The chemistry of beryl as a tool to understand non-emerald bearing pegmatites

A química de berilo como ferramenta para entender os pegmatitos não portadores de esmeralda

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Abstract: The study of non-emerald-bearing beryl pegmatites unveils secrets about the formation and development of pegmatites, paving the way to comprehend these geological formations. As a borosilicate, beryl occurs in various colors and forms, reflecting the geochemical conditions and impurities of its environment. Therefore, analyzing the chemical composition of beryl reveals details about its crystallization. Such chemical variations signal the processes of magmatic differentiation that influence the mineral diversity of pegmatites. This in-depth study not only elucidates the geological mechanisms behind the genesis of non-emerald-bearing pegmatites but also expands the understanding of mineral and valuable element distribution in the Earth's crust. The study of beryl also offers insights into the geological evolution of areas abundant in pegmatites. This article provides a detailed review of the characteristics and chemical behavior of beryl, as well as describing a routine for determining the chemical formula of beryls through stoichiometry, using electronic microprobe analyses.

Keywords: Mineral chemistry; Beryl formula calculation; Pegmatite Geochemistry.

Resumo: O estudo do berilo de pegmatitos não portadores de esmeralda desvenda segredos sobre a formação e desenvolvimento dos pegmatitos, abrindo caminhos para compreender essas formações geológicas. Como um silicato de boro, o berilo se apresenta em diversas cores e formas, refletindo as condições geoquímicas e as impurezas de seu ambiente. Portanto, a análise da composição química do berilo revela detalhes sobre a sua cristalização. Tais variações químicas sinalizam os processos de diferenciação magmática que influenciam a diversidade mineral dos pegmatitos. Este estudo aprofundado não apenas esclarece os mecanismos geológicos por trás da gênese dos pegmatitos sem esmeralda, mas também expande o entendimento sobre a distribuição de minerais e elementos valiosos na crosta terrestre. O estudo do berilo oferece ainda perspectivas sobre a evolução geológica de áreas abundantes em pegmatitos. Este artigo traz uma revisão detalhada das características e comportamento químico do berilo, além de descrever uma rotina para a determinar da fórmula química de berilos por estequiometria, usando análises de microssonda eletrônica.

Palavras-chave: Química mineral; Cálculo de fórmula do berilo; Geoquímica de pegmatitos.

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1. Introduction

Beryl ($Be_3Al_2Si_6O_{18}$) is a mineral that stands out due to its rarity and the specificity of the geological environments in which it occurs, being most commonly found in granitic pegmatites. This occurrence also extends to hydrothermal deposits linked to granites, such as greisens and quartz-cassiterite veins, as well as occurring in rhyolites and, under certain conditions, in metamorphic rocks, including schists and skarns (London, 2015; Turner & Groat, 2007).

The complexity and coarse graining of pegmatites pose a challenge for sampling and detailed geochemical studies. However, minerals such as beryl, quartz and minerals from the feldspar, mica and tourmaline groups are crucial for characterizing the geochemistry of pegmatites and elucidating their evolutionary processes (Černý, 1975).

By examining the composition and structure of beryls, geoscientists can gain insights into the temperature, pressure, and composition of the magmatic fluid at different stages in the evolution of a pegmatite (Aurisicchio et al., 2012; Bacík et al., 2019; Daneshvar et al., 2021; Fan et al., 2022; Jiang et al., 2023; Lum et al., 2016; Neiva A & Neiva J, 2005; Pauly et al., 2021; Suo et al., 2022; Uher et al., 2010; Viana et al., 2002). Changes in the chemical composition of beryl, especially in the content of alkalis (Na, Li, Cs), water (H_2O) and divalent metals (Fe, Mg), show a strong correlation with the geochemical and genetic characteristics of the host geological systems, as well as with the beryl-bearing pegmatites themselves (Aurisicchio et al., 1988; Černý, 1975).

This study does not deal with pegmatites containing emerald, as its presence in pegmatites is uncommon and usually occurs due to later processes. Emerald is a beryl with chromophores such as chromium (Cr) and vanadium (V), which results in green crystals, occasionally with bluish or yellowish tones. Emerald formation is limited by geological conditions that favor the concentration of beryllium (Be), Cr and/or V. Be is often found in granites, pegmatites and metamorphic equivalents, while Cr in dunite, peridotite, basalt and their metamorphic equivalents, and V in organic and iron-rich sediments and their metamorphic equivalents. The occurrence of these elements together is unusual, as Cr and V are generally not present in Be-rich environments. Therefore, dynamic geological and geochemical conditions are necessary for these elements to meet. Traditionally there are three types of emerald deposits. The first involves desilicate pegmatites formed by the interaction of metasomatic fluids with Be-rich pegmatites, or similar granitic bodies, which intrude Cr- or V-rich rocks, such as ultramafics and volcanics. The second type is sedimentary, in which Be-rich crustal brines interact with shales and other sedimentary rocks containing Cr and/or V along faults and fractures. The third type is metamorphic-metasomatic, in which deeper crustal fluids interact with metamorphosed shales, carbonates and ultramafic rocks along faults or shear zones, transporting Be and Cr (and occasionally V) to depositional sites (Giuliani et al., 2019; Groat et al., 2008).

The aim of this article is to review the characteristics and properties of beryls. This paper looks at how the chemical composition of beryl, including its trace elements, can provide valuable information about the environmental conditions present during the crystallization of pegmatites. In addition, this paper presents the step-by-step process for calculating the chemical composition of beryls from electron microprobe analysis of oxides. The approach is outlined in seven steps, focusing on the precise determination of the proportions of cations and anions, specifically oxygen, in the mineral formula based on the amount of oxides present.

2. Beryl Mineralogy and Crystallography

The minerals of the beryl group are avdeevite, bazzite, beryl, johnkoivulaite, pezzottaite and stoppaniite, which are silicates of beryllium and aluminum, represented by the general crystallochemical formula $(M^{3+},M^{2+})_4[Be_6Si_{12}O_{36-z}(OH)_z] \cdot (H_2O)_y A_x$, where A = mainly Na and x = probably not greater than 1. The mineral beryl has the formula $Be_3Al_2Si_6O_{18}$, with approximate values of BeO $\cong$ 14%, Al_2O_3 $\cong$ 19% and SiO_2 $\cong$ 67% (Klein & Dutrow, 2012). The usual impurities, which make up a substantial part of most beryl varieties, are alkalis (Na, Li, Cs, Rb, K) and to a lesser extent H_2O, Ca, Mg, Mn, Fe^{2+}, Fe^{3+}, Cr, CO_2, He and Ar (Beus, 1966). However, the presence of alkalis (Na and Rb) and Li can considerably reduce the percentage of BeO (Bragg & Langworthy, 1926; Klein & Dutrow, 2012).

The constitution of beryl is marked by the formation of hexagonal rings, each composed of six Si-O tetrahedrons, which organize continuous channels along the c-axis of the crystal, spaces which can accommodate ions and/or molecules. Between these rings, the beryllium and aluminum atoms are arranged alternately, with each aluminum atom surrounded by an octahedron made up of six oxygen atoms and each beryllium atom linked to four oxygen atoms, forming an asymmetrical tetrahedron (Bragg & Langworthy, 1926; Klein & Dutrow, 2012) (Figure 1).
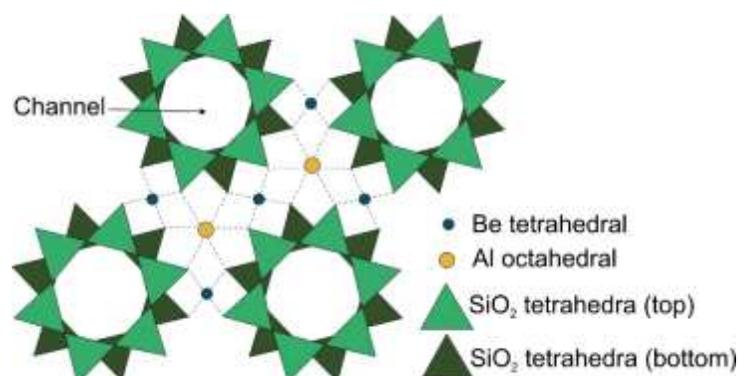
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Figure 1 – Beryl structure projected in (0001), looking down the c-axis.
Source: Adapted from de Klein & Dutrow (2012).

Beryl is characterized by having four crystallographic axes, three of which are coplanar and form angles of 120º to each other, while the fourth axis is orthogonal to the others. Its shape can vary from elongated prismatic to short, tending towards a tabular shape. Beryl is often found in the form of isolated, well-formed crystals and rarely in aggregates. Usually, the prismatic faces are the most prominent, occurring in combination with the basal pinacoid faces, while the bipyramid and diaxegonal prism faces are less common (Bragg & Langworthy, 1926).

From the analysis of studies on isomorphic substitutions in the crystal structure of beryl, often associated with alkaline elements, it is possible to suggest a generalized formula that incorporates mono- and bivalent ions. These ions are crucial for investigating the factors responsible for beryl's colors, which are defining characteristics of its different varieties. As proposed by Gaines et al. (1997) apud Gandini et al. (2001), the formula can be represented as $[A]X_3Y_2T_6O_{18}$. In the "A" position, we can find H_2O, OH, Na, Ca, Fe^{2+}, K, Cs, Rb. Interestingly, this position can also be empty. The "X" site is occupied by elements that prefer the tetrahedral configuration, such as beryllium (Be), aluminum (Al), lithium (Li) and silicon (Si^{4+}). The "Y" site accommodates ions in octahedral configurations, such as Al, Fe^{2+}, Mg, Fe^{3+}, Ca, Mn^{2+}, Cr^{3+}, V^{5+}, Te^{4+}, Sc. At the "T" site, we only have silicon (Si4+) in a tetrahedral configuration (Gandini et al., 2001).

Based on this information, we have the following substitutions (Table 1): octahedral substitution by Al^{3+}, tetrahedral substitution by Be^{2+}, and a limited tetrahedral substitution by Be^{2+} followed by octahedral substitution by Al^{3+}. Table 1 gives a summary of how changes in the chemical composition of beryl influence the occupation of specific places within its crystal structure.

Table 1 – Ionic substitutions in beryl

Sítio	Element	Observations
Tetrahedral	Si^{4+}	In $(SiO_4)^{4-}$ tetrahedrons. Replaces Be in the tetrahedron $(BeO_4)^{6-}$ if it is in excess.
Octahedral	Al^{3+}	It enters tetrahedrons replacing Si and Be when in excess.
	Fe^{2+}, Fe^{3+}, Mg^{2+}, Cr^{3+}, Sc^{3+}	Replaces Al in octahedrons.
	Li^+	It fills vacancies when there is a deficiency in Al, it does not replace it.
Tetrahedral	Be^{2+}	In tetrahedrons (BeO4)6- or together with Si in tetrahedrons $(SiO_4)^{4-}$. Al substitution if Si and Al are missing.
	Li^+	In Be's positions.
Canal	Na^+, Ca^{2+}	In the channels between two HOH groups and, rarely, in the empty spaces between the rings.
	K^+	In positions similar to the HOH group within the channels.
	Rb^+	In the channels between HOH and three oxygens of a ditrigonal ring, with strong deformation.
	Cs^+	In the channels, analogous to the Rb^+, but with only a slight distortion of the rings.
	$Fe2^+$	It can be in the channels or occupy vacancies when it exists

Source: Gandini et al. (2001).

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According to Bakakin et al. (1970) and Aurisicchio et al. (1994) it is possible to classify beryl polytypes into: normal type (N) and tetrahedral type (T) and a transition sample between the normal and tetrahedral types. The N-type of beryl is the one that comes closest to the theoretical formula, with no cation substitution. In the T-type there is partial substitution of beryllium with lithium and sometimes with silicon, which causes alkaline elements to enter the channel.

Beryl, from a mineralogical point of view, is notable for its wide range of colors, a phenomenon resulting from the presence of small amounts of impurities in its crystal structure, especially transition metals such as Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{3+}, Cr^{3+}, e V^{3+}, or by color centers (Klein & Dutrow, 2012). These elements can occupy the places normally filled by Al^{3+} and Be^{2+}, causing the color variations that characterize its gemological varieties: emerald, green in color, owes its hue to chromium and/or vanadium (Figure 2-A); aquamarine (Figure 2-B) shows blue to bluish-green hues, resulting from the interaction of Fe^{2+} in the structural channels with Fe^{3+} in the octahedral sites; morganite (Figure 2-C) shows a spectrum from pink to salmon, thanks to the presence of manganese. 2-C) shows a spectrum ranging from pink to salmon, thanks to the presence of manganese; heliodorite (Figure 2-D), with its golden yellow to amber color, owes its color to the charge transfer from Fe3+ to the adjacent oxygens, which intensely absorbs the blue light of the spectrum; goshenite (Figure 2-E), transparent and almost free of impurities; and red beryl (Figure 2-F), whose color comes from manganese. These distinct hues not only embellish the mineral, but also provide clues about the geochemical and geological conditions of its formation (Gandini et al., 2001).

Figure 2 – A) Esmeralda (Brumado, Bahia) measuring 3.2 cm x 1.4 cm x 1.2 cm. B) Group of aquamarine crystals with an unusual morphology, in an albite matrix with muscovite (Fazenda Concórdia pegmatite, Mimoso do Sul, Espírito Santo), specimen size: 4.8 cm x 4.1 cm x 3.9 cm. C) Morganite (Urucum deposit, Barra do Cuieté, Conselheiro Pena, Minas Gerais), dimensions: 16.8 cm x 16 cm x 14.3 cm. D) Heliodoro (Itinga, Minas Gerais), dimensions 4.4 cm x 1.7 cm x 1.5 cm. E) Goshenite (Ponto do Marambaia mine, Caraí, Minas Gerais), dimensions: 5.2 cm x 2.5 cm x 1.9. F) Red Beryl (Ruby Violet deposit, Beaver County).
Source: www.mindat.org.

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Aurisicchio et al. (1994) identified, by means of absorption spectroscopy in the infrared spectral range, two distinct arrangements of water molecules within the structural channels of beryl. The so-called Type I arrangement occurs when the axis of the H-H dipole is aligned parallel to the c-axis of the beryl crystal, and the Type II arrangement when this axis is perpendicular to the c-axis (Figure 3). This observation suggests that the presence of alkalis as contaminants in the channels generates an electrostatic force that induces the rotation of the water molecule, so that the O^{2-} ion is positioned next to the alkali.
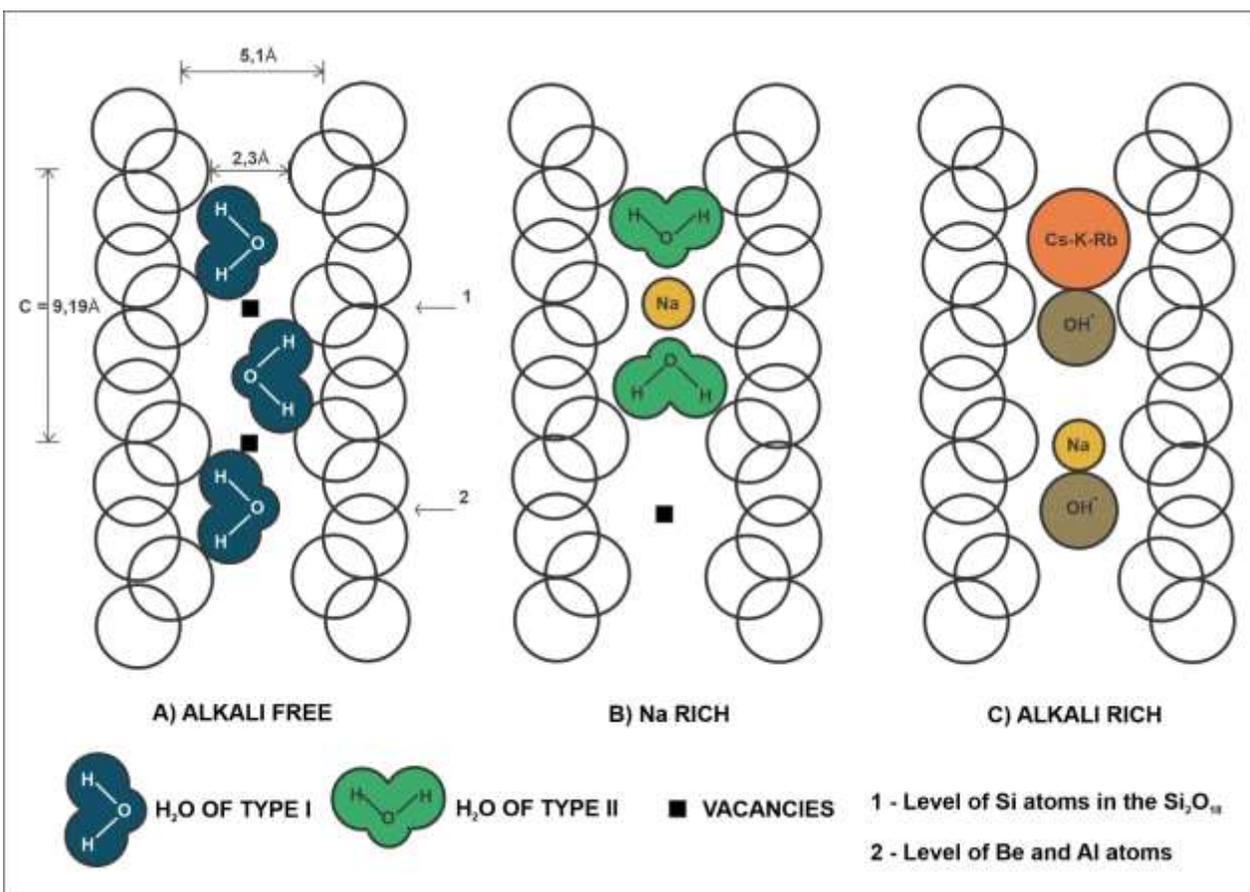

Figure 3 – Diagrams parallel to the c-axis showing the spatial positioning of the H_2O type I and H_2O type II molecules in the beryl structure.
Source: Aurisicchio et al. (1994).

3. Beryllium (Be) deposits and beryl formation.

The formation of beryl is intrinsically linked to specific geochemical factors, such as the availability of beryllium (Be), silicon (Si), and aluminum (Al) in the magma or hydrothermal fluids. In addition, the presence of other elements can determine the color and characteristics of the beryl formed; for example, chromium or vanadium can give the emerald its characteristic green color, while iron can color aquamarine blue.

Beryllium minerals are mainly found in environments associated with felsic magmatism, but they also occur in a wide variety of geological contexts, from the surface to the deep crust. The host rocks range from feldspathic to carbonate and ultramafic. The related igneous rocks are characteristically felsic, with low calcium and high fluorine concentrations, showing diversity in composition, from peraluminous to peralkaline and even undersaturated in silica. In addition, beryllium minerals are also found in metamorphic environments and are redistributed by surface processes (Barton & Young, 2002).

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Barton & Yong (2002) present the main geological environments in which beryllium deposits are found, identifying two broad categories: one linked to igneous processes and the other to processes of non-igneous origin. They expand on this classification by considering the particularities of the magma involved and the specific properties of the rocks that host these deposits.

Considering the low abundance of the element beryllium in the Earth's crust, beryl is a surprisingly common mineral in pegmatites. It is the first of the truly exotic minerals to crystallize in the LCT (Lithium-Cesium-Tantalum) rare element pegmatite evolution sequence. In the chemically simplest pegmatites (granitic composition), beryl usually forms blue-green prisms that appear first in the wall zone and inside the center of the pegmatite body. A beryl fringe is also common at the margin between the intermediate zone of blocky microcline and the quartz core, and this paragenesis persists throughout the evolution of the LCT pegmatite subtypes. Furthermore, beryl from miarolitic cavities is highly valued as mineral specimens and gem minerals (London, 2008, 2015).

Despite the scarcity of data, it has been determined that beryllium-rich pegmatites contain, on average, approximately 145 parts per million (ppm) of beryllium. London & Evensen (2002) defined a "beryllium threshold" - the minimum amount of beryllium, around 70 ppm, required in a molten mass of granitic composition to allow the formation of beryl. Starting from an initial felsic magma with 6 ppm beryllium, they proposed a process by which several phases of fractional crystallization and the separation of residual fusions could lead to the formation of beryl in pegmatites. However, this would only occur after more than 95% of the initial magma had crystallized. Thus, the occurrence of beryl in igneous formations signals an advanced process of fractionation by melting and the effective separation of residual melts.

The widely accepted genetic relationship between granites and granitic pegmatites is based on the observation that pegmatite swarms commonly occur in or around granite intrusions (Černý 1991, Černý & Ercit 2005). Some of these swarms show distinct chemical zonation, suggesting a genetic association and possibly a regional tectono-magmatic event (Figure 4).
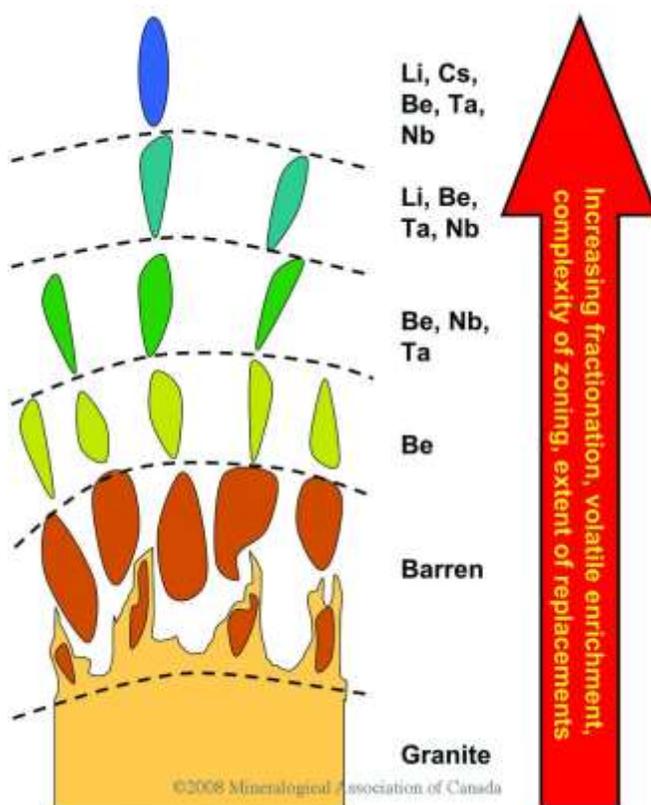

Figure 4 – Chemical evolution through a lithium-rich pegmatite group with distance from the granite source.
Source: Trueman & Černý (1982).

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4. How to calculate the formula of beryls

Minerals are identified by their physical characteristics and by techniques such as X-ray diffraction and microscopy. To analyze the composition, methods such as spectroscopy and traditional chemical analysis are used. Tools such as X-ray fluorescence (XRF), mass spectrometry (AES/MS) and scanning electron microscopy coupled with energy dispersive spectrometry (SEM-EDS) are essential for characterizing minerals and for geochemical research. The choice of technique depends on the objectives of the study, the type of sample and the resources available. Using several techniques together improves understanding of minerals, contributing to the advancement of geosciences. Let's explore the importance of the electron microprobe in this context.

Electron probe microanalysis (EPMA) is a non-destructive method that determines the chemical composition of small areas of solid materials. It uses an electron beam focused on the sample, while a spectrometer measures the X-rays generated, enabling chemical analysis. The technique can also create images of the sample by scanning the area with the electron beam, similar to how a scanning electron microscope (SEM) works. X-ray detection can be done by wavelength dispersion (WDS), which offers high resolution and better signal distinction, but requires a variety of crystals to cover the entire X-ray spectrum and imposes limitations on sample and detector positioning. Specialized EPMA equipment has spectrometers that contain several crystals, allowing precise quantitative analysis of elements down to levels as low as 100 ppm (Reed, 2005). However, EPMA has limitations, including the inability to analyze volatile (such as H_2O and CO_2) and light elements (H, F, B, Li), as well as the difficulty in determining oxidation states of certain elements (Fe, Mn, Cu) (Reed, 2005).

Before carrying out chemical analysis on mineral samples, it is crucial to examine them first. This initial examination includes looking at the samples with a magnifying glass or microscope and carrying out basic tests. It is also very important to take care with the purity of the sample. The main precautions include avoiding contamination during preparation, ensuring that the minerals are not mixed or separated correctly, checking for small inclusions or variations in the mineral's composition, and considering changes in the mineral caused by hot water, substitution of elements, exposure to radiation, among others. These steps are crucial to ensuring that the analysis results are reliable and accurate.

Determining the chemical formula of beryl through oxide analysis using electron microprobe requires a meticulous procedure. This process involves converting the percentage composition data of the oxides into molar ratios, then adjusting them to align with the mineral's unit formula, $Be_3Al_2Si_6O_{18}$. Considering the possibility of isomorphic substitution which can alter this basic composition, and the fact that the microprobe does not directly detect beryllium (Be) or water ($H2O$), these components are inferred and calculated stoichiometrically. Here is a detailed guide to calculating the chemical formula of beryl (Fig 5). In addition, a table containing the formulas corresponding to each stage of this process can be accessed and downloaded from Supplementary Material 1.

4.1 First Step: Calculating the Molecular Mass of the Oxides

The analysis begins by calculating the molecular mass of each oxide present in the sample. The molecular mass is the sum of the atomic masses of the constituent atoms. For example, sodium oxide ($Na2O$) has its molecular mass calculated by adding the atomic masses of two sodium atoms (22.99 u each) and one oxygen atom (15.99 u), giving a total of 61.97 u (atomic mass units) or g/mol. This calculation is repeated for all the oxides identified, providing the basis for subsequent analyses.

4.2 Step Two: Calculating the Molecular Ratio

Once the molecular masses have been determined, the molecular proportion of each oxide is calculated. This is done by dividing the percentage weight of the oxide (obtained from the analysis) by its molecular mass. This procedure makes it possible to quantify the contribution of each oxide to the overall composition of the sample in molecular terms.

$$Molecular\ ratio\ of\ Na_2O\ = \frac{Percentage\ weight\ of\ Na_2O}{Molecular\ Mass\ Na_2O}$$

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4.3 Step Three: Calculating the Ratio of Cations

The proportion of cations is calculated by adjusting the molecular proportions by the amount of cations in each oxide. The number of cations is multiplied by the result of the molecular proportion, which adjusts the contribution of each cation to the total composition.

Cation ratio = Molar ratio × Number of cations

4.4 Step Four: Calculating the Ratio of Anions

Similarly, the proportion of anions (in this context, oxygen) is determined by multiplying the number of oxygen atoms by the result of the molecular proportion of each oxide. This step is crucial for balancing the proportion of oxygen in the mineral formula.

Oxygen ratio = Molar ratio × Oxygen number

4.5 Step Five: Adding up the Oxygen Ratio

All the oxygen ratio values are added together to obtain the total oxygen present in the sample. This value is essential for the subsequent steps that seek to normalize the mineral formula.

4.6 Step Six: Calculating the Oxygen Factor

The general formulation of beryls contains 18 oxygens. To normalize the proportion of cations in relation to these 18 oxygens, the "oxygen factor" is calculated by dividing 18 by the total proportion of oxygen obtained in the previous step.

$$Oxygen\ factor = \frac{18}{\Sigma\ oxygen\ ratio}$$

4.7 Step Seven: Cation Normalization

Multiplying the column of cations by the oxygen factor gives the proportion of cations based on 18 oxygens, normalizing all the cations in the formula for a direct comparison with the theoretical formulation of beryls.

Number of cations (apfu)= ratio of cations × oxygen factor.

4.8 Note on BeO

Specifically for beryllium oxide (BeO), it is considered necessary to adjust the analysis to reflect 3 apfu (atoms per unit formula) of Be, as indicated in line 85 of supplementary material 1. This implies adjusting the percentage values of BeO, which vary between 11 and 15%, to ensure consistency with the defined parameters.
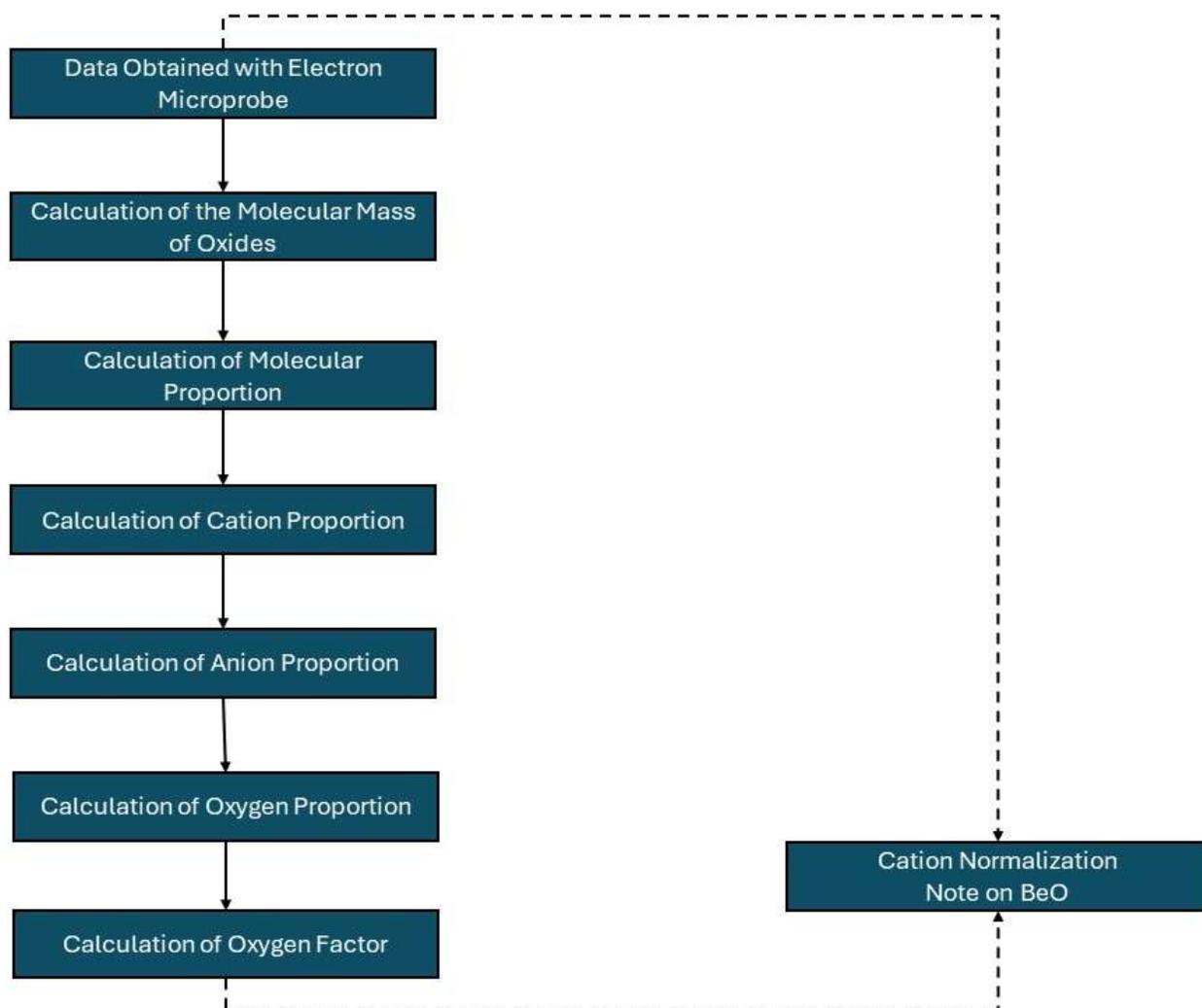
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Figure 5 – Step-by-step flowchart for calculating the beryl formula based on electron microprobe analysis.
Source: Authors (2024).

5. What the minor and trace elements in beryls tell us about pegmatites

As the crystallization of a magma progresses, the distribution of trace elements changes significantly. Whether these trace elements become more concentrated in the remaining magma or distributed throughout the minerals that form depends mainly on how well these elements fit into the minerals compared to the magma, which changes with temperature. Instead of looking at trace elements in isolation, petrologists and geochemists examine the ratios between them as a way of understanding how magma separates and evolves chemically quimicamente (London & Evensen, 2002; Uher et al., 2010). Variations in Fe, Na, Li and Cs contents in beryl are measures of fractionation within rare element pegmatites. From a petrological point of view, caesium is the most interesting and useful of the trace elements sequestered by beryl; few other minerals record Cs accumulation at easily measurable values (London, 2008, 2015).

Černý (1975) established a new classification for beryl, modifying the one proposed by Beus (1966), based on the variation in the alkali content present in its crystal structure, thus dividing it into five types, described in Table 2.

Table 2 – Classification of beryl types according to the concentration of alkali in their structure.

Type of Beryl	Classification	Alkali concentration (% by weight)	General characteristics
1	Alkali-free beryl	Total alkali contents < 0,1	occurs mainly in small cavities of dominantly graphite, or in pegmatite bands and pockets in granites
2	Potassium and sodium-potassium beryl poor in alkali	K contents between 0,5 e 1,0	It occurs in pegmatite bands and pockets in granites and in the quartz cores of "simple" pegmatites
3	Sodium beryl	Na contents between 0,5 e 1,0	Occurs in pegmatites with albitic paragenesis, but very poor in rare alkalis
4	Lithiniferous sodium beryl	Na contents between 0,0 e 2,0 Li contents reaching a 0,6 Low levels of Cs	Occurs in Li-bearing pegmatites
5	Cesium-lithiniferous beryl	Cs contents > 0,5 High concentrations of Na and Li	It occurs in Li-rich, extremely differentiated pegmatites, often bearing pollucite and with late units rich in lepidolite

Fonte: Černý (1975).

According to Kahwage & Mendes, (2005) beryl can be chemically subdivided into alkaline and non-alkaline, based on the Li, Cs and Rb contents that are placed in its structure through isomorphic substitutions or by filling open channels. In differentiated pegmatites, the alkali content in beryl is much higher than in crystals from poorly differentiated pegmatites. However, iron in these specimens shows the opposite behavior to alkalinity, being more concentrated in the non-alkaline specimens of poorly differentiated pegmatites.

Information about the beryl's habit can also be obtained from its alkalinity; beryls poor in alkali form prismatic crystals. The prismatic habit appears in the final stage of pegmatite evolution. In addition, alkaline substitution in Be-tetrahedrons causes lateral growth (Černý et al., 2003). Thus, the transition from a prismatic pattern to a tabular pattern with alkali-rich beryl reflects the hydrothermal process in the final stage of pegmatite evolution, this occurs with the accommodation of alkaline elements such as Li, Na, K, Rb and Cs and the substitution of Be^{2+} and Li^+ in the beryl structure along the c-axis (Černý et al., 2003; Wang et al., 2009).

When positioned on the refractive index versus alkali content diagram, beryl can show differences due to variations in Li^+, Cs^+ and Na^+ content (Sinkankas & Read, 1986). According to Kahwage & Mendes (2005), beryls with a flattening along the c-axis exhibit the highest refractive index values. This is due to Li^+ being replaced by Be^{2+} in the tetrahedral site and charge compensation by alkalis with large ionic radii, such as Cs+ and Rb+, in the channels. These cations cause electrostatic repulsion between the channels, hindering growth along the c-axis and altering both the structure and the optical properties of this mineral (refractive index).

Černý (1975) carried out a quantitative analysis of the alkaline contents in beryl, proposing that the relationship between the Na/Li and Cs contents could reflect the degree of evolution and fractionation in the last generations of beryl associated with different types of rare element pegmatites. This proposal was visually represented by Trueman & Černý (1982) (Figure 6), in which pegmatites are classified into four distinct categories: A) Barren pegmatites, characterized by the presence of Be, Nb, Ta and low content of rare alkalis; B) Pegmatites rich in Be and rare alkalis; C)Pegmatites containing spodumene; and D) Pegmatites with mineralizations rich in Li, Rb, Cs, Be and Ta.
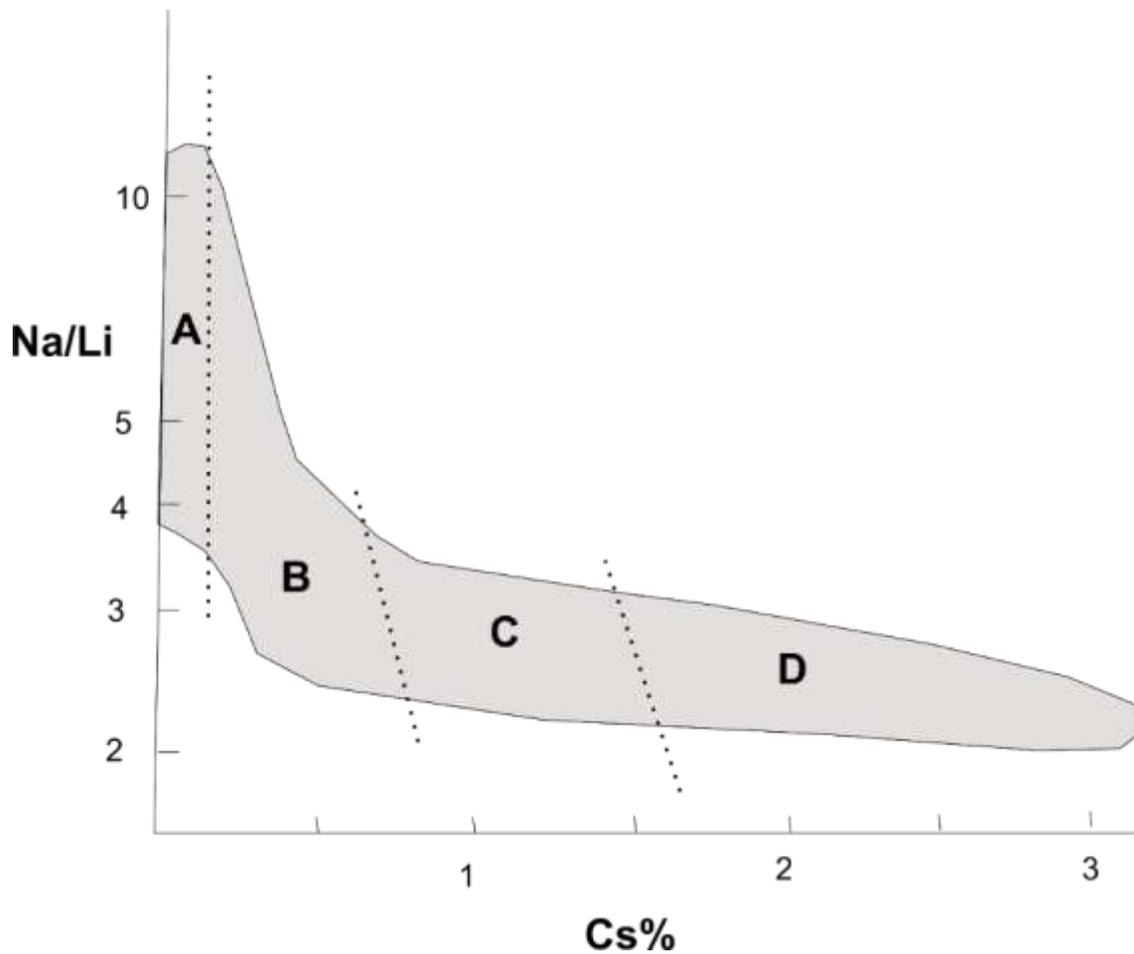
Figure 6 – Classification of pegmatites based on chemical analysis of beryls.
Source: Trueman and Černý (1982).

According to Černý et al. (1985), in a fertilized system, there is a gradual increase in lithophile rare earth elements (RTEs) throughout the crystal fractionation process, which extends from granite to pegmatite. Rare alkaline elements such as Rb and Cs, together with high field strength elements (HFSE) such as Nb and Ta, as well as certain ratios such as Rb/Sr, Nb/Ta and Zr/Hf, are considered crucial indicators of this granite fractionation. They can also signal proximity to a parent body of granite. It has been observed that highly differentiated granites have low Nb/Ta and Zr/Hf ratios (Dostal & Chatterjee, 2000). It can be seen that the most differentiated (or most evolved) pegmatites are located distally from the parent granite, while the least differentiated (or least evolved) are located proximally. Thus, distance from the parent magma can be a determining factor in the degree of pegmatite differentiation (Steiner, 2019).

Barton & Young (2002) compared the composition of various Be-bearing host rocks on the basis of alkaline components, silica and alumina in total alkali, adapting Wilson's (1989) compositional division of alkaline and subalkaline (Figure 7).
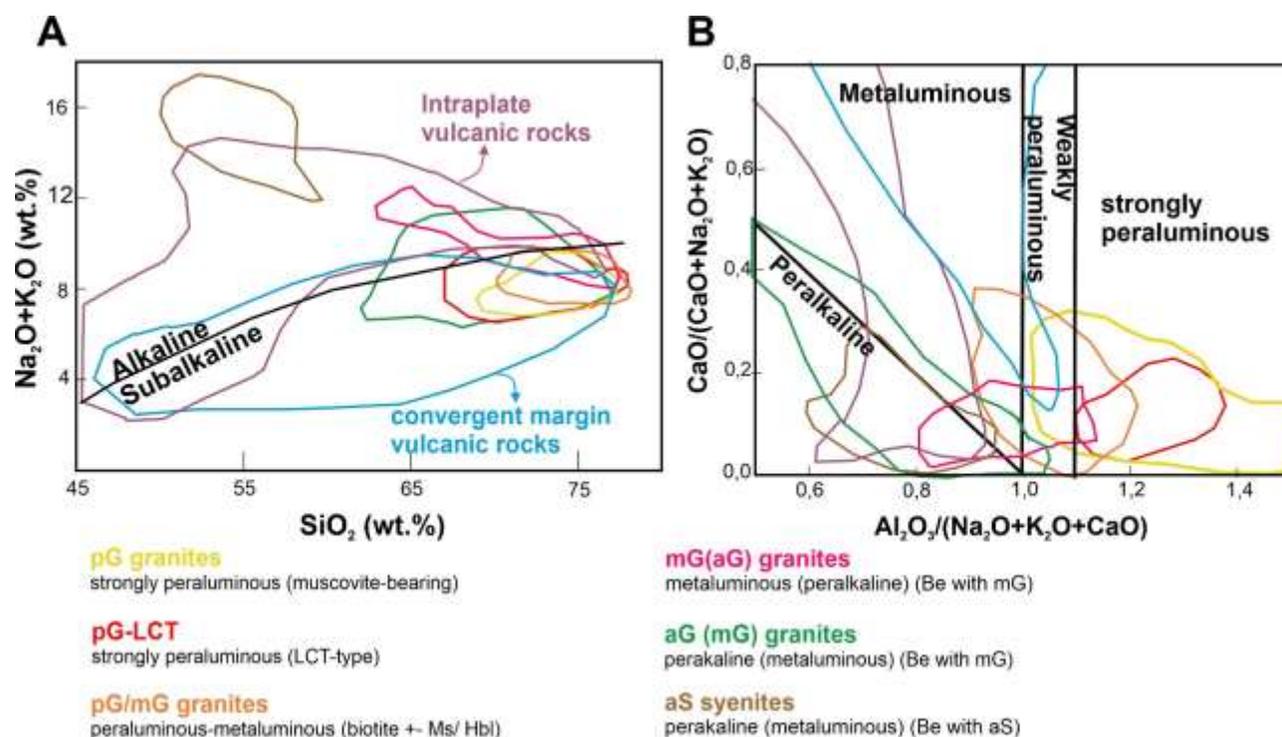
Figure 7 – a) Total alkali vs. silica graph with whole rock chemical data fields selected from Be deposits (Barton; Young, 2002). The compositional division of alkaline and subalkaline is from Wilson (1989). (b) Graph CaO/(Na2O + K2O + CaO) vs. Al2O3 /(Na2O + K2O + CaO) (% by weight) with projection of composite data from Be deposit (Barton; Young, 2002). PG-LCT = LCT type; PG = strongly peraluminous; PG/MG = peraluminous granite; MG (AG)= metaluminous granite; AG (MG) = peralkaline; (AG) = peralkaline syenites.
Source: Authors (2024).

Barton & Young (2002) classified beryllium-bearing igneous rocks into four categories, taking into account the levels of Al_2O_3 and SiO_2: (1) from strong to moderate peraluminous, grouped in the BeO-Al_2O_3-SiO_2-H_2O (BASH) family; (2) from metalluminous to slightly peraluminous, with varying enrichments of Nb, Ta, F, Sn, Mo and Li - these have minerals from the phenacite, bertrandite and helvite group; hydrothermal alteration of Li-Fe micas is characteristic; (3) peralkaline to metaluminous, with quartz saturation and rich in Nb-Y-F, with phenacite, bertrandite and Ca-Na-Be silicates; feldspathic hydrothermal alteration is characteristic; (4) peralkaline (undersaturated quartz), characterized by a high concentration of Nb-ETR-Y together with Ca-Na-Be silicate and helvite group minerals; feldspathic hydrothermal alteration is characteristic.

Merino et al. (2013) conducted a detailed analysis of the co-occurrence of gahnite, chrysoberyl and beryl as accessory minerals in a highly evolved peraluminous pluton, specifically the Belvís de Monroy leucogranite, located in Cáceres, Spain. In their study, the authors used the Na_2O versus FeO diagram (expressed as a percentage by weight) (Figure 8) as a key analytical tool to infer the possible origins of the beryls examined. This diagram was drawn up on the basis of beryl analyses previously carried out by Uher et al. (2010), thus enabling a more in-depth comparison and interpretation of the potential sources of these minerals in the geological context of the pluton studied.
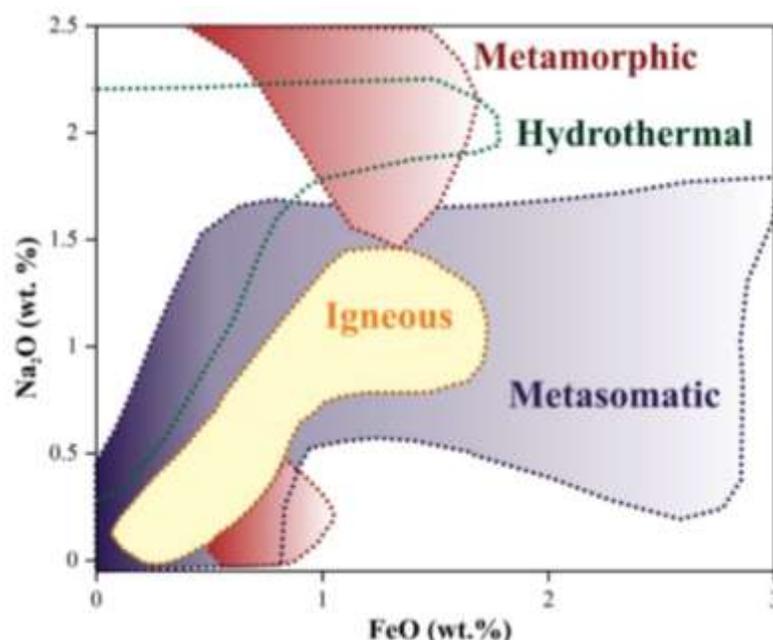
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Figure 8 – Diagram of Na2O vs. FeO (in weight%). The composition of beryl from other global tectonic contexts has been plotted for comparison, as well as the magmatic trend found in other magmatic beryl crystals.
Source: Merino et al., (2013).

6. Conclusions

The association of beryls with non-emerald-bearing pegmatites has significant petrogenetic implications, which provide information about the formation of the beryls and the geological conditions of their host environments, the pegmatites. The implications include:

- Pegmatites are intrusive bodies that crystallize from granitic or alkaline magmas under conditions of low cooling speed, allowing the growth of large crystals. The presence of beryl in these environments suggests that beryl-forming elements, such as beryllium (Be), were available in the final stages of magma crystallization. However, the absence of emerald indicates that the environment lacked chromium (Cr) or vanadium (V), the elements needed to give emerald its characteristic green color.

- The formation of beryl in pegmatites suggests a magma with a specific composition, rich in silica and alkaline elements, but poor in chromophore elements. This reflects the differentiation of the magma, where the lighter and more incompatible elements, such as Be, are concentrated in the residual liquid phases.

- The beryllium needed to form beryl can be derived from deep magmatic sources or from metasedimentary rocks that have undergone anatexis (partial melting) processes.

- Beryls in pegmatites can form in more stable tectonic environments, where differentiated magma can intrude and crystallize into large pegmatitic bodies.

- The formation of beryl in pegmatites indicates processes of magmatic enrichment and differentiation that allow Be to be concentrated in residual solutions. The transition from a prismatic to tabular habit is indicative of an increase in alkalis, the result of a hydrothermal process in the final stage of the pegmatite's evolution.

Acknowledgements

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