fe) atomic rates 1:1 and 1:2.

Fig. 5: (a, b, c, d) Plots of Li, Ge, Al and Ti contents from whole rock vs trace element contents from quartz analyses (e) Ge/Ti vs Al/Ti from bulk rock.

Fig. 6: Plot of (a) Li vs Ba, and (b) Rb vs Ba, for different bodies from Tres Arroyos area, and the possible path of fractional crystallization of a parent magma with the composition of the Nisa-Alburquerque monzogranite. Filled symbols represent our data, empty symbols represent data from Gallego-Garrido, 1992, half-filled symbol represents data from González-Menéndez, 1998.

Fig. 7: Variations in the Ti and Al contents in the different facies from the Tres Arroyos system and comparison with quartz from other granitic and pegmatitic quartz occurrences (data modified from (Breiter et al., 2013): Nejdek pluton (Breiter and
Müller, 2009), Central Moldanubian and Rozvadov (Breiter et al., 2013); Ruby mountains granites (Deans, 2010); Norwegian Precambrian granites (Jcamon and Larsen, 2009); and, Borborema pegmatites (Beurlen et al., 2011)).

Table 1: Mineralogy and petrography of the different facies from the Tres Arroyos aplite-pegmatite-granite system.

Table 2: Detection limits of trace elements of LA-CP-MS analyses (in μgg⁻¹).

Table 3: Range of values of trace elements in quartz from the different granite and pegmatite types, analyzed by LA-ICP-MS (all values given in μgg⁻¹).

Table 4: Average values and their standard deviation of trace element in quartz from different layers from the three types of aplite-pegmatites, analyzed by LA-ICP-MS.

Table 5: Mineral modes from a representative monzogranite and partition coefficients used in the modelling of fractional crystallization. For quartz, K-feldspar, plagioclase and muscovite, data compiled by Jollif et al., 1992; for biotite, data compiled by Icenhower and London, 1995.
Monzogranite
Marginal granitic facies
Barren aplite-pegmatites
Intermediate aplite-pegmatites
Li-rich aplite-pegmatites
Li-rich aplite-pegmatites (not outcropping)
Dumps

CZ=Cantabrian Zone
WALZ=West Asturian-Leonese Zone
CIZ=Central Iberian Zone
GTMZ=Galicia Tras Os Montes Zone
OMZ=Ossa Morena Zone
SPZ=South Portuguese Zone

Schist Metagreywacke Complex (SMC)

Rivera del Arconeo

N

39.25°
-7.08°
Type I (very fine-grained layers)
Type II (fine-grained layers)
Type III (medium-grained layers)
A) Barren aplite-pegmatites

B) Intermediate aplite-pegmatites

C) Intermediate aplite-pegmatites

D) Li-rich aplite-pegmatites

**A-B-C (I)**

**D-E-F (II)**

**A-B (II)**

**C-D-E (I)**

**F-G-H (II)**

**A-B-C (I)**

**D (II)**

**E (II)**

**G-H-J-K (III)**

**A (II)**

**B-C-D (II)**

**E-F (II)**

**A-B (II)**

**C-D-E (I)**

**F-G-H (II)**

**A (II)**

**B-C-D (II)**

**E-F (II)**

**A-B-C (I)**

**D (II)**

**E (II)**

**G-H-J-K (III)**
Central Moldanubian
Rozvadov
Monzogranite
Marginal granitic facies
Barren aplite-pegmatites
Intermediate aplite-pegmatites
Li-rich aplite-pegmatites
Norway
Ruby Mts.
Borborema
Nedjek

Al µgg⁻¹

Ti µgg⁻¹
<table>
<thead>
<tr>
<th>LITHOLOGY</th>
<th>MINERALOGY</th>
<th>QUARTZ GRAIN SIZE</th>
<th>QUARTZ HABIT</th>
<th>ROCK TEXTURE (quartz texture)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porphyritic monzogranite</td>
<td>Quartz, K-feldspar, plagioclase, biotite, muscovite, cordierite, andalusite, tourmaline, zircon, apatite, oxides</td>
<td>Fine to medium 0.1-1 cm</td>
<td>Subrounded Anhedral</td>
<td>Oriented porphyritic feldspar crystals Oxides and zircon (with metamictic halos) crystals usually inside or close to biotite. (Quartz with undulose extinction)</td>
</tr>
<tr>
<td>Marginal granitic facies</td>
<td>Quartz, K-feldspar, plagioclase, tourmaline, biotite, cordierite, andalusite, muscovite, Fe-Li-muscovite, ilmenite.</td>
<td>Very fine to fine 0.1-0.5 cm</td>
<td>Subrounded Anhedral</td>
<td>Biotite frequently concentrated in layers, Biotite-Muscovites intergrowths. Accessory tourmaline prisms Aplitic texture Chloritization and serizitation of the Al-silicates (Single quartz crystals with undulatory extinction + anhedral quartz aggregates + very fine (&lt;2 mm) inclusions in tourmaline)</td>
</tr>
<tr>
<td>Barren aplite-pegmatites</td>
<td>Quartz, plagioclase, K-feldspar, muscovite, tourmaline, zinnwaldite, topaz, Fe-Mn phosphates, apatite, Sn-Nb-Ta oxides</td>
<td>Very fine to medium Pegmatitic layers: &lt;3 cm Aplitic layers: &lt;0.5 cm</td>
<td>Subrounded Anhedral</td>
<td>Layered texture, alternating pegmatic and aplitic layers Locally greenish color in hand sample due to Fe-Mn phosphates (Single quartz crystals + anhedral quartz aggregates + quartz occasionally occurs as comb shaped aggregates of very fine sized subrounded crystals (&lt;0.3 cm) + very fine inclusions in tourmaline and feldspar)</td>
</tr>
<tr>
<td>Intermediate aplite-pegmatites</td>
<td>Quartz, plagioclase, K-feldspar, muscovite, topaz, Li-Al phosphates, Fe-Mn phosphates, Sn-Nb-Ta oxides, apatite</td>
<td>Very fine to medium 0.1 – 2.5 cm</td>
<td>Subrounded Anhedral Largest ones: elongated</td>
<td>Simple pattern layering, alternating albite rich layers with quartz rich layers, the grain size also may change. Ablite radial small flakes (Single quartz crystal with irregular contact some of them showing a weak undulose extinction + quartz occasionally occurs as comb shaped aggregates (up to 2.5 cm) of fine sized subrounded crystals (&lt;0.5 cm))</td>
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<td>Li-rich aplite-pegmatite</td>
<td>Quartz, plagioclase, K-feldspar, Li-Al-mica, topaz, Li-Al phosphates, Sn-Nb-Ta oxides, apatite</td>
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<td>Rhythmic layering, some with a complex pattern, with alternating albite-rich and Li-mica rich layers. Fan-shaped micas with patchy-zoning (Single quartz crystals in aplitic layers + subrounded quartz aggregates, &lt;0.8 cm)</td>
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Very fine< 3mm; Fine=3-6mm; Medium>6mm
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