Apatite Geochemical Characteristics for Mineralization in Granitic Pegmatite-Type Lithium Deposits

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Abstract: Granitic pegmatite-type lithium deposits are a crucial source of lithium resources, with their mineralization temporally coupled with the convergent orogenic processes of supercontinents, primarily occurring in the middle to late stages of these tectonic events. In China, most identified granitic pegmatite-type lithium deposits are located in the western regions, where they were formed in post-collisional tectonic environments of the Paleozoic era, with mineralization periods extending into post-orogenic tectonic settings. Apatite, a widely present accessory mineral in granite, holds significant value for understanding pegmatite evolution and mineralization, as its trace-element composition can record and preserve evidence of magmatic and hydrothermal activity. This study takes apatite from the Zhawulong and Koktokay granitic pegmatite-type lithium deposits as examples to explore the influence of magmatic oxygen and hydrothermal activities on the mineralization of pegmatite-type lithium deposits during diagenesis and mineralization. The findings indicate that the geochemical characteristics of apatite effectively serve as indicators for the mineralization processes of granitic pegmatite-type lithium deposits.

Keywords: Apatite; Geochemistry; Granitic pegmatite; Lithium deposit

1. Introduction

With the rapid development of strategic emerging industries, rare metals and other critical metal resources have become increasingly indispensable. As one of the globally strategic critical metals, lithium is vital, with granitic pegmatite-type lithium deposits serving as an important source of lithium resources. The metallogenic fluid characteristics and genetic mechanisms of these deposits are currently a research focus in global metallogeny. Granitic pegmatites are classified into LCT (Li-Cs-Ta), NYF (Nb-Y-F), and LCT+NYF types. Among these, LCT-type pegmatites are enriched with rare elements, including Li, Rb, Cs, Be, Ga, Sn, Ta, Nb, and fluxing agents such as B, P, and F, and are commonly associated with late-orogenic and post-orogenic S-type granites in extensional tectonic settings. Previous studies on the spatiotemporal distribution of pegmatite-type lithium deposits worldwide have shown that the mineralization periods of these deposits coincide with the convergent orogeny of supercontinents, primarily occurring in the middle to late stages of such tectonic processes. Comprehensive studies on the metallogenic characteristics, distribution, research progress, and exploration potential of lithium deposits in three typical pegmatite-type lithium belts in Western China-West Kunlun, Western Sichuan Songpan-Ganzi, and Altay-have suggested that the coupling relationships among tectonic, magmatic, metamorphic, and metallogenic processes are critical scientific issues controlling lithium mineralization and enrichment patterns [1].

2. Temporal and Spatial Distribution of Granite-Pegmatitic Lithium Deposits

The formation of granite pegmatite-type (LCT) lithium deposits is closely coupled with the timing of supercontinent assembly driven by collisional orogenesis in globall. The peak formation times of LCT pegmatite lithium deposits are 2825 Ma, 2625 Ma, 2075 Ma, 1875 Ma, 975 Ma, 525 Ma, and 275 Ma. Previous studies have shown that the frequency and temporal distribution of LCT pegmatites globally correspond to the supercontinent assembly events of Kenor, Nuna, Rodinia, Gondwana, and Pangea [1]. Most LCT pegmatite lithium deposits form during the middle to late stages of supercontinent convergence and orogeny, typically lagging behind tectonic deformation. Although global LCT pegmatite lithium resources are abundant, they display significant heterogeneity in terms of time, space, and tectonic settings. LCT pegmatites are generally closely associated with the modification or exposure of deep continental crust in high-grade metamorphic terranes. Numerous examples of the relationship between LCT pegmatites and high-grade metamorphic terranes can be found worldwide, such as the Neoproterozoic granulite belt in northern Scotland, the Archaean-Proterozoic greenstone belts in Canada, Africa, and Australia, and the Phanerozoi cmountain belts, particularly the European Variscan fold belt extending into the New England Province of North America along the Alleghanian orogeny [1,2].

3. Temporal and Spatial Distribution and Mineralization of Pegmatite in China

Previous research has shown that discovered lithium pegmatite deposits (spodumene type) in China are primarily located in the western regions, while the eastern regions are dominated by granite-type (lepidolite) lithium deposits. Most of China's known pegmatite lithium deposits formed in Paleozoic post-collisional tectonic settings, with mineralization periods extending into post-collisional orogenic environments [3]. The element combinations in these deposits largely exhibit characteristics of LCT-type pegmatites, with Late Indosinian deposits representing the majority in terms of both quantity and resources. China lithium pegmatite deposits are spatially concentrated and distributed across nine rare metal metallogenic belts: Altay, West Kunlun–Karakoram, Songpan–Garze in western Sichuan, East Tianshan, East Qinling, Altyn, northern Qaidam margin, Jiangnan, and southern Tibet in the Himalayas [4].

The Zhawulong-Caolong rare metal deposit spans the counties of Shiqu in Sichuan and Yushu in Qingha. The exposed strata mainly consist of Triassic Xikang Group rocks, covered by Quaternary deposits at over 50% of the surface. The deposit's exposed plutons are muscovite granites intruding into the Xikang Group strata along the Zhawulong Anticline in an irregular spindle shape, covering approximately 58 km². The upper portion of the pluton locally retains remnants of the Xikang Group wall rock. This is a typical granite pegmatite rare metal deposit with geological characteristics similar to the Jiajika rare metal deposit found within the orogenic belt [5]. The Altai region in Xinjiang is one of the largest and most significant pegmatite provinces worldwide, with over 100,000 pegmatite dikes identified across an area of approximately 20,000 km². Concentrated within the Central Altai and Qiongkur terranes in a NW-SE orientation, this area also includes the famous Koktokay No. 2 pegmatite field, which covers about 110 km² [3]. Thus, this study focuses on the geochemical characteristics of apatite within the Zhawulong granitic pegmatite deposit in western Sichuan and the Koktokay pegmatite-type lithium deposit in Xinjiang to explore the application of apatite in lithium pegmatite deposit exploration [6].

Current mainstream theories propose two main formation mechanisms for granite pegmatites: fractional crystallization of granitic magma and partial melting of ore-bearing material from the lower crust or mantle (deep melting). Fluid immiscibility and compositional purification are important processes for the further enrichment of rare metals during the magmatic-hydrothermal evolution. In the formation of granite-pegmatite-type rare metal deposits, the metallogenic fluids typically become enriched in volatile components (such as B, P, F, and H2O) and metallogenic elements. These fluids are characterized by low viscosity, low nucleation rates, high element solubility, and strong mobility, which contribute significantly to the transport and concentration of rare metals [7]. Regardless, it is clear that magmatic differentiation and hydrothermal alteration play pivotal roles in the formation of granite pegmatite-type rare metal deposits. Apatite, a widespread accessory mineral in granites, can capture and preserve information on magmatic and hydrothermal processes. In the first model, highly fractionated granitic melts remain after granite crystallization, concentrating near the upper parts of the pluton and forming pegmatite veins that intrude surrounding rock fractures and faults. Such LCT-type pegmatites generally appear within a 10 km radius from the rare-metal-bearing granite, with the degree of differentiation, rare element concentration, volatile content, and zonal complexity increasing with distance from the granite source rock [8,9].

4. Geochemical Characteristics of Apatite in Pegmatite

Apatite, as an accessory mineral, is widely distributed in various types of igneous, metamorphic, and sedimentary rocks, displaying high stability across geological processes. Apatite demonstrates notable stability under metamorphic and hydrothermal conditions [9]. The trace element composition of apatite can provide insight into the redox state of magma, its formation environment, and source characteristics. The F and Cl content in apatite varies based on the environment in which it was formed [10]. Apatite's geochemical characteristics are valuable for understanding the evolution of granite pegmatite and the processes of crystallization and mineralization. The Th/U ratio in apatite, for example, can reflect the fluid activity during magma formation, as apatite subjected to intense fluid interactions often exhibits lower Th/U ratios. Apatite found in Rb-rich pegmatites typically contains higher MnO and Cl levels, along with a lower F/Cl ratio [10]. Furthermore, the geochemical characteristics of elements like Na, Si, S, Mn, Sr, U, Th, and rare earth elements (REE) in apatite can provide information about its source rock [11].

Research shows that the chemical composition of apatite is influenced not only by the host magma composition but also by the processes of magma crystallization and the interaction with hydrothermal fluids [12]. Belousova (2002) [12] observed that the continual decrease in Sr content within apatite correlates with early fractional crystallization of plagioclase during magma evolution. Prowatke and Klemme (2006) [13] experimentally demonstrated that elements such as rare earth elements (La, Ce, Pr, Sm, Gd, Lu), Y, Sr, U, and Th are compatible in apatite, with Th being more compatible than U in silicate and carbonate melt systems, while large lithophile elements (Cs, Rb, Ba) are strongly incompatible in apatite. Therefore, Sr content in apatite is considered an important indicator of magma evolution. A distribution coefficient of approximately 0.69 was empirically established for Sr in magma evolution through linear fitting, with Sr content in highly fractionated granites and granite pegmatites typically below 100 ppm. Significant changes in Sr content in apatite reflect the melt evolution from high Sr to low Sr content [13]. Many researchers now focus on using Eu anomalies in hydrothermal minerals to infer oxygen fugacity in fluids [14]. Macrae (1992) [15] found that crystal fractionation in apatite also enhanced positive Eu anomalies in the melt, influenced not only by plagioclase and monazite fractionation but also by magma oxygen fugacity. A negative Eu anomaly in apatite indicates the presence of Eu^{2+}, reflecting a reduced environment, whereas a positive Eu anomaly suggests an oxidizing environment. Thus, the Eu anomaly in apatite is often interpreted as a proxy for magma fO_2 [12].

In the Zhawulong and Koktokay pegmatite-type lithium ore veins, apatite exhibits a marked decline in Sr content (Figure.1), indicating that the fractional crystallization of the melt primarily governed the Sr distribution in apatite during mineralization. During the mineralization process, the total REE (rare earth elements) content of some apatite in Koktokay is notably lower than that of Zhawulong apatite (Figure.1a), which could be attributed to two factors: (1) the presence of REE-rich minerals in Koktokay, such as monazite, zircon, garnet, apatite, and titanite, which competed with apatites for REEs in the melt during crystallization. These REE-rich minerals crystallized extensively during the granite melt stage, consuming substantial REEs from the melt and thereby contributing to the low REE content in apatite during the pegmatitic stage; (2) hydrothermal alteration affecting apatite in the later stages of formation. Eu and Ce, two elements with distinct properties, show opposite distribution characteristics in apatite under varying oxidation states. Results in Figure.1b and Figure.1d reveal that the initial melt in both Zhawulong and Koktokay granite pegmatites was characterized by a reducing nature. In Zhawulong, as Sr content decreased, the Eu/Eu* ratio in apatite showed an upward trend, while the Ce/Ce* ratio decreased. Some apatite samples in Zhawulong maintained a constant Eu/Eu* ratio. In contrast, in Koktokay, despite a significant reduction in Sr content, the Eu/Eu* and Ce/Ce* ratios in apatite remained relatively stable. Additionally, the Ce/Yb ratio in Zhawulong apatite increased considerably (Figure.1c), while no significant change was observed in Koktokay apatite. The Th/U ratio of Zhawulong apatite remains constant despite increasing Rb/Sr ratios, whereas the Th/U ratio in Koktokay apatite shows a marked increase. This observation suggests that Koktokay apatite is of hydrothermal origin, while Zhawulong apatite is of magmatic origin (Figure.1f). The REE distribution patterns (Figure.1e) show that Zhawulong apatite exhibits a distinctive "M"-shaped tetrad effect, with some samples depleted in heavy REEs (HREE) and enriched in elements such as Ce, Nd, Sm, Tb, and Dy. This REE enrichment likely reflects more pronounced differentiation and elemental enrichment experienced by the magmatic-fluid phase, indicating that the REE enrichment resulted from the intensified differentiation and enrichment within the magmatic-fluid system. In contrast, Koktokay apatite displays a pattern of light REE (LREE) enrichment and HREE depletion, suggesting that HREE-rich minerals co-crystallized during its formation. In conjunction with previous research findings, the variations in the Eu/Eu* and Ce/Ce* ratios in Zhawulong apatite can be attributed to shifts in the system's oxygen fugacity. These changes in oxygen fugacity likely occurred as the pegmatitic melt, separating and migrating from granite, transitioned from a relatively closed to a relatively open structural environment. This transition facilitated the escape of reducing components such as H_2, increasing the system's oxygen fugacity and altering the Eu/Eu* and Ce/Ce* ratios in Zhawulong apatite. Conversely, during the crystallization of Koktokay pegmatite, there was no significant change in the oxygen fugacity of the hydrothermal system. As magmatic evolution progressed, the REE content in Zhawulong apatite decreased, indicating an increase in late-stage volatiles, including H_2O, within the melt. This suggests that Zhawulong apatite was metasomatized by F-rich fluids exsolved during the late magmatic-hydrothermal stage.

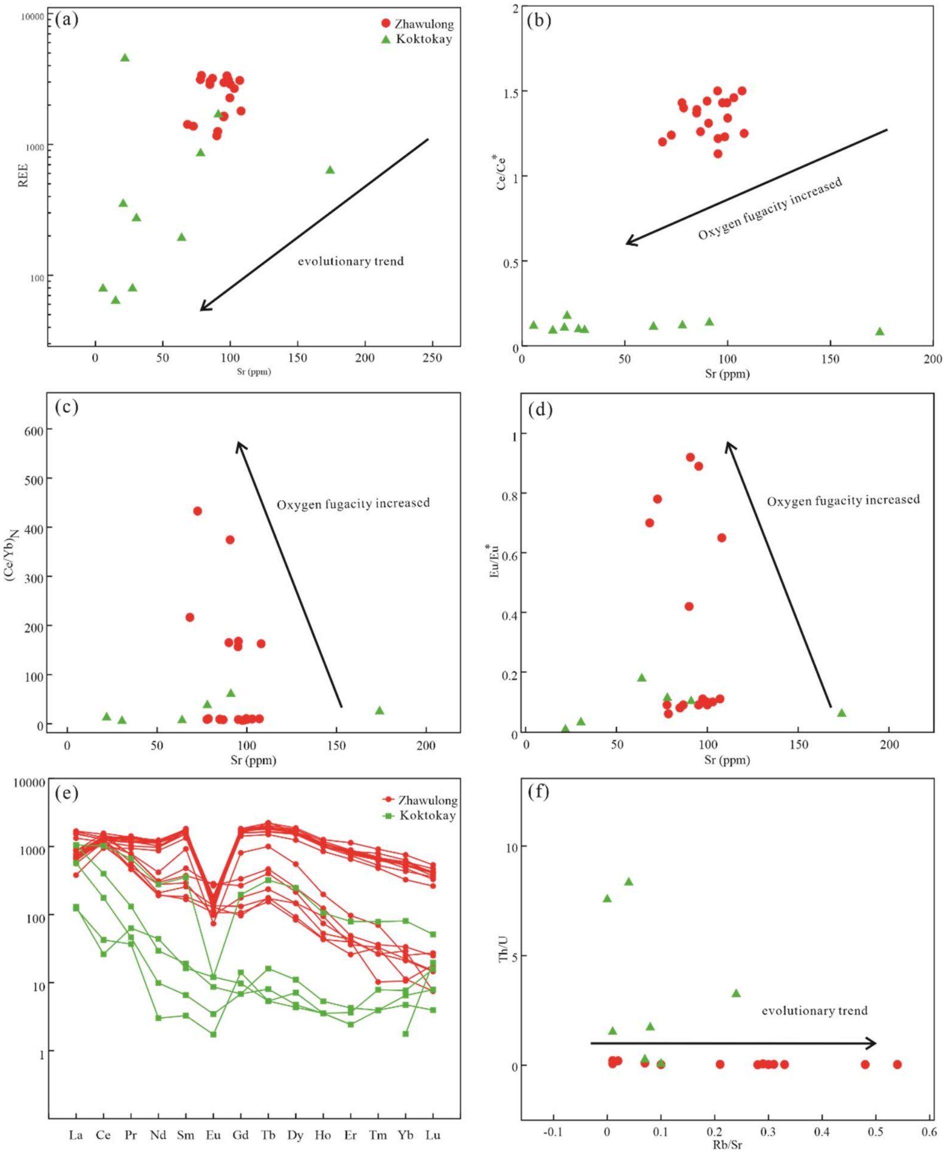

Figure 1: Diagram of Apatite Trace Element Diagram from Zhawulong Lithium Mine and Koktokay Pegmatite Deposit.

5. Conclusion

The formation of global LCT (Lithium Cesium Tantalum) granite pegmatites is closely linked to the assembly of supercontinents, with a strong relationship to the metamorphism or exposure of the deep continental crust in high-grade metamorphic terranes. In China, granite pegmatite-type (spodumene) lithium deposits are primarily distributed in the western regions, mainly formed under a Paleozoic post-collisional tectonic environment, with mineralization continuing into post-collisional orogenic environments.

The trace element characteristics of apatite in pegmatites can provide valuable information about fluid alteration and magmatic evolution during mineralization. The Sr content in apatite decreases during the mineralization process, while the Rb/Sr ratio increases and the REE content shows a downward trend. The rare earth element distribution diagram exhibits an "M"-shaped quadripartite effect and negative Eu anomalies. In the lithium deposits of Zhawulong and Koktokay, the trace element characteristics of apatite indicate that the former experienced intense fluid exsolution and significant changes in magmatic oxygen fugacity during its formation, whereas the latter also underwent fluid exsolution during mineralization, but with little change in magmatic oxygen fugacity.

Therefore, a positive correlation between the REE and Sr content in apatite, the appearance of the "M"-type tetrad effect in the REE distribution diagram, and significant variations in the Eu/Eu* and Ce/Ce* ratios suggest that the magmatic-hydrothermal system of the apatite underwent high differentiation, changes in oxygen fugacity, and late-stage fluid exsolution. These processes are crucial for the formation of granite pegmatite-type deposits. Hence, the trace element characteristics of apatite have significant implications for the exploration and prospecting of granite pegmatite-type lithium deposits.

Funding

(1) Scientific Research Fund of Hunan Provincial Education Department (NO. 23B0953).
(2) Open Research Fund Program of Hunan Mine Carbon Sequestration and Sink Enhancement Engineering Technology Research Center (NO. 2024KSGTZH01).

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