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Primary rare earth element enrichment in carbonatites: evidence from melt inclusions in Ulgii Khiid carbonatite, Mongolia

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Abstract

Carbonatites are abundant in the rare earth elements (REE), and they host the most important REE resources in the world. However, the mechanisms that concentrate these elements during carbonatitic magmatic processes are still poorly constrained. Here, we report the occurrence of apatite-hosted melt inclusions from the Ulgii Khiid carbonatites, Mongolia, and use these to reconstruct the evolution of REE concentrations and patterns in early, primary carbonatite magma. The melt inclusions consist of a varied polycrystalline assemblage of daughter minerals, including calcite, diopside, phlogopite, magnetite, pyrite, monazite, parisite, and a phosphate glass which is remarkably enriched in REE. Heating-quenching experiments show that the homogenization temperatures of the inclusions are above 1200 °C and produce three immiscible liquid phases (i.e., phosphate-, silicate-, and Fe-silicate-melt). The phosphate melt has much higher REE content than the silicate melts. We, therefore, suggest that the melt inclusions trapped a REE-, P- and silicate-enriched carbonate melt produced via carbonate-silicate liquid immiscibility. During this process, both REE and P preferentially incorporated into the carbonate melt. With subsequent crystal fractionation of REE- and P-poor carbonate and silicate minerals, the separated carbonatitic melt becomes P-REE-saturated, forming REE minerals and an immiscible REE-rich phosphate melt. The phosphate melt is highly efficient at concentrating REE during the immiscibility process and plays a crucial role in controlling the REE budget in the P-rich carbonatite magmas.

Keywords: carbonatite; melt inclusion; REE, phosphate; immiscibility; mineralization;

Ulgii Khiid

1. Introduction

Carbonatites are igneous rocks dominated (>50 modal %) by carbonate minerals. They form essential repositories of many “critical metals” (e.g., REE and Nb, etc.), which are vital to the development of new energy technologies. Presently, the dominant REE resources in the world’s market come from carbonatite-hosted REE deposits (Chakhmouradian and Wall, 2012; Liu and Hou, 2017; Song et al., 2016) and the demand for REE is expected to multiply over the next decade (Weng et al., 2015). Though carbonatites are well known to be enriched in REE, the processes that concentrate these elements to an economic level (wt. %) are still poorly constrained. REE mineralization in carbonatites can be of magmatic origin, and, in most cases, there is evidence of hydrothermal re-mobilization of primary formed REE-bearing minerals (e.g., carbonates, burbankite, apatite, and monazite; Wall and Mariano, 1996; Chakhmouradian and Wall, 2012; Downes et al., 2014; Trofanenko et al., 2016; Song et al., 2018 and references therein). Therefore, pre-enrichment of REE in igneous carbonatite is the prerequisite for a carbonatite system to form high-grade REE ores.

Carbonatites are rich in salt components such as sulfate, phosphate, fluorine, and chlorine (Chakhmouradian et al., 2017; Doroshkevich et al., 2010; Jago and Gittins, 1991; Kamenetsky et al., 2015). Multiphase silicate-carbonate-salt (fluoride, sulfate, phosphate and chloride) immiscibility has been proposed to play a significant role in petrogenesis of the carbonatites and to have role in controlling their diversity (Andreeva et al., 2007; Andreeva and Kovalenko, 2003; Panina, 2005; Panina and Motorina, 2008; Fulignati et al., 2011; Potter et al., 2017). However, few studies focus on the role of such salt melts in

the formation of REE mineralization. Recently, Kynický et al. (2018) suggested that preferentially partitioning of the REE into the carbonate-fluoride fraction separated from a carbonated silicate melt was the principal ore genetic mechanism for the formation of the Lugiin Gol REE deposit in Mongolia. Besides fluoride, phosphate is another essential component usually enriched in carbonatites. Both experimental (Baker and Wyllie, 1992; Ryabchikov and Hamilton, 1993) and melt inclusion (Andreeva and Kovalenko, 2003; Guzmics et al., 2008a, b) investigations show that the P_2O_5 contents of carbonate melts are relatively high, ranging from 5 to 24 wt. %. Moreover, both monazite and apatite are the dominate phosphate minerals in carbonatites, and the latter also can host a significant amount of REE (up to ~15 wt. % REO, Enkhbayar et al., 2016), indicating that phosphorus may be critical in controlling fractionation of the REE in carbonatites.

Southern Mongolia is one of the most important polymetallic ore areas in Central Asia (Enkhbold et al., 2007; Pavlova et al., 2009; Pirajno et al., 2009). Magmatism and mineralization are widely developed in the area. REE mineralization is closely related to carbonatite-alkaline complexes (Nie et al., 2010; Baatar et al., 2013; Vladykin et al., 2013). Here, we report an investigation of REE-P-rich melt inclusions hosted by apatite from the Ulgii Khiid carbonatite-syenite complex, Southern Mongolia. The composition of the daughter minerals and quenched immiscible melts after heating of the melt inclusions had been determined using both the scanning electron microscope with energy dispersive spectrometer (SEM-EDS) and electron microprobe analysis (EMPA) methods. Based on these results, we present a model for the REE enrichment and evolution of the studied carbonatitic melts and highlight that the presence of phosphate melt can be significant in

controlling the REE contents of the carbonatite magmas.

2. Geologic background

The southern Mongolian alkaline province is well known for many alkaline-carbonatite volcano-plutonic complexes and associated REE and rare metal deposits (e.g., Lugiin Gol, Mushgai Khudag, Bayan Khoshuu and Ulgii Khiid, Baatar et al., 2013). Geologically, Mongolia is divided into northern and southern domains by the main Mongolian lineament (Fig. 1a, b). The alkaline-carbonatite complexes are mainly distributed within the area of Southern Mongolia. Southern Mongolia is dominated by Lower to Middle Paleozoic arc-related volcanic and volcanoclastic rocks, followed by ophiolite remnants, Silurian and Devonian limestones, as well as terrigenous and volcanoclastic rocks (Badarch et al., 2002). The alkaline-carbonatite complexes occur along the Gobi-Tien Shan fold belt and controlled by east-west faults formed in a continental rift environment (Fig. 1b). Mushgai Khudag (MKC) and Bayan Khoshuu (BAK) occur along the main Mongolian lineament, and Lugiin Gol (LG) and Ulgii Khiid are along the Sulinkheer suture zone (SKSZ). The southern part of the Sulinkheer zone is dominated by the Paleozoic ophiolitic rocks, whereas the northern is covered by the Late Paleozoic sediments (Baatar et al., 2013 and therein references).

The alkaline-carbonatite complexes are mainly potassic syenite volcanic and plutonic rocks and carbonatite dykes or veins (Baatar et al., 2013). According to the previous chronological studies (Samoylov, and Kovalenko, 1983; Baatar et al., 2013; Yarmolyuk et al., 2015), most of these complexes were formed during the Late Paleozoic-Early

Mesozoic (e.g., Lugiin Gol: ~244Ma, Baatar et al., 2013) and Late Mesozoic (e.g., Mushgai Khudag: ~138Ma and Bayan Khoshuu: ~134Ma, Baatar et al., 2013; Ulgii Khiid: 147-158Ma, Samoylov, and Kovalenko, 1983). However, the genesis and tectonic environment of these complexes remain controversial. Many studies have suggested that melting could have been triggered either by a mantle plume, or by upwelling of hot asthenospheric mantle materials following post-collisional delamination (Kovalenko et al., 2004; Yarmolyuk et al., 2004; Vladyskin, 2009; Kuzmin and Yarmolyuk, 2014). It was also proposed that the alkaline-carbonatite complexes originated from enriched sources similar to EMII which should occur within post-collisional arc tectonic settings (e.g., Gerel et al., 2005).

The Ulgii Khiid carbonatite-alkaline complex is located at the southeastern side of the Gobi-Tien Shan fold belt and along the Sulinkheer suture zone (SKSZ) (Fig.1b). The complex intrudes into a Lower Carboniferous volcano-sedimentary sequence composed of andesites and basaltic andesites, most of which are metamorphosed to greenschist facies. A NE-trending fault disrupted its southern part and produced breccia zones (Fig.1c). The complex covers an area of 3 km² and shows a ring structure with alkaline syenite in the center, then syenites and outer alkaline granites. Carbonatites occur as radially distributed veins and dykes (up to 1.5 m in width and more than 200 m in length) cross-cutting the syenite. Carbonatite breccias outcrop along the fault. Other rock types observed include porphyric microsyenite veins, apatite-magnetite veins, and carbonatite breccias. The syenite age was determined using K-Ar techniques and ranges from 147 Ma to 158 Ma (Samoilov and Kovalenko, 1983).

The carbonatites are mainly composed of medium- to coarse-grained calcite (2-5 mm in diameter) and apatite (typically, 0.5-12 mm in diameter) (Fig. 2a-b). Subordinate minerals include diopside, phlogopite, barite, strontianite, pyrite, quartz, synchysite and monazite (Fig. 2c-h). The occurrence of the apatites is relatively simple and without any obvious hydrothermal alteration. They occur as euhedral to subhedral, individual, isolated grains (Fig. 2a, c) or mineral aggregates (Fig. b, f-h) within the calcites of the carbonatites. Some apatites are closely associated with the diopsides. A few diopsides are present as mineral inclusions within the apatite, indicating diopside precipitated earlier than the apatite during the crystallization of the carbonatitic magma (Fig. 2c). Most diopsides show irregular grain shapes, forming mineral aggregates together with phlogopite and/or apatite (Fig. 2b, g, h). Phlogopites mainly exist as schistose or platy crystals, up to 2mm in length and most of them are intergrown with diopside (Fig. 2e, g). Quartz, pyrite, barite, strontianite, synchysite and monazite are found as small or tiny mineral grains distributed randomly in the calcite matrix of the carbonatites (Fig. 2d-g).

3. Sample preparation and experimental methods

Representative samples of 10~15 cm blocks from diverse carbonatite dyke and vein outcrops were selected for this study. Samples used for investigation of the melt inclusions are apatite-rich (more than 5% in volume) carbonatite rocks. We studied more than 200 apatite grains (0.5~2mm in diameter) which come from different carbonatite rocks.

3.1 Melt inclusion petrography and preparation

Primary melt inclusions have been recognized from transmitted light microscopy, randomly distributed within the apatite (Fig.3a). They show elliptical to spherical, or irregular shapes and with sizes from 20-50 μ m. The intact melt inclusions observed contain a complex and varied assemblage of solid phases and a CO₂ bubble (confirmed by microthermometry) (Fig.3b). However, it is difficult to determine the mineral phase in situ by Raman spectroscopy due to the small size and mobility of the solids. To expose the melt inclusions, separated apatite grains were embedded in epoxy mounts and polished by Al₂O₃ sandpaper without using any liquid (e.g., water or oil) to avoid dissolution of salt phases. The exposed melt inclusions were examined using the high-resolution SEM-EDS at the School of Earth and Space Sciences, Peking University, with a conductive carbon layer (thickness of 10 nm) in High Vacuum Mode at typical working conditions of accelerating voltage 25 kV, working distance 15 mm. The BSE images were used to select inclusion mineral grains, which are relatively large and with a flat surface for further quantitative electron probe microprobe (EMPA) analyses.

3.2 Microthermometry and heating and quenching experiments

Microthermometric experiments for apatite slices were undertaken in the Lithosphere Fluid Research Laboratory, the Guilin University of Technology, using a Linkam TS 1500 high-temperature stage mounted on a Nikon Eclipse E600 polarizing microscope. To reproduce the melt phases of the crystallized melt inclusions at the time of entrapment, we carried out heating-quenching experiments, using a high-temperature furnace at School of Earth and Space Sciences, Peking University. The separated apatite grains were used and encapsulated in graphite containers to prevent oxidation. The maximum heating

temperature was chosen to be 1300°C according to the homogenization temperatures (see below). The heating rate was 300°C/h to 1300°C, and the quenching rate was 350-400°C/s. The recovered apatite grains were embedded in epoxy mounts and polished to check the produced melts.

3.3 Mineral and melt composition analysis

Major element compositions of the mineral and melt phases were analyzed using an EPMA-JXA-8230 electron microprobe with wavelength-dispersive X-ray spectrometry (WDS) at the Institute of Mineral Resources, Chinese Academy of Geological Sciences. The measurements were carried out using a 15 kV accelerating voltage and 20 nA beam current, with an electron beam of 1-5 μm . According to the components and sizes of the minerals, a set of appropriate matrix-specific standards (including natural and synthetic minerals) and similar instrumental conditions (including beam diameter, detector type, and counting statistics) were utilized. All data were corrected with standard ZAF correction procedures. Analytical precision for most of the elements analyzed is better than 0.1% relative to oxides. The standards used were Jadite (for Si, Al, and Na), K-feldspar (for K), Mg-olivine (for Mg), wollastonite (for Ca), magnetite (for Fe), apatite (for P), and synthetic oxides for other elements. The raw WDS data from REE-bearing minerals were corrected empirically for interferences between the REE using well-characterized synthetic standards, REE glasses, and orthophosphates.

The LA-ICP-MS analyses of the calcite and apatite were performed at the School of Earth and Space Sciences, Peking University. The diameter of the ablation spot is 32 μm and NIST 610 glass was used as a calibration standard for all samples. The element used

for the internal standard was Ca, measured as ^{43}Ca and expressed as CaO, which was independently measured by electron microprobe. During analysis, the signal intensities of indicative trace elements were monitored to ensure that the laser beam did not penetrate any mineral inclusions but stayed within the phase selected. A comparison of analytical and reference results of NIST 610 indicates that the systematic error is <5% at the ppm level.

4. Results

4.1 Compositions of the carbonatite minerals

The EMPA results from the primary minerals in the Ulgii Khiid carbonatites are listed in Table 1, and LA-ICPMS analysis data from calcite and apatite are presented in Table 2. Our study shows that the Ulgii Khiid carbonatite is relatively simple in mineralogy and mainly consists of calcite and apatite, as well as a small amount of diopside, phlogopite and REE minerals such as monazite and parisite.

Calcite is the dominant carbonate mineral in the carbonatites. The CaO contents range from 54.5-56.0 wt. % and SrO is relatively high (1.6-2.2 wt. %). LA-ICP-MS analysis shows that, besides high Sr (17144-21943 ppm) concentrations, the calcites contain moderately elevated Ba concentrations (24-307 ppm). The total REE content ranges from 380 ppm to 1220 ppm. After being normalized to the values of the primitive mantle (McDonough and Sun, 1995), the trace element distribution pattern shows positive Ba, Sr, REE, and negative Rb, Th, Nb, Ta, Zr and Hf anomalies (Fig.4a). The

chondrite-normalized REE distribution patterns are LREE enriched, with $(\text{La}/\text{Nd})_{\text{CN}}$ and $(\text{La}/\text{Yb})_{\text{CN}}$ values from 2.5 to 4 and 49 to 104, respectively (Fig.4b).

The apatites contain high levels of F (3.9-5.9 wt. %) and are fluorapatite. Minor Na_2O (up to 0.25 wt. %) was detected. The chlorine contents are very low (<0.03 wt. %). The Sr (SrO : 0.7-1.7 wt. %) contents are similar to those analyzed by LA-ICPMS (Sr: 10911-15016 ppm). Note that both Ulgiu Khiid calcites and apatites show high Sr contents, typical of carbonatitic primary calcite and apatite worldwide (Bühn et al., 2001; Chakhmouradian et al., 2016; 2017). The apatites show enrichment of Th, U, REE and negative high field strength elements (HFSE, e.g., Nb, Ta, Zr, and Hf) anomalies in trace element diagrams (Fig.4c). The total REE concentrations are between 2125-2656 ppm and with $(\text{La}/\text{Nd})_{\text{CN}}$ (1.99-2.23) and $(\text{La}/\text{Yb})_{\text{CN}}$ (62-103) values (Fig.4d) similar to the calcites. All the studied apatites show relatively consistent major and trace element compositions.

The diopsides and phlogopites are the main silicate minerals found in carbonatites. They are texturally in equilibrium with the carbonatite, demonstrating a primary magmatic origin. The diopsides show no significant compositional differences and with relatively consistent $\text{Mg}/(\text{Mg} + \text{Fe})$ values (0.84-0.87). Minor amounts of Al_2O_3 (0.75-2.13 wt. %), MnO (0.7-3.4 wt. %) and Cr_2O_3 (0.23-0.85 wt. %) are also present in the diopsides. Their TiO_2 concentrations are below or close to the detection limit of the EMPA.

All analyzed phlogopite in carbonatites show characteristically low contents of Na_2O (0.05–0.29 wt.%) and with very high $\text{K}/(\text{K}+\text{Na})$ ratios (0.97-0.99). The $\text{Mg}/(\text{Mg}+\text{Fe})$ values of the phlogopite are variable (0.76-0.95). The mineral also contains small amounts of

TiO₂ (up to 3.19 wt. %) and Cr₂O₃ (0.29-1.27 wt.%). Their compositions are similar to primary phlogopites in other carbonatites (Reguir et al., 2009).

4.2 Composition of the melt inclusions

Based on the SEM-EDS and EMPA analyses on the exposed melt inclusions, the daughter mineral phases found in the melt inclusions are calcite, diopside, phlogopite, magnetite and pyrite, as well as REE minerals including monazite and parisite. Among them, calcites are the most common daughter mineral and have been found in nearly all the investigated melt inclusions. They occur as subhedral-euhedral crystals and occupy the main space of the melt inclusions in most cases (Fig. 5a-f). Euhedral diopsides occur with calcite and phlogopite in the inclusions (Fig. 5a, d). Phlogopites are easy to identify and usually occur as schistose or small columnar crystals (Fig. 5a, e). Magnetite was identified by SEM-EDS and showed a close association with pyrite and REE minerals in the melt inclusions (Fig. 5c, f). Pyrites exist as anhedral-subhedral grains, and some of them are intergrown with magnetite (Fig. 5b, c, d, and f). The REE minerals, including parisite and monazite, occur as tiny mineral grains or irregular fillings between other daughter minerals within the melt inclusions (Fig. 5a-d, f). It is noted that there is a remarkable REE-rich phosphate glass phase occurring around the inner edge of the melt inclusions (Fig. 5a-e). Compositions of these mineral and glass phases are shown in Table 3.

Calcites in melt inclusions show similar compositions to the rock-forming calcites of the carbonatites, except the former (SrO: 0.01-3.48 wt. %) have significant variable and a little higher Sr contents than the later (SrO: 1.6-2.2 wt. %).

The chemistry of diopsides from the melt inclusions show relatively higher contents of Al_2O_3 (3.2-5.9 wt. %) and FeO (3.0-5.9 wt. %), but lower levels of MgO (10.8-12.2 wt. %), compared to those from the host rocks. The $\text{Mg}/(\text{Mg} + \text{Fe})$ values of the diopsides in melt inclusions vary from 0.61 to 0.77. The compositional differences between minerals from carbonatite and melt inclusions are probably caused by crystal differentiation.

Compared to the phlogopite from the carbonatites, the phlogopite within the melt inclusions shows similar $\text{K}/(\text{K}+\text{Na})$ (0.97-0.98) values but relatively consistent $\text{Mg}/(\text{Mg}+\text{Fe})$ ratios (0.78-0.81). Besides, the inclusion minerals show relatively higher levels of Al_2O_3 (15.2-16.7wt %) and Na_2O (0.21-0.34 wt. %).

All the analyzed pyrites from the melt inclusions show similar compositions. Besides Fe and S, these pyrites contain high amounts of Cu (~ 5 wt.%) and a small amount of Mo (~ 0.6 wt.%). High Cu contents have also been reported in sulfide melts from the carbonate melt inclusions in Kerimasi volcano, Tanzania (Guzmics et al., 2012). Other elements like As, Cu, Zn, Co, Ni, Ag, and Au are below or close to the limit detection of the EMPA.

Monazite and parisite are the REE minerals found in the melt inclusions. The total REE oxide contents and La/Ndn values of the monazite and parisite are 64-70 wt. % and 2.6-5.74 and, 50-54 wt. % and 4.39-5.83, respectively. Their La/Ndn values are similar to the primary magmatic monazite reported from Miaoya REE carbonatite deposit, China (~4, Xu et al., 2010).

The phosphorus melts are quite unusual and characterized by very high REE contents (Total REE oxides: 51.01~53.76 wt. %). They also contain high contents of P_2O_5

(26.4~28.3 wt. %), CaO (28.8~30.0 wt. %), and F (1.30~3.49 wt. %). Recently, similar REE-rich (>40 wt. %) phosphate-fluoride (P_2O_5 : 3.7-4.8 wt. %; F: 5-8 wt. %) melt composition has been reported in the Longs Peak-St. Vrain aplite from Colorado by Stern et al. (2018).

4.3 Homogenization temperature and compositions of the heated-quenched melts

The homogenization temperature of the apatite-hosted melt inclusions is high. All the solid phases completely melt beyond 1200°C. However, the bubble continues to exist in most cases. Most melt inclusions investigated could not be entirely homogenized as they decrepitated above 1250°C. This is probably due to heterogeneous entrapment of the melt and fluid phase (Andreeva and Kovalenko, 2003; Guzmics et al., 2011; Panina, 2005). The temperature of at least 1200°C can still be considered to represent the minimum possible trapping temperature of the melt inclusion (Panina, 2005).

Three immiscible liquid phases coexisted in melt inclusions after the heat and quench, namely phosphate melt, silicate melt and Fe-rich silicate melt (Fig. 6 and Table 4). Texturally, distinct boundaries have been observed between the different immiscible compositions. However, there is no carbonate melt observed in the quenched melt inclusions, probably because the carbonate melts decomposed during heating at high temperatures but low pressure (Canil, 1990). Phosphate melts are richer in CaO (33.8-54.5 wt. %), P_2O_5 (29.4-36.9 wt. %), F (1.25-4.60 wt. %), and particularly REE (La_2O_3 =0.84-5.09 wt. %; Ce_2O_3 =2.17-11.91 wt. %; Nd_2O_3 =0.57-4.67), but lower in SiO_2 (3.08-6.92 wt. %) and FeO (0.14-4.24 wt. %), compared to the other two silicate melts (Fig. 7). In contrast, silicate melts contain a higher level of SiO_2 (29.4-33.8 wt. %), FeO

(14.3-19.2 wt. %), Al_2O_3 (3.88-9.34 wt. %), lesser CaO (21.1-24.7 wt. %) and P_2O_5 (11.5-15.3 wt. %). The REE concentrations ($\text{La}_2\text{O}_3=0.02\text{-}0.69$ wt. %; $\text{Ce}_2\text{O}_3=0.09\text{-}1.20$ wt. %; $\text{Nd}_2\text{O}_3<0.53$ wt. %) of the silicate melts are much lower than the phosphate melts. Compare to the silicate melts, the Fe-rich silicate melts show higher FeO (39.3~51.7 wt. %), but relatively lower SiO_2 (18.2~28.2 wt. %) and similar CaO (17.7~23.9 wt. %) contents. Their REE contents are very low ($\text{La}_2\text{O}_3=0.27\text{-}0.69$ wt. %; $\text{Ce}_2\text{O}_3=0.81\text{-}2.10$ wt. %; $\text{Nd}_2\text{O}_3<0.73$ wt. %) compared to the phosphate melts.

5. Discussion

5.1 Composition of the parent melts

The melt inclusions studied in this work contain a phosphate-rich melt phase and a varied polycrystalline assemblage of daughter minerals (Fig. 5). Besides phosphate melts, the daughter mineral assemblage (e.g., calcite + diopside + phlogopite + monazite + parisite, Fig. 5a) shows almost complete agreement with the mineral association of the carbonatites (calcite + apatite + diopside + phlogopite + monazite, Fig. 2). The chemical compositions of the solid minerals are also similar to corresponding primary minerals in carbonatites (Table 1 and 3). Additionally, the high homogenization temperature ($>1200^\circ\text{C}$) of the inclusions is similar to the normal liquidus temperature of the carbonate melt (Dalton and Presnall, 1998; Gudfinnsson and Presnall, 2005; Guzmics et al., 2011). This evidence demonstrates that the inclusions are crystallized melt inclusions from the trapped carbonate melt.

The melt is inferred to have been carbonate-dominated because calcite occurs as a predominant daughter mineral phase and is always present in the inclusions. The occurrence of phlogopite ($K_2O \sim 10$ wt. %, Table 1 and 3) both within the carbonatite and melt inclusions requires a K_2O -bearing carbonate melt to saturate this mineral (Weidendorfer et al., 2016). The presence of phosphate melt and minor monazite indicates the primary melt was rich in phosphorus. Primary P-rich (P_2O_5 up to 20 wt. %) carbonate melt has also been reported from the Mongolia Mushgai Khudag carbonatite-alkaline complex (Andreeva and Kovalenko, 2003). Pyrite is the only sulfide phase in the inclusions and is usually associated with the REE minerals. Sulfide melt has also been found in primary carbonate melts from Kerimasi, Tanzania (Guzmics et al., 2012).

Notably, a remarkable characteristic of the studied melt inclusions is their enrichment in REE, reflected in the presence of daughter REE minerals (e.g., monazite and parisite) and REE-rich phosphate melts (e.g., $Ce_2O_3 = 2.17 \sim 11.91$ wt. %). This indicates that the primary magmas were characterized by high REE contents. Therefore, the presence of abundant carbonates, silicates, REE minerals and phosphate melts within the melt inclusions demonstrate that the Ulgii Khiid carbonatites were formed from an REE-, P-, silicate- and potassium-bearing carbonate melt at a high temperature $>1200^\circ C$.

5.2 Origin of the Ulgii Khiid carbonatites

The genesis of carbonatitic parental magmas has been extensively investigated from both experimental and natural systems in the past several decades. The petrogenetic models include: (1) direct low degree partial melting of a carbonated mantle (e.g., Wallace

and Green, 1988; Sweeney, 1994; Dalton and Presnall, 1998) (2) extreme fractional crystallization of a carbonated silicate magma (e.g., Watkinson and Wyllie, 1971; Lee and Wyllie, 1994; Veksler et al., 1998); and (3) immiscibility from carbonated silicate magmas (e.g., Brooker and Kjarsgaard, 2011; Lee and Wyllie, 1997; Martin et al., 2013). Partial melting alone cannot be the origin of carbonatites. Previous studies have suggested that the carbonatitic melts produced in this process, are characterized by a dolomitic composition (Dalton and Presnall, 1998; Guzmics et al., 2008a,b; Sweeney, 1994; Wallace and Green, 1988) and are low in REE concentration (Foley et al., 2009), in contrast to the Ulgii Khiid carbonatite and melt inclusions. Fractional crystallization models suggest that the carbonatite represents the last stage residual liquid produced by fractional crystallization of a coexisting carbonated silicate melt. This means the remaining melts would crystallize at low temperatures according to experimental and melt inclusion studies (e.g., 600-1000 °C, Watkinson and Wyllie, 1971; Veksler et al., 1998), unlike the high formation temperature (>1200 °C) of the Ulgii Khiid melt inclusions. Veksler et al. (1998) studied melt inclusions from carbonatite and silicate rocks of the Kovdor and Gardiner complexes and concluded that the fractional residuals might have higher MgO (i.e. more dolomitic) and HFSE concentrations (occurrence of pyrochlore, baddeleyite, etc.) than immiscible products. However, these were not observed in the studied carbonatite, ruling out fractional crystallization as the origin of the Ulgii Khiid carbonatite.

Alternatively, we suggest melt immiscibility for the genesis and REE enrichment of the Ulgii Khiid carbonatite. Firstly, the carbonatite is temporally (carbonatite: apatite U-Pb: 165±10 Ma, Feng, et al., unpublished data; Syenite: K-Ar: 147-158Ma, Samoylov, and

Kovalenko, 1983) and spatially (Fig. 1c) associated with the syenite. Then, the very high homogenization temperatures obtained from the melt inclusion are comparable to those inferred for silicate-carbonate liquid immiscibility processes (Brooker and Kjarsgaard, 2011; Panina, 2005). Furthermore, the coexistence of calcite and silicate minerals with high variability in volume in the inclusions (Fig. 4) probably indicates heterogeneous trapping of immiscible silicate-carbonate phases. Unfortunately, we failed to reproduce the carbonate melts during heating although calcite is always present in the melt inclusions. This is probably due to the decomposition of the carbonate melt at a high heating temperature and low pressure (Canil, 1990). The phosphate melts with very high CaO (33.8~54.5 wt. %) contents are probably the products of the original phosphate-rich carbonate melt which decomposed, released CO_2 and the remaining CaO was incorporated into the phosphate melts. There is no corresponding rock type to the Fe-silicate melt found in the studied area presently. However, Petrella et al. (2014) proposed that the REE-bearing quartz-fayalite dykes/veins in the Misery syenite, Canada, are the products of an immiscible FeO-SiO₂-rich magma which separated from the conjugate syenitic melt.

Experimental studies of element partitioning have shown that in the carbonate-silicate liquid system, the REE partition coefficients vary broadly with melt composition (Martin et al., 2013; Veksler et al., 2012). Veksler et al. (2012) proposed that REE will not or only slightly (D_{La} and D_{Lu} up to 1.05 and 0.25, respectively) partition into the carbonate melt relative to co-existing immiscible silicate melts. However, Martin et al. (2013) subsequently found that in the H₂O-potassium-rich system, which is similar to Ulgii Khiid,

the carbonate melts will have much higher REE concentrations relative to the conjugate silicate melt ($D_{\text{REE}}=6-38$). Kynický et al. (2018) also argued that the anionic components of the melt could have a significant impact on REE partitioning, and, in particular, proposed that carbonate-fluoride melts should preferentially incorporate the REE relative to silicate melts.

It is worth noting that natural carbonatite systems are not a simple silicate-carbonate composition. Our work shows that the parental melt of the Ulgii Khiid carbonatite was rich in P, which invariably partitions into the carbonate melt during carbonate-silicate liquid immiscibility ($D_{\text{P}_2\text{O}_5}=2-9$, Guzmics et al., 2015; $D_{\text{P}_2\text{O}_5}$ up to 13.5, Martin et al., 2013). The heating-produced phosphate melts, which are inferred to initially be phosphate-rich carbonate melt, as mentioned above, contain much higher levels of REE ($\text{La}_2\text{O}_3=0.84\sim5.09$ wt. %; $\text{Ce}_2\text{O}_3=2.17\sim11.91$ wt. %) than the silicate melts. Moreover, the P_2O_5 and Ce_2O_3 contents in phosphate melts are positively correlated (Fig.8). Also, strong REE-enrichments were also observed experimentally in phosphate-silicate ($D_{\text{REE}}>100$) immiscible systems (Veksler et al., 2012). All these results suggest that phosphate and the REE had a solid binding ability in the melt. Carbonate melts rich in phosphate will extract much more REE from the conjugate immiscible silicate melt. Though we failed to obtain carbonate melt during the heating-quenching experiments, the bulk rock composition of the Ulgii Khiid carbonatites could represent the composition of the carbonate melt to a great extent and supports the above conclusion. According to Kynický and Chakhmouradian (2010), two reported whole-rock data show that the carbonatites are CaO (46.5 wt. % and 50.2 wt. %)-dominated and the total REE (1.8 wt. % and 2.5 wt. %)

and P (5.7 wt. % and 9.9 wt. %) contents are positively correlated. Therefore, it is reasonable to conclude that the Ulgii Khiid magmas are the products of liquid immiscibility from a P-rich, carbonated, parental silicate melt. Similarly, the REE-P-F-rich globular segregations found in the aplite were also considered to be the products of liquid immiscibility from an initially single homogeneous silicate magma (Stern et al., 2018).

Experimental studies have shown that phosphate-rich carbonate melts are formed by the melting of the P-bearing mantle materials and the melts will intensely extract REE from the mantle sources (e.g., Ryabchikov et al., 1993; Hammouda et al., 2010). This is consistent with our results and suggests that the P-rich characteristic of the mantle source is probably due to the input of subducted phosphatic sediments (Rosenbaum et al., 1997; Hammouda et al., 2010). However, as mentioned above, the tectonic settings of apatite-enriched carbonatite complexes are still under debate and further, detailed, isotopic studies of these rocks are desirable.

5.3 Carbonatitic magma evolution

After separation from the silicate melt, the P-REE-rich Ulgii Khiid carbonatitic magmas began to evolve by crystal fractionation and potentially volatile exsolution. According to the melt inclusion results, we propose a combined model of crystal fractionation and subsequent carbonate-phosphate immiscibility contributed to the final formation of the carbonatites.

The carbonatite mineralogy indicates that calcite, diopside (included within apatite, Fig. 2a) and phlogopite were the early crystallizing minerals. Many studies have shown that the partition coefficients between calcite and carbonatitic melt are below 1 (e.g., Bühn

et al., 2001; Hornig-Kjarsgaard, 1998; Xu et al., 2007, 2010). Phlogopite and diopside occurring in the melt inclusions show higher Al_2O_3 (15.2-16.7 wt. % and 3.2- 5.9 wt. %, respectively) contents than those (11.6-14.2 wt. % and 0.75- 2.13 wt. %, respectively) in the carbonatites. Also, the diopsides from the melt inclusions have slightly higher SiO_2 (51.3-54.9 wt. %) than those (49.8- 53.0 wt. %) from the carbonatites. These differences are probably due to crystallization of the silicate-bearing minerals such as phlogopite and pyroxene which normally precipitated during the early stage of the evolution of the parental carbonatitic magma (Requir et al., 2009, 2012). The extensive precipitation of those REE- and P-poor calcite, silicates, magnetite and pyrite may drive the residual carbonatitic melt to become saturated with P- and REE-bearing phases. The REE minerals started to precipitate at this time, and phosphate-carbonate immiscibility occurred. After separation of the phosphate, the later carbonatitic magmas will not form immiscible melts due to their extremely low viscosities (Kono et al., 2014), but continue to crystallize. This better explains the phase association observed in our melt inclusions. A similar evolution trend has been proposed by Panina (2005), who found that early silicate-carbonate liquid immiscibility (1230-1250 °C), followed by carbonate-salt (e.g., phosphate, sulfate) immiscibility was the origin of the Krestovskiy massif in Siberia. Andreeva and Kovalenko (2003) also proposed liquid immiscibility is crucial for the formation of ore-bearing rocks of the Mushgai Khudag carbonatite-alkaline complex. Besides, there is also a possibility that carbonate-silicate-phosphate immiscibility would occur during the evolution of the carbonate-silicate magmas. The multiphase immiscibility has also been described by previous study (e.g., carbonate-silicate-sulfide

melt, Guzmics et al., 2012). However, further investigation on the inclusions with more coexisting melts is desirable.

5.4 Implications for REE carbonatitic ore deposits

Our melt inclusion results show that phosphorus potentially plays a key role in controlling the REE budget in the evolution of the carbonatites, and have implications for models of genesis of carbonatite-hosted REE ores. The presence of phosphate will help the carbonatitic magmas concentrate more REE during low degree partial melting and/or carbonate-silicate immiscibility processes. However, in the evolution of the carbonatitic stage, if the magmas are initially rich in P and become phosphate-saturated due to crystal fractionation as discussed above, then they may have the potential to separate REE-rich immiscible phosphate melts (and/or to crystallize monazite and apatite preferentially, Xu et al., 2010), causing later carbonatitic magmas to be depleted in REE. Thus, economic REE mineralization would not occur in late stage carbonatites. Apatites from the Mushgai Khudag complex in the region, which have a high REE content (> 10 wt. % REO, Enkhbayar et al., 2016), may formed from an immiscible, residual, REE-rich phosphate melt because silicate-phosphate and phosphate-carbonate immiscibility have occurred (Andreeva and Kovalenko, 2003). On the contrary, a carbonatite magma relatively low in P may not reach P saturation, leading to the concentration of REE in residual carbonatitic liquids or fluids, subsequently forming REE mineralization. This inference is consistent with mineralogical observations from the world's second and third largest REE deposits at Mountain Pass (Castor, 2008; Wyllie et al., 1996) and Maoniuping (Liu et al., 2016; Liu and Hou, 2017; Xu et al., 2008). The Mountain Pass deposit is considered to have formed

during carbonatitic magmatic process based on mineral texture and experimental studies (Jones et al., 1983; Mariano, 1989; Wyllie et al., 1996). Melt and melt-fluid inclusions have been found in the Maoniuping REE deposits (Xie et al., 2009), indicating the presence of the carbonatitic magmatic stage. Xie et al. (2009) found that these inclusions are dominated by the sulfates but poor in phosphorus components, suggesting the melts in charge of REE mineralization are also depleted in P. In addition, detailed mineralogical studies (Castor, 2008; Liu and Hou, 2017) have shown that both of the above two deposits are poor in apatite but rich in fluorides and sulfates.

The occurrence of large amounts of primary magmatic apatite in carbonatite rocks could be an indicator of the P saturation in the melt, which may also explain why, in many carbonatites, the apatites have become important economic resources, but with less REE mineralization (as summarized by Mariano, 1989). In the case of the Ulgii Khiid carbonatites, although initial carbonatitic magma was rich in REE as evidenced from the melt inclusions, economic REE mineralization was not well developed in these rocks. The nearby Lugiin Gol carbonatite-hosted REE mineralization occurs as and calcite-fluorite veins, and originated from a REE-rich carbonate-fluoride melt which separated from the alkaline silicate melt by immiscibility (Kynicky et al., 2018). Moreover, recent study has demonstrated that the REE minerals in the Mushgai Khudag complex were precipitated from late stage carbonate-chloride-(fluoride)-sulfate hydrothermal fluids which dissolved the early-formed REE-rich apatite (Nikolenko et al., 2018). Therefore, it is suggested that carbonatites, with mineralogy relatively poor in apatite but rich in barite, celestine and fluorite, may be prospective targets for REE mineral exploration in the region and

elsewhere.

6. Conclusion

Primary melt inclusions have been recognized randomly distributed within apatite from the Ulgii Khiid carbonatite-alkaline complex, South Mongolia. The melt inclusions are polycrystalline and contain a complex and varied assemblage of phases and a CO₂ vapour bubble. Calcite, diopside, phlogopite, magnetite, pyrite, monazite, and parisite, as well as an extremely REE-enriched phosphate melt, have been identified by SEM-EDS and EMPA as the main components of the inclusions. Heating-quenching experiments produced three immiscible liquid phases, namely phosphate-, silicate-, and Fe-silicate-melt. Based on these results, we propose that the Ulgii Khiid carbonatite was produced by silicate-carbonate liquid immiscibility processes with subsequent crystal differentiation and phosphate-carbonate immiscibility. The REE, together with P, were preferentially incorporated in the residual phosphate melt during the immiscibility process. The presence of the phosphate melt plays a vital role in the REE behavior in carbonatites and associated ore mineralization.

References

- Andreeva, I.A., Kovalenko, V.I., 2003. Magma compositions and genesis of the rocks of the Mushugai-Khuduk carbonatite-bearing alkaline complex (southern Mongolia): evidence from melt inclusions. *Per. Mineral*, 72, 95-105.

- Andreeva, I.A., Kovalenko, V.I., Nikiforov, A.V., Kononkova, N.N., 2007. Compositions of
magmas, formation conditions, and genesis of carbonate-bearing ijolites and
carbonatites of the Belaya Zima alkaline carbonatite complex, eastern Sayan.
Petrology. 15(6), 551-574.
- Baatar, M., Ochir, G., Kynický, J., Lizumi, S., Comin-Chiaramonti, P., 2013. Some Notes
on the Lugiin Gol, Mushgai Khudag and Bayan Khoshuu Alkaline Complexes,
Southern Mongolia. *International Journal of Geosciences*. 4(8), 1200-1214.
- Badarch, G., Cunningham, W. D., Windley, B. F., 2003. A new terrane subdivision for
mongolia: implications for the Phanerozoic crustal growth of central Asia. *Journal of
Asian Earth Sciences*, 21(1), 87-110.
- Baker, M.B., Wyllie, P.J., 1992. High-pressure apatite solubility in carbonate-rich liquids:
Implications for mantle metasomatism. *Geochimica et Cosmochimica Acta*. 56 (9),
3409-3422.
- Brooker, R.A., Kjarsgaard, B.A., 2011. Silicate-carbonate liquid immiscibility and phase
relations in the system $\text{SiO}_2\text{-Na}_2\text{O-Al}_2\text{O}_3\text{-CaO-CO}_2$ at 0.1-2.5 GPa with applications
to carbonatite genesis. *Journal of Petrology*. 52(7-8), 1281-1305.
- Bühn, B., Wall, F., Le Bas., 2011. Rare-earth systematics of carbonatitic fluorapatites and
their significance for carbonatite magma evolution. *Contributions to Mineralogy and
Petrology*. 141, 572-591.
- Canil, D., 1990. Experimental study bearing on the absence of carbonate in
mantle-derived xenoliths. *Geology*. 18(10), 1011-1013.
- Castor, S.B., 2008. Rare earth deposits of North America. *Resource Geology*. 58(4),

337-347.

Chakhmouradian, A.R., Wall, F., 2012. Rare earth elements: minerals, mines, magnets (and more). *Elements*. 8, 333-340.

Chakhmouradian, A.R., Reguir, E.P., Couëslan, C., Yang, P., 2016. Calcite and dolomite in intrusive carbonatites. II. Trace-element variations. *Mineralogy and Petrology*. 110, 361-377.

Chakhmouradian, A.R., Reguir, E.P., Zaitsev, A.N., Couëslan, C., Xu, C., Kynický, J., Mumin, A.H., Yang, P.S., 2017. Apatite in carbonatitic rocks: Compositional variation, zoning, element partitioning and petrogenetic significance. *Lithos*. 274-275, 188-213.

Dalton, J.A., Presnall, D.C., 1998. Carbonatitic melts along the solidus of model lherzolite in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2$, from 3 to 7 GPa. *Contributions to Mineralogy and Petrology*. 131(2-3), 123-135.

Doroshkevich, A.G., Ripp, G.S., Moore, K.R., 2010. Genesis of the Khaluta alkaline-basic Ba-Sr carbonatite complex (west Transbaikala, Russia). *Mineralogy and Petrology*. 98(1-4), 245-268.

Downes, P.J., Demény, A., Czuppon, G., Jaques, A.L., Verrall, M., Sweetapple, M., Adams, D., McNaughton, N.J., Gwalani, L.G., Griffin, B. J., 2014. Stable H-C-O isotope and trace element geochemistry of the Cummins Range Carbonatite Complex, Kimberley region, Western Australia: implications for hydrothermal REE mineralization, carbonatite evolution and mantle source regions. *Mineralium Deposita*. 49(8), 905-932.

Enkhbold, J., Gantulga, J., Dambinyan, M., 2007. A summary of the White Hill Cu-Zn

deposit, Southern Mongolia. Unpublished Technical report of the Universal Copper Corp. 1-168.

Enkhbayar, D., Seo, J., Choi, S.G., Lee, Y.J., Knkhbayar, B., 2016. Mineral Chemistry of REE-Rich Apatite and Sulfur-Rich Monazite from the Mushgai Khudag, Alkaline Volcanic-Plutonic Complex, South Mongolia. *International Journal of Geosciences*. 7(1), 20-31.

Foley, S.F., Yaxley, G.M., Rosenthal, A., Buhre, S., Kiseeva, E.S., Rapp, R.P., Jacob, D.E., 2009. The composition of near-solidus melts of peridotite in the presence of CO₂ and H₂O between 40 and 60 kbar. *Lithos*. 112 (Suppl 1), 274-283.

Fulignati, P., Kamenetsky, V.S., Marianelli, P., Sbrana, A., Meffre, S., 2011. First insights on the metallogenic signature of magmatic fluids exsolved from the active magma chamber of Vesuvius (AD 79 "Pompei" eruption). *Journal of Volcanology and Geothermal Research*. 200(3-4), 223-233.

Gerel, O., Munkhtsengel, B., Enkhtuvshin, H., Iizumi, Sh., 2005. Mushgai Khudag and Bayan Khushuu volcanic-plutonic alkaline complexes with REE Ta, Nb, Fe carbonatite mineralization. In: *Geodynamics and Metallogeny of Mongolia with Special Emphasis on Copper and Gold Deposits* (R. Seltmann, O. Gerel, D. Kirwin, eds.) London, 215-221.

Guzmics, T., Zajacz, Z., Kodolányi, J., Halter, W., Szabó, C., 2008a. LA-ICP-MS study of apatite- and K-feldspar-hosted primary carbonatite melt inclusions in clinopyroxenite xenoliths from lamprophyres Hungary: implication for significance of carbonatite melts in the Earth's mantle. *Geochimica et Cosmochimica Acta*. 72, 1864-1886.

- Guzmics, T., Kodolányi, J., Kovács, I., Szabó, C., Bali, E., Ntaflos, T., 2008b. Primary carbonatite melt inclusions in apatite and in K-feldspar of clinopyroxene-rich mantle xenoliths hosted in lamprophyre dikes (Hungary). *Mineralogy and Petrology*. 94, 225-242.
- Guzmics, T., Mitchell, R.H., Szabó, C., Berkesi, M., Milke, R., Abart, R., 2011. Carbonatite melt inclusions in coexisting magnetite, apatite and monticellite in Kerimasi calciocarbonatite, Tanzania: melt evolution and petrogenesis. *Contributions to Mineralogy and Petrology*. 161(2), 177-196.
- Guzmics, T., Mitchell, R.H., Szabó, C., Berkesi, M., Milke, R., Ratter, K., 2012. Liquid immiscibility between silicate, carbonate and sulfide melts in melt inclusions hosted in co-precipitated minerals from Kerimasi volcano (Tanzania): evolution of carbonated nephelinitic magma. *Contributions to Mineralogy and Petrology*. 164(1), 101-122.
- Guzmics, T., Zajacz, Z., Mitchell, R.H., Szabó, C., Wälle, M., 2015. The role of liquid–liquid immiscibility and crystal fractionation in the genesis of carbonatite magmas: insights from Kerimasi melt inclusions. *Contributions to Mineralogy and Petrology*. 169(2), 17.
- Gudfinnsson, G.H., Presnall, D.C., 2005. Continuous gradations among primary carbonatitic, kimberlitic, melilititic, basaltic, picritic, and komatiitic melts in equilibrium with garnet lherzolite at 3–8 GPa. *Journal of Petrology*. 46, 1645-1659.
- Hammouda, T., Chantel, J., Devidal, J.L., 2010. Apatite solubility in carbonatitic liquids and trace element partitioning between apatite and carbonatite at high pressure. *Geochimica et Cosmochimica Acta*, 74(24), 0-7235.

- Hornig-Kjaarsgaard, I., 1998. Rare earth elements in sövittic carbonatites and their mineral phases: *Journal of Petrology*. 39, 2105-2121.
- Jago, B.C., Gittins, J., 1991. The role of fluorine in carbonatite magma evolution. *Nature*, 349 (6304), 56-58.
- Jones, A.P., Wyllie, P.J., 1983. Low-temperature glass quenched from a synthetic, rare earth carbonatite: Implications for the origin of the Mountain Pass deposit, California: *Economic Geology*, 78, 1721-1728.
- Kamenetsky, V.S., Mitchell, R.H., Maas, R., Giuliani, A., Gaboury, D., Zhitova, L., 2015. Chlorine in mantle-derived carbonatite melts revealed by halite in the St.-Honore intrusion (Quebec, Canada). *Geology*, 43(4), 687-690.
- Kono, Y., Kenney-Benson, C., Hummer, D., Ohfuji, H., Park, C., Shen, G., Wang, Y., Kavner, A., Manning, C.E., 2014. Ultralow viscosity of carbonate melts at high pressures. *Nature communications*, 5 (5), 5091.
- Kovalenko, V.I., Yarmolyuk, V.V., Kovach, V.P., Kotov, A.B., Kozakov, I.K., Salnikova, E.B., Larin, A.M., 2004. Isotope provinces, mechanisms of generation and sources of the continental crust in the Central Asian mobile belt: geological and isotopic evidence. *Journal of Asian Earth Sciences*. 23(5), 605-627.
- Kuzmin, M.I., Yarmolyuk, V.V., 2014. Mantle plumes of Central Asia (Northeast Asia) and their role in forming endogenous deposits. *Russian Geology and Geophysics*. 55(2), 120-143.
- Kynický, J., Chakhmouradian, A.R. 2010. Exotic rocks and REE apatite mineralization of Ulugei Khid massif in the Mongolia. *Geoscience Research Reports*, 44, 205-210 (In

Czech with English abstract).

- Kynický, J., Smith, M.P., Song, W.L., Chakhmouradian, A.R., Xu, C., Kopriva, A., Galiova, M.V., Brtnický, M., 2019. The role of carbonate-fluoride melt immiscibility in shallow REE deposit evolution. *Geoscience Frontiers*, 10, 527-537.
- Lee, W.J., Wyllie, P., 1994. Experimental Data Bearing on Liquid Immiscibility, Crystal Fractionation, and the Origin of Calciocarbonatites and Natrocarbonatites. *International Geology Review*. 36(9), 797-819.
- Lee, W.J., Wyllie, P.J., 1997. Liquid immiscibility between nephelinite and carbonatite from 1.0 to 2.5 GPa compared with mantle melt compositions. *Contributions to Mineralogy and Petrology*. 127(1-2), 1-16.
- Liu, Y., Hou, Z.Q., 2017. A synthesis of mineralization styles with an integrated genetic model of carbonatite-syenite-hosted REE deposits in the Cenozoic Mianning-Dechang REE metallogenic belt, the eastern Tibetan Plateau, southwestern China. *Journal of Asian Earth Sciences*. 137, 35-79.
- Liu, Y., Hou, Z.Q., Tian, S., Zhang, Q., Zhu, Z., Liu, J., 2015. Zircon U-Pb ages of the Mianning-Dechang syenites, Sichuan Province, Southwestern China: constraints on the giant REE mineralization belt and its regional geological setting. *Ore Geology Reviews*. 64(8), 554-568.
- Martin, L.H.J., Schmidt, M.W., Mattsson, H.B., Guenther, D., 2013. Element partitioning between immiscible carbonatite and silicate melts for dry and H₂O-bearing systems at 1-3 GPa. *Journal of Petrology*. 54(11), 2301-2338.
- Mariano, A.N., 1989, Nature of economic mineralization in carbonatites and related rocks,

- in Bell, K., ed., Carbonatites: Genesis and Evolution: London, Unwin Hyman. 149-175.
- McDonough, W.F., Sun, S.S., 1995. The composition of the Earth. *Chemical Geology*. 120, 223-253.
- Nie, F.G., Jiang, S.H., Bai, D.M., Hou, W.R., Liu, Y.F., 2010. Types and Temporal-Spatial Distribution of Metallic Deposits in Southern Mongolia and Its Neighboring Areas. *Acta Geoscientica Sinica*. 31(3), 267-288.
- Nikolenko, A.M., Redina A.A., Doroshkevich A.G., Prokopyev, I.R., Alexey, L.R., Vladykin, N.V., 2018. The origin of magnetite-apatite rocks of Mushgai-Khudag complex, South Mongolia: Mineral chemistry and studies of melt and fluid inclusions. *Lithos*. 320-321, 567-582.
- Panina, L.I., Motorina, I.V., 2008. Liquid immiscibility in deep-seated magmas and the generation of carbonatite melts. *Geochemistry International*. 46(5), 448-464.
- Panina, L.I., 2005, Multiphase carbonate-salt immiscibility in carbonatite melts: data on melt inclusions from the Krestovskiy massif minerals (Polar Siberia). *Contributions to Mineralogy & Petrology*. 150(1), 19-36.
- Pavlova, C.G., Borisenko, A.S., 2009. The age of Ag-Sb deposits of central Asia and their correlation with other types of ore system and magmatism. *Ore Geology Reviews*. 35, 164-185.
- Pirajno, F., Ernst, R.E., Borisenko, A.S., 2009. Intraplate magmatism in Central Asia and China and associated metallogeny. *Ore Geology Reviews*. 35(2), 114-136.
- Potter, N.J., Kamenetsky, V.S., Simonetti, A., Goemann, K., 2016. Different types of liquid

- immiscibility in carbonatite magmas: A case study of the Oldoinyo Lengai 1993 lava and melt inclusions. *Chemical Geology*, 455, 376-384.
- Reguir, E.P., Chakhmouradian, A.R., Halden, N.M., Malkovets, V.G., Yang, P., 2009. Major-and trace-element compositional variation of phlogopite from kimberlites and carbonatites as a petrogenetic indicator. *Lithos*. 112(Suppl 1), 372-384.
- Reguir, E.P., Chakhmouradian, A.R., Pisiak, L., Halden, N.M., Yang, P., Xu, C., Kynický, J., Coueslan, C. G., 2012. Trace-element composition and zoning in clinopyroxene- and amphibole-group minerals: implications for element partitioning and evolution of carbonatites. *Lithos*, 128(1), 27-45.
- Rosenbaum, J.M., Wilson, M., Condliffe, E., 1997. Partial melts of subducted phosphatic sediments in the mantle. *Geology*, 25(1), 77-80.
- Ryabchikov, I.D., Orlova, G.P., Senin, V.G., Trubkin, N.V., 1993. Partitioning of rare earth elements between phosphate-rich carbonatite melts and mantle peridotites. *Mineralogy and Petrology*. 49(1-2), 1-12.
- Petrella, L., Williams-Jones, A.E., Goutier, J., Walsh, J., 2014. The nature and origin of the rare earth element mineralization in the misery syenitic intrusion, northern Quebec, Canada. *Economic Geology*, 109(109), 1643-1666.
- Samoilov, V.S., Kovalenko, V.I., 1983. Complexes of alkaline rocks and carbonatites in Mongolia. Nauka, Moscow. 195.
- Song, W.L., Xu, C., Veksler, I.V., and Kynický, J., 2016, Experimental study of REE Ba, Sr, Mo and W partitioning between carbonatitic melt and aqueous fluid with implications

- for rare metal mineralization: Contributions to Mineralogy and Petrology. 171, 1-12.
- Song, W., Xu, C., Smith, M.P., Chakhmouradian, A.R., Brenna, M., Kynický, J., Chen, W., Yang, Y.H., Deng, M., Tang, H.Y. 2018. Genesis of the world's largest rare earth element deposit, Bayan Obo, China: Protracted mineralization evolution over~1 b.y. Geology. 46(4), 323-326.
- Stern, C. R., Allaz, J. M., Raschke, M. B., Farmer, G. L., Skewes, M. A., Ross, J. T. 2018. Formation by silicate-fluoride+phosphate melt immiscibility of REE-rich globular segregations within aplite dikes. Contributions to mineralogy and petrology, 173:65.
- Sweeney, R.J., 1994. Carbonatite melt compositions in the Earth's mantle. Earth and Planetary Science Letters. 128, 259-270.
- Trofanenko, J., Williams-Jones, A.E., Simandl, G.J., Migdisov, A.A., 2016. The nature and origin of the REE mineralization in the Wicheeda carbonatite, British Columbia, Canada. Economic Geology. 111(1), 199-223.
- Veksler, I.V., Dorfman, A.M., Dulski, P., Kamenetsky, V.S., Danyushevsky, L.V., Jeffries, T., Dingwell, D.B., 2012. Partitioning of elements between silicate melt and immiscible fluoride, chloride, carbonate, phosphate and sulfate melts, with implications to the origin of natrocarbonatite. Geochimica et Cosmochimica Acta, 79, 20-40.
- Veksler, I.V., Nielsen, T.F.D., Sokolov, S.V., 1998. Mineralogy of crystallized melt inclusions from Gardiner and Kovdor ultramafic alkaline complexes: implications for carbonatite genesis. Journal of Petrology, 39(11-12), 2015-2031.
- Vladykin, N.V., 2009. Potassium alkaline lamproite-carbonatite complexes: petrology,

- genesis, and ore reserves. *Russian Geology and Geophysics* 50(12), 1119–1128.
- Vladykin, N.V., 2013. Petrology and composition of rare-metal alkaline rocks in the South Gobi Desert, Mongolia. *Russian Geology and Geophysics*. 54(4), 416-435.
- Wall, F., Mariano, A.N., 1996. Rare earth minerals in carbonatites: a discussion centred in the Kangankunde carbonatite, Malawi. In: Jones A P, Wall F, Williams C T. (Eds.), *Rare earth minerals: chemistry, origin and ore deposits*. Mineralogical Society Series, vol.7. Chapman and Hall, London. 193-225.
- Wallace, M.E., Green, D.H., 1988. An experimental determination of primary carbonatite magma composition. *Nature*. 335(6188), 343-346.
- Watkinson, D.H., Wyllie, P.J., 1971. Experimental study of composition join $\text{NaAlSi}_3\text{O}_8\text{-CaCO}_3\text{-H}_2\text{O}$ and genesis of alkali rock-carbonatite complexes. *Journal of Petrology*. 12(2), 357-378.
- Weidendorfer, D., Schmidt, M.W., Mattsson, H.B., 2016. Fractional crystallization of Si-undersaturated alkaline magmas leading to unmixing of carbonatites on Brava Island (Cape Verde) and a general model of carbonatite genesis in alkaline magma suites. *Contributions to Mineralogy and Petrology*. 171(5), 43.
- Weng, Z., Jowitt, S.M., Mudd, G.M., Haque, N., 2015. A detailed assessment of global rare earth element resources: Opportunities and challenges: *Economic Geology and the Bulletin of the Society of Economic Geologists*. 110, 1925-1952.
- Wyllie, P.J., Jones, A.P., Deng, J., 1996. Rare earth elements in carbonate-rich melts from mantle to crust. In: Jones, A.P., Wall, F., Williams, C.T. (Eds.), *Rare Earth Minerals: Chemistry, Origin and Ore Deposits*. The Mineralogical Society Series,

vol.7. Chapman and Hall, London. 7, 77-103.

Xie, Y., Hou, Z., Yin, S., Dominy, S.C., Xu, J., Tian, S., Xu, W., 2009. Continuous carbonatitic melt-fluid evolution of a REE mineralization system: Evidence from inclusions in the Maoniuping REE Deposit, Western Sichuan, China. *Ore Geology Reviews*, 36(1), 90-105.

Xu, C., Campbell, I.H., Allen, C.M., Huang, Z.L., Qi, L., Zhang, H., Zhang, G.S., 2007. Flat rare earth element patterns as an indicator of cumulate processes in the Lesser Qinling carbonatites, China. *Lithos.* 95(3), 267-278.

Xu, C., Campbell, I.H., Kynicky, J., Allen, C.M., Chen, Y.J., Huang, Z.L., Qi, L., 2008. Comparison of the Daluxiang and Maoniuping carbonatitic REE deposits with Bayan Obo REE deposit, China. *Lithos.* 106(1), 12-24.

Xu, C., Kynicky, J., Chakhmouradian, A.N., Campbell, I.H., Allen, C.M., 2010. Trace-element modeling of the magmatic evolution of rare-earth-rich carbonatite from the Miaoya deposit, central China. *Lithos.* 118(1-2), 145-155.

Yarmolyuk, V.V., Kudryashova, E.A., Kozlovsky, A.M., Lebedev, V.A., Savatenkov, V.M., 2015. Late Mesozoic-Cenozoic intraplate magmatism in Central Asia and its relation with mantle diapirism: Evidence from the South Khangai volcanic region, Mongolia. *Journal of Asian Earth Sciences*. 111,604-623.

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Figure Captions

Fig.1 (a) Position of the South Mongolia alkaline province; (b) Simplified geotectonic map of the South Mongolia alkaline province showing the distribution of carbonatite-alkaline complexes (MKC, Mushgai Khudag; BAK, Bayan Khoshuu; LG, Lugiin Gol) modified after Samoilov and Kovalenko (1983) and Baatar et al. (2013); SKSZ, Sulinkheer suture zone; (c) Geological map of the Ulgii Khiid carbonatites and associated syenitic rocks from Kynicky and Chakhmouradian (2010).

Fig.2 Photomicrograph (a-b) and back-scattered electron (BSE) images (c-h) showing the main mineral assemblages of the Ulgii Khiid carbonatites. (a, b) Photomicrograph showing the occurrence of single euhedral elongated apatite grain and apatite aggregates within the carbonatite, (c) Diopside included within the apatite in the carbonatite; (d, f) Tiny monazite grains occur as disseminations within the calcite matrix of the carbonatite; (g, h) Phlogopite and diopside occur together and associated with the apatites in the carbonatite. Abbreviations: Cc-Calcite; Ap-Apatite; Di-Diopside; Mnz-Monazite; Q-Quartz; Phl-Phlogopite; Py-Pyrite.

Fig.3 Apatite-hosted melt inclusions in Ulgii Khiid carbonatites. (a)-Photomicrographs showing that the melt inclusions are distributed randomly within the apatite, (b) A representative intact melt inclusion containing a complex solid phase and liquid CO₂ bubble. L_{CO2}- liquid CO₂ confirmed by microthermometry.

Fig.4 Distribution of trace elements normalized to primitive mantle and

chondrite-normalized REE patterns for calcite (a, b) and fluorapatite (c, d). Normalizing values for trace elements are from McDonough and Sun (1995).

Fig.5 BSE images of exposed melt inclusions in apatites from Ulgii Khiid carbonatites showing varied assemblage and volume of calcite, diopside, phlogopite, monazite, parisite, magnetite, pyrite daughter mineral phases, as well as a phosphate melt. The hole indicates former fluid and CO₂ phases existed in the open part of the inclusions.

Abbreviations: Ap-Apatite; Cc-Calcite; Di-Diopside; Phl-Phlogopite; Mag-Magnetite; Mnz-Monazite; Par-Parisite; Py-Pyrite; PM-phosphate melt.

Fig.6 BSE images of the immiscible melt in the melt inclusions of apatites produced by heating-quenching experiments. (a-b) The presence of three immiscible phases namely, phosphate, silicate, and Fe-silicate melt phases. (c) Immiscible phosphate and silicate melt. (d) Immiscible silicate and Fe-silicate melt. Abbreviations: PM-Phosphate melt; SM-Silicate melt; Fe-SM, Fe-silicate melt.

Fig. 7 Compositions of the heated and quenched immiscible melts plotted on the P₂O₅–SiO₂–FeO diagram.

Fig.8 P₂O₅ versus Ce₂O₃ content diagram of the heated and quenched phosphate melts showing a positive relationship.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Tables

Table 1 Compositions of the rock-forming minerals in the Ulgii Khiid carbonatite.

Table 2 Trace-element compositions of calcite and apatite in the Ulgii Khiid carbonatite.

Table 3 Major-element compositions of phases in apatite-hosted melt inclusions in the Ulgii Khiid carbonatite.

Table 4 Compositions of the immiscible melts after heating-quenching experiments of the apatite-hosted melt inclusions.

Table 1 Compositions of the rock-forming minerals in Ulgi Khiid carbonatite.

Calcite							Apatite								
SiO ₂							0.01	0.11	0.02	0.02	0.18	0.04	0.05	0.05	0.16
FeO	0.02	0.01	0.02	-	0.01	-	0.34	0.37	0.19	-	-	0.06	0.31	0.21	0
MnO	0.05	0.05	0.11	0.14	0.05	0.06	0.23	0.1	0.08	0.08	-	0.04	0.14	0.17	0.02
MgO	0.03	0.02	0.03	0.01	0.03	0.02	-	-	-	-	-	-	-	-	-
CaO	54.79	55.9	55.28	55.76	54.79	56.03	57.97	56.91	57.53	57.19	56.55	56.72	57.2	57.75	56.32
SrO	1.88	2.16	1.58	1.18	1.16	1.32	0.64	1.12	1.46	0.75	1.7	1.84	0.69	0.78	1.54
BaO	-	-	-	0.01	0.04	0.02	-	-	-	0.03	-	-	-	0.03	0.05
Na ₂ O							0.19	0.1	0.02	0.13	0	0.07	0.25	0.13	0.04
K ₂ O							-	0.11	0.03	0.03	0.03	0.04	0.02	0.06	-
P ₂ O ₅							38.57	38.8	39.14	39.07	38.27	38.02	38.2	38	38.48
ThO ₂							0.02	-	-	0.03	0.01	0	-	-	-
UO ₂							0.01	-	-	-	0.02	0.01	-	0.03	0.02
PbO							0.04	0.03	-	-	0.03	-	-	-	0.07
SO ₃							0.48	0.58	0.31	0.47	0.32	0.34	0.61	0.57	0.3
F							4.17	5.85	5.11	4.99	4.83	3.86	4.22	4.77	5.23
Cl							0.02	0.03	0.01	0.02	-	0.01	0.02	0.01	-
-O=(F,Cl) ₂							-1.76	-2.47	-2.15	-2.1	-2.03	-1.63	-1.78	-2.01	-2.2
Total	56.76	58.14	57.01	57.1	56.07	57.46	100.92	101.62	101.74	100.69	99.89	99.41	99.93	100.54	100.01

Note: "-" -below the detection limit; Blank—not analyzed.

Continued Table 1 Compositions of the rock-forming minerals in Ulgii Khiid carbonatite.

	Phlogopite											Diopside					
SiO ₂	39.12	38.35	39.06	37.32	36.93	37.61	37.64	38.54	37.80	38.36	37.89	52.77	53.05	51.39	51.20	49.75	52.83
Cr ₂ O ₃	0.93	1.02	0.68	0.77	1.27	0.69	0.68	0.76	0.56	0.68	0.29	0.85	0.84	0.23	0.75	0.53	0.52
TiO ₂	0.17	0.00	2.90	2.88	3.19	2.00	2.10	2.06	1.91	2.17	1.83	-	0.01	-	0.03	0.03	0.14
Al ₂ O ₃	12.01	14.19	12.69	12.99	12.66	11.97	11.57	13.70	13.32	12.28	12.94	2.13	2.13	0.75	1.45	1.16	1.49
FeO	1.02	1.68	3.55	3.41	3.98	5.35	5.59	4.36	4.57	5.62	5.37	1.85	2.01	1.85	1.80	2.01	2.34
MnO	0.37	0.21	0.11	0.11	0.12	0.11	0.14	0.18	0.16	0.15	0.16	1.10	1.09	3.41	0.66	1.61	0.73
MgO	27.17	27.24	24.31	24.13	22.88	22.62	22.35	23.30	23.42	23.12	23.40	16.56	16.02	14.59	16.43	14.69	16.35
CaO	0.61	0.38	0.17	0.19	0.62	0.74	0.30	0.54	0.10	0.47	0.19	26.40	26.45	26.32	27.38	28.55	26.73
BaO	0.19	0.54	0.25	0.11	0.22	0.05	0.21	0.51	0.39	0.21	0.30	0.05	-	-	-	0.02	0.01
Na ₂ O	0.20	0.27	0.05	0.09	0.09	0.29	0.19	0.18	0.22	0.18	0.20	0.19	0.19	0.24	0.26	0.30	0.41
K ₂ O	10.89	10.14	10.36	10.98	10.99	10.96	10.51	10.40	10.87	10.26	10.65	0.04	-	0.25	0.14	0.06	-
F	2.71	2.31	1.83	2.13	1.66	1.74	1.88	1.94	2.09	2.35	2.10	-	-	0.05	0.02	-	-
Cl	0.01	-	0.01	0.02	0.01	0.03	0.07	-	-	0.01	-	-	-	0.02	-	-	-
-O=(F,Cl) ₂	-1.14	-0.97	-0.78	-0.90	-0.70	-0.74	-0.81	-0.82	-0.88	-0.99	-0.88	-	-	-	-	-	-
Total	94.25	95.33	95.20	94.21	93.91	93.42	92.42	95.64	94.52	94.85	94.42	101.93	101.78	99.09	100.13	98.71	101.55

Table 2 Trace-element compositions of calcite and apatite in the Ulgii Khiid carbonatites.

	Calcite						Apatite					
Rb	0.1	0.13	0.06	0.74	0.17	0.06	0.05	0.05	0.05	0.05	0.05	0.04
Sr	21943	21637	19443	17144	20928	17462	10911	11179	13511	15016	13834	13369
Y	38.9	41.8	24.3	26.4	20.5	20	87.6	89.3	86.5	72.4	82.4	60.1
Zr	0.08	0.05	0.11	5.96	0.06	0.06	3.49	3.48	7.39	8.63	7.78	3.22
Nb	0.02	0.03	0.02	0.95	0.03	0.04	0.02	0.04	0.05	0.03	0.06	0.02
Ba	229	172	145	307	132	23.8	15.7	14.8	15.5	15.1	16.5	14.8
La	356	235	217	213	180	95	508	531	606	479	610	489
Ce	552	383	318	463	294	166	1046	1084	1175	966	1172	955
Pr	55.4	40.1	30.9	43.1	30.8	18.7	123	128	137	113	136	108
Nd	193	145	110	171	113	73.8	504	520	551	457	541	431
Sm	24	19.3	12.9	17.2	13.5	9.55	68.1	70.7	74.3	62.4	70.8	56.1
Eu	10.8	9.76	6.78	6.89	6.72	4.12	26.3	27	29.1	25.8	28.8	23.1
Gd	13.1	12.1	7.41	7.73	6.61	5.94	39.2	40.6	41.6	35.1	39.3	32.8
Tb	1.45	1.41	0.77	1.07	0.74	0.66	4.23	4.22	4.37	3.65	4.14	3.47
Dy	6.41	7.08	3.92	4.63	3.22	3.29	19.3	19.5	19.5	16.6	18.3	14.4
Ho	1.08	1.26	0.67	0.89	0.64	0.66	3.37	3.28	3.17	2.82	3.14	2.56
Er	2.99	3.4	1.55	2.1	1.53	1.41	7.21	7.48	7.74	6.32	6.72	5.25
Tm	0.41	0.4	0.21	0.17	0.18	0.16	0.92	0.94	0.9	0.72	0.84	0.66
Yb	2.46	3.15	1.51	1.81	1.3	1.39	5.66	6.1	5.4	4.35	4.78	3.4
Lu	0.35	0.42	0.24	0.33	0.19	0.11	0.77	0.81	0.65	0.55	0.66	0.48
Hf	0.08	0.13	0.09	0.19	0.14	0.11	0.09	0.08	0.08	0.08	0.09	0.07
Ta	0.02	0.04	0.03	0.15	0.03	0.03	0.02	0.02	0.03	0.02	0.02	0.02
Pb	8.8	5.67	4.81	4.85	5.91	3.4	2.79	2.41	2.36	2.55	2.39	2.2
Th	0.09	0.07	0.05	0.53	0.1	0.11	6	5.79	7.42	12.9	7.27	5.97
U	0.04	0.06	0.04	1.41	0.06	0.06	2.09	2.05	3.73	4.11	4.49	2.84

Table 3 Major-element compositions of phases in apatite-hosted melt inclusions in the Ulgii Khiid carbonatite.

Calcite										Phlogopite								Diopside							
SiO ₂										38.2	38.2	38.2	38.2	38.7	38.2	38.8		54.9	54.4	53.9	53.7	51.3	52.6	51.8	
TiO ₂		-								0.41	1.51	1.65	1.31	0.71	1.21	1.84		0.2	0.02	-	0.03	0.06	-	-	
Al ₂ O ₃										16.7	15.9	15.2	16	15.6	16	15.7		3.18	4.03	4.04	4.04	5.92	4	5.8	
FeO	0.1	-	0.59	0.05	-	0.57	0.05	0.15	-	4.16	4.93	5.08	4.6	3.81	4.44	4.56		3.79	5.1	5.17	3	5.73	4.05	5.94	
MnO	0.1	0.12	0.31	0.08	0.03	0.49	-	1.8	0.05	0.07	0.13	0.16	0.1	0.14	0.16	0.16		0.52	0.05	0.29	0.2	-	-	0.02	
MgO	0.05	0.01	0.37	0.16	0.03	0.65	0.11	0.08	0.03	23.7	23.9	24	24.7	24.5	23.6	23.8		12.1	10.8	11	12.8	11.8	12.2	12.1	
CaO	55.22	55.8	54.55	55.82	54.19	52.69	55.06	54.79	54.55	0.92	0.41	0.48	0.49	0.79	0.7	0.57		24.5	25.4	24.5	26.7	24	24.9	24.1	
SrO	3.43	0.96	0.04	0.05	1.28	0.02	0.01	0.07	3.12																
BaO	0.02	-	-	0.04	-	0.06	-	0.01	0.04	0.82	0.79	0.75	0.07	0.17	0.18	0.36		0.14	-	0.07	-	0.06	0.05	0.2	
Na ₂ O										0.3	0.32	0.34	0.21	0.42	0.38	0.32		0.31	0.62	0.61	0.37	0.21	0.3	0.3	
K ₂ O										10.6	9.6	10.2	9.34	10.5	10.1	9.4		0.05	-	-	-	0.34	0.4	0.39	
Total	58.71	56.77	54.95	56.07	55.5	53.42	55.24	56.88	57.77	95.88	95.69	96.06	95.02	95.34	94.97	95.51		99.69	100.42	99.58	100.84	99.42	98.5	100.65	

Note: "-"-below the detection limit; Blank-not analyzed.

Continued Table 3 Major-element compositions of solid and melt phases in apatite-hosted melt inclusions in Ulgii Khiid carbonatite.

Parisite					Monazite											Phosphorus melt				
SiO ₂	0.33	0.18	0.6	0.85	0.3	0.78	0.25	0.24	0.25	0.41	0.24	0.28	0.56	0.27	0.36	0.24	0.25	0.41	0.24	0.28
CaO	10.5	10.7	9.1	10	4.01	3.63	3.67	3.81	3.71	3.55	4.78	4.67	4.49	2.66	3.46	12.8	13.7	13.5	14.8	14.7
SrO	1.31	0.68	0.69	1.38	2.63	1.53	2.4	2.27	2.01	2.9	1.8	2.64	2.51	2.72	1.38	4.27	4.01	3.9	2.8	4.64
P ₂ O ₅	-	-	-	-	26.5	25.09	25.1	26.8	28.42	27.6	26.27	27.33	25.9	27.78	26.2	26.8	26.4	27.6	28.3	26.3
Y ₂ O ₃	-	-	-	-	-	-	-	-	0.26	0.16	-	0.16	0.15	0.3	0.55	-	-	-	-	-
ThO ₂	-	-	-	-	-	-	-	-	0.05	0.04	0.03	0.01	0.05	0.09	0.16	-	-	-	-	-
U ₂ O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
La ₂ O ₃	15	16.4	18.1	15.7	20.88	21.8	19.6	15.31	17.5	15.1	19.3	17.24	18.9	18.06	18.6	12.3	13.5	10.1	12.3	13.2
Ce ₂ O ₃	30.1	28.5	29.7	29.4	40.1	40.55	38.81	38.8	34.2	35.6	36.85	37.02	39.4	36.04	35.5	28.8	29.2	29.6	28.9	30
Pr ₂ O ₃	-	-	-	-	-	-	-	-	2.03	2.09	2.02	1.87	1.54	1.97	1.79	10.7	10.9	11.2	9.79	8.26
Nd ₂ O ₃	5.04	6.78	6.58	7	7.24	7.44	10.1	10.7	10.9	11.2	9.79	8.26	7.51	9.2	10.4	0.03	0.16	0.35	0.02	0.04
SO ₃					-	-	-	-	-	-	-	-	-	-	-					
F	4.14	4.6	5.64	5.7	0.33	0.37	0.74	0.47	0.3	0.49	0.59	0.69	0.67	0.58	1.03	2.47	1.3	3.49	2.59	2.69
-O=F	-1.74	-1.94	-2.37	-2.4	-0.14	-0.16	-0.31	-0.2	-0.13	-0.21	-0.25	-0.29	-0.28	-	-					
Total	64.68	65.9	68.04	67.63	101.85	101.03	100.36	98.2	99.5	98.93	101.42	99.88	101.4	99.67	99.43	98.41	99.42	100.15	99.74	100.11

Continued Table 3 Major-element compositions of solid and melt phases in apatite-hosted melt inclusions in Ulgii Khiid carbonatite.

Pyrite										
As	S	Fe	Cu	Zn	Co	Ni	Ag	Au	Mo	Total
-	45.28	47.70	5.51	0.06	0.05	-	-	-	0.59	99.18
0.01	44.93	49.77	4.37	0.07	0.06	-	-	-	0.65	99.90
0.01	45.28	48.21	5.41	0.07	0.06	-	-	-	0.65	99.72
-	44.84	48.14	5.42	0.04	0.05	0.01	-	-	0.64	99.36
-	45.92	49.03	4.27	0.03	0.06	-	-	-	0.59	99.91

Table 4 Compositions of the immiscible melts after heating-quenching experiments of the apatite-hosted melt inclusions.

	Phosphorus melt												
SiO ₂	3.11	4.76	4.32	3.73	3.63	4.93	6.92	3.24	4.09	4.31	3.08	3.34	5.46
TiO ₂	0.02	-	0.13	-	0.03	0.06	0.26	0.01	0.09	0.08	-	-	0.07
Al ₂ O ₃	0.19	-	0.25	0.11	0.07	0.53	0.04	0.06	-	0.05	-	-	0.41
FeO	0.6	0.32	4.24	1.48	1.63	1.19	1.48	0.32	1.59	1.09	0.17	0.19	1.94
MnO	0.02	0.01	0.04	0.06	0.04	0.01	-	-	0.03	0.03	0.01	0.02	0.03
MgO	0.25	0.01	0.46	0.05	0.77	0.08	0.03	0.02	0.01	0.03	0.01	0.01	0.58
CaO	43.3	52.9	49.9	51.9	54.2	34.5	33.8	54.5	54.4	52.3	53.2	52	50.8
SrO	-	-	-	-	-	-	-	-	-	-	-	-	-
BaO	-	0.13	0.18	-	-	-	0.06	0.13	0.81	0.56	-	0.07	-
Na ₂ O	-	-	0.07	0.06	0.83	0.05	0.04	0	0.15	0.11	0.23	0.2	0.3
K ₂ O	0.01	-	0.01	0	0.34	-	0.01	0.03	-	0.01	-	0.02	0.07
P ₂ O ₅	34.9	29.6	30.3	31.6	29.4	36.4	36.9	32.7	30.9	32	31.9	32.9	30.8
La ₂ O ₃	2.67	0.84	2.69	2.82	1.5	5.09	4.72	1.24	1.03	1.67	0.86	1.11	1.28
Ce ₂ O ₃	9.54	2.13	4.41	4.5	3.16	11.91	11.19	2.29	2.54	3.17	3.77	3	3.07
Pr ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-	-	-
Nd ₂ O ₃	2.51	0.52	0.77	1.02	1.08	4.67	3.57	0.57	0.96	0.78	0.9	1.03	0.61
SO ₃	0.88	2.91	0.38	1.21	0.34	0.15	0.32	0.24	0.32	0.4	2.23	2.33	0.62
F	2.81	4.6	3.31	2.69	1.25	1.52	1.24	3.71	1.71	2.46	3.13	4.6	2.67
Cl	0.04	0.07	0.03	0.02	-	0.03	0.04	0.01	-	0.03	0.03	-	0.04
Total	100.85	98.8	101.49	101.25	98.27	101.12	100.62	99.07	98.63	99.08	99.52	100.82	98.75

Note: "-" below the detection limit

Continued Table 4 Compositions of the immiscible melts after heating-quenching experiments of the apatite-hosted melt inclusions.

	Silicate melt										Fe-rich Silicate melt						
SiO ₂	31.70	32.00	29.70	33.40	32.70	31.50	29.40	30.70	33.80	32.20	18.20	18.20	28.10	28.20	20.10	20.30	19.70
TiO ₂	0.88	0.19	0.24	1.69	0.08	0.02	0	0.06	2.6	1.48	0.13	0.25	0.14	0.13	0.00	0.00	0.00
Al ₂ O ₃	9.34	7.65	6.86	6	5.65	5.01	3.88	4.59	7.16	6.87	1.45	1.36	0.25	0.24	0.98	1.09	1.15
FeO	14.3	15.7	16.7	15.30	17.70	17.70	19.20	17.30	17.70	16.90	51.70	51.80	39.40	39.30	45.87	46.61	45.26
MnO	0.1	0.12	0.03	0.08	0.07	0.14	0.46	0.37	0.13	0.23	0.28	0.27	0.50	0.53	0.19	0.18	0.20
MgO	2.73	3.13	2.14	3.78	2.78	2.41	2.69	2.84	1.36	2.05	1.95	1.00	0.42	0.42	0.92	0.87	0.81
CaO	23.7	22.1	24.7	21.9	22.8	21	24	22.8	21.3	21.1	18.00	17.70	22.60	22.50	23.90	23.00	23.40
SrO	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BaO	0.23	-	0.07	-	-	-	-	-	-	-	0.00	0.03	0.05	-	0.70	0.90	0.71
Na ₂ O	0.57	0.37	0.31	0.94	0.5	0.66	0.9	1.07	0.65	0.83	0.21	0.20	1.01	0.95	1.40	1.28	1.25
K ₂ O	0.83	0.27	0.16	0.21	0.18	0.04	0.08	0.01	1.57	0.43	0.06	0.07	0.23	0.24	0.12	0.17	0.15
P ₂ O ₅	14.1	15	15.3	12.7	14.8	14.6	13.8	12.7	11.5	13.9	0.31	0.32	1.76	1.72	0.60	0.50	1.00
La ₂ O ₃	0.12	0.03	0.02	0.61	0.2	0.69	0.05	0.54	0.02	0.25	0.61	0.69	0.27	0.27	0.60	0.56	0.53
Ce ₂ O ₃	0.24	0.09	0.11	1.04	0.28	1.2	0.67	0.84	0.3	0.29	2.10	1.95	0.81	0.93	1.52	1.38	1.50
Pr ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Nd ₂ O ₃	0.13	0.03	-	0.41	0.17	0.53	0.19	0.30	0.12	0.11	0.72	0.73	0.23	0.31	0.45	0.46	0.34
SO ₃	0.8	0.72	0.97	0.43	0.38	1.53	2.92	2.62	0.54	0.54	4.31	4.35	4.15	4.17	3.56	3.69	3.67
F	0.08	0.28	0.07	0.49	0.6	0.15	0.52	0.60	-	0.05	0.08	0.32	0.05	0.33	0.25	0.20	0.66
Cl	-	0.03	0.02	0.01	0.02	0.03	0.01	-	0.03	-	-	0.01	0.02	-	0.05	0.04	0.05
Total	99.85	97.71	97.40	98.99	98.91	97.21	98.77	97.34	98.78	97.23	100.11	99.25	99.99	100.24	101.21	101.23	100.38

Abbreviations: Ap-Apatite; Cc-Calcite; Di-Diopside; Phl-Phlogopite; Mag-Magnetite; Mnz-Monazite; Par-Parisite; Py-Pyrite; PM-phosphate melt.

BSE images of the exposed melt inclusions in apatites from Ulgi Khiid carbonatites showing varied assemblage and volume of calcite, diopside, phlogopite, monazite, parisite, magnetite, pyrite daughter mineral phases, as well as a phosphate melt. Hole indicates former fluid and CO₂ phases

existed in the open of the inclusions. We proposed that the Ulgii Khiid carbonatite was produced by silicate-carbonate liquid immiscibility processes with subsequent crystal differentiation and phosphate-carbonate immiscibility. The REE, together with P, preferentially incorporated the residual phosphate melt during the immiscible process. The phosphate melt plays a vital role in the REE behavior in carbonatites and associated ore mineralization.

Highlights

The varied assemblage of calcite, silicates, Fe- and REE minerals, and a REE-rich phosphate melt had been found in the melt inclusions of apatite from Ulgii Khiid carbonatites.

The carbonatite was produced by silicate-carbonate liquid immiscibility processes with subsequent crystal differentiation and phosphate-carbonate melt immiscibility.

The phosphate melt is efficient for extract REE during the immiscible process and plays a crucial role in controlling REE budget and ore genesis in the P-rich carbonatite magmas.