

Mineralogical and geochemical study of apatite and dolomite from the Bayan Obo giant Fe-REE-Nb deposit in Inner Mongolia: New evidences for genesis



Yisu Ren^{a,b}, Xiaoyong Yang^{a,b,*}, Shuangshuang Wang^c, Hüseyin Öztürk^d

^a CAS Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China, Hefei 230026, China

^b CAS Center for Excellence in Comparative Planetology, University of Science and Technology of China, Hefei 230026, China

^c Xi'an Center of Geological Survey, China Geological Survey, Xi'an 710054, China

^d Department of Geological Engineering, Avcilar Campus, Istanbul University, Istanbul TR-34850, Turkey

ARTICLE INFO

Keywords:

Apatite
EPMA and LA-ICPMS
REE remobilization
Multi-stage metasomatism
Genesis
Bayan Obo Fe-REE-Nb deposit

ABSTRACT

The Bayan Obo Fe-REE-Nb deposit is the world's largest resource of REE and its origin still remains controversial. To decipher the genesis of this unique deposit, we conducted a detailed mineralogical observations using scanning electron microscope (SEM), cathodoluminescence (CL) and in-situ micro-analyses on chemical compositions of the dolomite and apatite by EPMA and LA-ICPMS techniques. A wide range in SrO contents in dolomite mineral grains from coarse-grained dolomite marble has been observed. The SrO contents in the margin of the dolomite mineral reach up to 1.04 wt%, while the SrO contents in the core are as low as 0.16 wt%. In contrast, the SrO contents of the dolomite minerals of fine-grained dolomite marble are basically invariable, mainly concentrating on the range of 0.1 wt%–0.2 wt%. The MnO and FeO concentrations of dolomite mineral grains from the coarse-grained dolomite marble (MnO, 0.24 wt%–0.45 wt%; FeO, 2.27 wt%–3.42 wt%) are significantly lower than those of dolomite from fine-grained dolomite marble (MnO, 0.84 wt%–3.32 wt%; FeO, 3.59 wt%–12.16 wt%). The big differences in major elements between two types of the H8 dolomite marble imply different forming processes. Three types of apatite show big differences in cathodoluminescent signatures, major and trace elements. Type I fluorapatite has few REE mineral inclusions and Type II fluorapatite hosts abundant tiny REE mineral (monazite) inclusions. Type III fluorapatite from strongly deformed coarse-grained dolomite marble forms abnormally large monocrystals with elongated orientation. Both Type I and Type II fluorapatite from fine-grained dolomite marble samples display the heterogeneous component regions under BSE, with obvious depletion in Na and REE in BSE-dark areas observed in the X-ray compositional maps. Unaltered (BSE-bright) regions in Type I and Type II fluorapatite have high REE (17470–77090 ppm), Y (714–8162 ppm), Na (2023–10258 ppm), Sr (2126–6422 ppm) concentrations, obviously different from Type III fluorapatite (REE, 2452–7496 ppm; Y, 157–285 ppm; Na, 501–1464 ppm; Sr, 6878–9949 ppm). The REE, Na, Th and Pb depletion in BSE-dark regions in Type I and Type II apatite correspond to two styles of REE remobilization during fluid-induced dissolution-precipitation processes. Late-stage REE, Na, Ba, CO₃²⁻, SO₄²⁻-rich mesothermal hydrothermal fluid evolved from carbonatite was responsible for REE leaching in Type I fluorapatite. The Sr-rich, Na-poor, REE-poor Type III fluorapatite and associated elevated SrO contents in the margin of dolomite imply that the deposit underwent subsequent fluid infiltration by Sr-rich, REE-poor, Na-poor metamorphic fluid, causing the REE leaching in Type II fluorapatite and the consequent formation of monazite inclusions. As a common REE-bearing mineral in Bayan Obo deposit, apatite displays a diversity of textures and occurrences, fingerprints multi-stage metasomatic fluids and provides new insights into the mechanism of REE enrichment and remobilization.

1. Introduction

The Bayan Obo REE-Fe-Nb deposit in the Inner Mongolia is the

world's largest rare-earth element resource, accounting for approximately 80% of world's REE reserves. Reserves for the main and east orebodies were estimated to be 57.4 Mt at 6 wt% REE₂O₃ (Fan et al.,

* Corresponding author at: CAS Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China, Hefei 230026, China.
E-mail address: xyyang@ustc.edu.cn (X. Yang).

<https://doi.org/10.1016/j.oregeorev.2019.04.020>

Received 20 July 2018; Received in revised form 21 March 2019; Accepted 25 April 2019

Available online 27 April 2019

0169-1368/ © 2019 Elsevier B.V. All rights reserved.

2014; Xie et al., 2016). The unique giant REE deposit is extremely geologically complex with at least 11 stages from deposition, through metamorphism and mineralization, to the intrusion of Hercynian granitoid to the south of the deposit (Chao et al., 1992, 1995, 1997; Smith et al., 2000). The mineral paragenesis of the Bayan Obo ore is exceedingly complex with over 170 minerals identified (IGCAS, 1988). Despite many studies over the last 80 years on the REE mineralogy, mineralization age and geochemistry of the deposit, the genesis and the mineralizing age still remain intense debate. Most scholars agree that carbonatite dykes intruded into the basement rocks or the Bayan Obo Group at around 1.4 Ga (Le Bas et al., 2007; Yang et al., 2011; Fan et al., 2014, 2016; Zhu et al., 2015; Zhang et al., 2017; Liu et al., 2018b) and remobilization of REE occurred due to subduction of the Palaeo-Asian oceanic plate during the Caledonian (Ling et al., 2013; Campbell et al., 2014; Lai et al., 2015; Smith et al., 2015; Zhu et al., 2015; Liu et al., 2018b).

The origin of the ore-hosting dolomite and the timing of the main REE mineralization are still controversial. The proposed genetic models of the ore-hosting dolomite include carbonatitic magmatism (Yuan et al., 1992; Le Bas et al., 1992, 1997, 2007; Yang et al., 2003, Yang and Le Bas, 2004; Yang et al., 2011; Sun et al., 2012, 2013; Campbell et al., 2014; Fan et al., 2014, 2016; Zhu et al., 2015; Liu et al., 2018a), hydrothermal alteration of sedimentary carbonate rocks (Chao et al., 1992, 1997; Wang et al., 1994; Xu et al., 2008; Yang et al., 2009, 2017; Lai et al., 2012; Lai and Yang, 2013; Lai et al., 2015, 2016; Ling et al., 2013; Smith et al., 2015) and submarine exhalative sedimentation (Tu, 1998; Gao et al., 1999). A close relationship between the Bayan Obo ore-bearing dolomite and carbonatitic magma has been demonstrated. The mineralized dolomite has obviously similar REE distribution patterns with the carbonatite (Yang et al., 2009; Yang et al., 2011). The narrow range of the near-zero $\delta^{56}\text{Fe}$ isotope values of fine-grained iron ores supports a magmatic origin (Sun et al., 2013). By contrast, carbon, oxygen and magnesium isotopes in mineralized dolomite marble vary significantly, and are distinctively different from those in mantle-derived carbonatite (Yang et al., 2009; Sun et al., 2012; Ling et al., 2013; Smith et al., 2015). There are big distinctions in chemistry between fine-grained and coarse-grained facies of H8 marble (Yang et al., 2011; Lai et al., 2012). Intensively REE-mineralized H8 dolomites have obviously different geochemical characteristics from those of dolomites with low REE contents (Yang et al., 2009; Lai and Yang, 2013). The dolomite crystals show decreases in Fe, Sr and REE from rim to core and vary greatly in REE patterns from LREE-rich in the rim to HREE-rich in the core (Ling et al., 2013; Smith et al., 2015). Therefore, the genetic model of metasomatism of sedimentary carbonate by REE-rich hydrothermal fluid cannot be ruled out.

The variable geochronological data lead to confusion in the interpretations of the time and episodes of ore mineralization. The isochron ages of Sm-Nd whole rocks of dolomite and REE minerals range from 1013 to 1592 Ma, with a clear frequency peak at 1.2–1.3 Ga (Yuan et al., 1992; Cao et al., 1994; Ren et al., 1994; Zhang et al., 1994, 2001, 2003; Liu et al., 2005; Yang et al., 2011; Zhu et al., 2015). SHRIMP Th-Pb geochronological data reveal the age of 1325 ± 60 Ma in zircon core derived from East orebody (Campbell et al., 2014), suggesting that the carbonatitic dykes and the H8 dolomite are broadly contemporaneous. The Mesoproterozoic carbonatite magmatism, associated with the final breakup of Columbia supercontinent (Zhao et al., 2003, 2004; Zhang et al., 2009), probably contributed to the formation of the giant REE deposit. However, Th-Pb isotopic measurements of the REE minerals, such as monazite and bastnaesite from orebodies mostly yield early Palaeozoic ages from 555 Ma to 398 Ma (Chao et al., 1992, 1995, 1997; Ren et al., 1994; Wang et al., 1994).

The objective of the present study is to further investigate the genesis of the Bayan Obo REE deposit accomplished by a detailed research by observations under SEM and CL, in-situ micro-analyses on the chemical compositions of the dolomite and apatite by EPMA and LA-ICPMS. Apatites derived from different rock types have distinctive

abundances of trace elements and display different chondrite-normalized REE patterns (Belousova et al., 2002). Cathodoluminescence is an important property of apatite that is caused by transition metal, REE and anion substitution (Waychunas, 2002). The concentrations of activators, particularly Mn/Fe, Na, S, and REE can be easily changed during hydrothermal mineralization and alteration. Therefore, CL properties combined with chemical compositions of apatite provide fast screening tools to assess multistage hydrothermal alteration (Bouzari et al., 2016). Apatite from the Bayan Obo deposit displays a diversity of textures and occurrences. Some scholars classified it into different types validly. Campbell and Henderson (1997) recognized four distinctive types of fluorapatite examined by cathodoluminescence properties and electron probe microanalyses. Deng et al. (2017) classified three types of apatite by different occurrences and chemical compositions with distinctly different Y/Ho ratios. In this study, we have identified three types of apatite based on the mineral morphology, internal structural features and trace elements composition. Based on the former studies of the apatites from the Bayan Obo deposit, we further investigated the heterogeneous composition zones and internal structure even in individual apatite particles. This study concentrates on the REE mineralization and remobilization in apatite and implies that two styles of REE leaching controlled by the fluids of different components, providing new insights into studying the behavior of REE during mineralization and hydrothermal metasomatism.

2. Geological setting

The Bayan Obo REE-Fe-Nb deposit is located in Inner Mongolia at the northern margin of North China Craton (NCC), separated from the Inner Mongolia Hercynian massif to the north by the Wulanbaolige deep fracture (Fig. 1a). The deposit possesses in excess of 57.4 Mt REE reserves with an average grade of 6% REE_2O_3 (Fan et al., 2014; Xie et al., 2016). It is also the largest niobium (Nb) deposit in China and a major iron deposit. The Bayan Obo Group was deposited in the Mesoproterozoic-Neoproterozoic (Liu et al., 2016; Zhong et al., 2015; Lai et al., 2016; Liu et al., 2017) and has been subdivided into eighteen lithological units, H1-H18 in ascending order (Bai and Yuan, 1985; IGCAS, 1988), principally consisting of low grade metamorphic clastic rock sequences, for instance, sandstones, slates, and carbonate. The Fe-Nb-REE deposit is contained within the H8 dolomite marble of Bayan Obo Group (Fig. 1b). The depositional age of the H8 dolomite marble was constrained by the U-Pb data from detrital zircons of the Hala-huogete (H7) formation of the Bayan Obo Group as 1710 ± 29 Ma (Zhong et al., 2015) and Re-Os geochronology of the black schist from Bilute (H9) with an age of 1447 ± 42 Ma (Liu et al., 2016).

The H8 dolomite marble unit hosting the majority of the ore, is confined to the south of Kuangou fault. The mine is composed of East, Main and West orebodies, showing as three spindles and occupying an area of approximately 18 km west to east and > 1 km north to south (Fig. 1a). The major ore minerals are monazite and (Ca-) REE fluorocarbonates, aeschynite and pyrochlore (Nb, REE), magnetite and hematite (Fe). Main gangue minerals include fluorite, barite, alkali amphibole, apatite, quartz and aegirine.

Detailed geological mapping has shown that there are nearly one hundred carbonatite dykes occurring adjacent to the Bayan Obo deposit (Fig. 1a). The majority of carbonatite dykes cut the Archean Wu Tai gneiss and some dykes intruded into the Bayan Obo group. They are usually 0.5 to 2.0 m wide and 10–200 m long. Carbonatite dykes can be divided into three types: dolomite, co-existing dolomite-calcite and calcite type. These dykes fenitized the country rocks on both sides of the contact zones. Zircon from the carbonatite dykes yielded an upper intercept age of 1417 ± 19 Ma and monazite gave an Sm-Nd isochronal age of 1275 ± 87 Ma (Fan et al., 2014), consistent with the Sm-Nd isochronal age of the whole rock (1354 ± 59 Ma) (Yang et al., 2011).

Later REE veins are also clearly identified in outcrop by the distinguishing feature of including very coarse-grained Huanghoite,

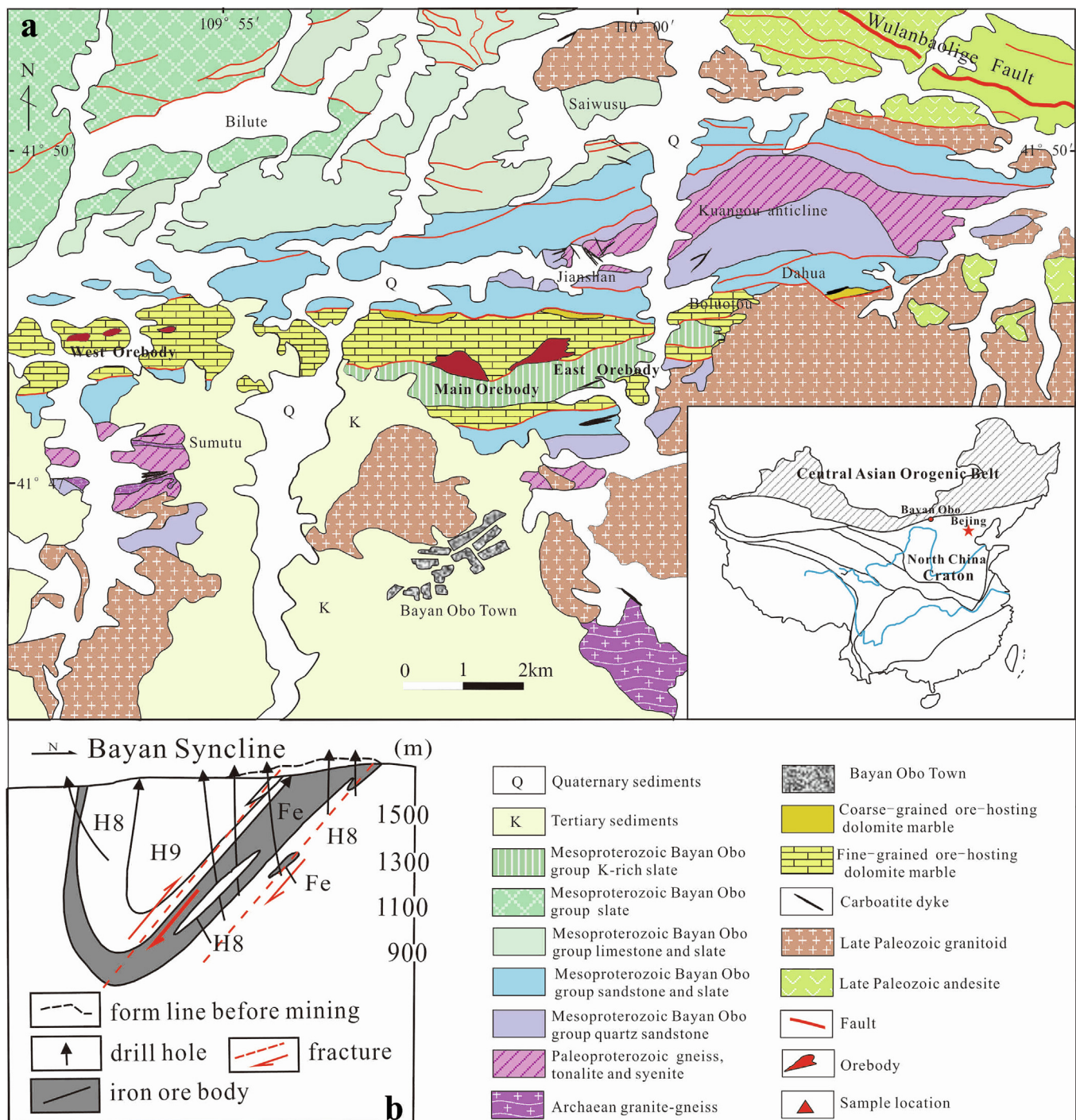


Fig. 1. (a) Geological sketch map of the Bayan Obo REE deposits (modified after Yang et al., 2011a); (b) geological cross section of the No. 10 exploration line in the main ore-body (Liu et al., 2006).

monazite and (Ca-) REE fluorocarbonates and accompanied gangue minerals fluorite, aegirine, alkali amphibole, biotite and pyrite. The late-stage veins cut across the massive Fe-Nb-REE ore. The Sm-Nd isotope age of REE minerals is 420 ± 46 Ma (Chao et al., 1995, 1997), gangue mineral is 442 ± 42 Ma (Hu et al., 2009) and Re-Os isochronal age of pyrite is 439 ± 86 Ma (Liu et al., 2004). A significant thermal event of Caledonian age resulted in the REE reactivation and the formation of late-stage veins. This event also affected the ore body and carbonatite dykes indicated by the facts that hydrothermal overgrowth of the ore body zircon has a U-Pb age of 455 ± 28 Ma (Campbell et al., 2014) with the U-Pb age on the core of zircon 1325 Ma and

hydrothermal zircons from the Wu dyke have a Caledonian age with the U-Pb age 381 ± 4 Ma (Liu et al., 2018a,b).

The H8 dolomite marble is grouped into coarse-grained (H8_c) and fine-grained (H8_f) types based on grain size (Le Bas et al., 1997; Yang and Le Bas, 2004). The coarse-grained (> 1 mm) variety is sparsely distributed along the south of the Kuangou fault (Fig. 1a), mainly consisting of coarse-grained dolomite and minor rounded, elongate apatite. Most apatite crystals are subprismatic to elongate with an orientation paralleling the lineation of the dolomite which resulted from shearing and deformation. The fine-grained variety constitutes the major REE ore-host rock. It occurs to the south of Kuangou fault zone,

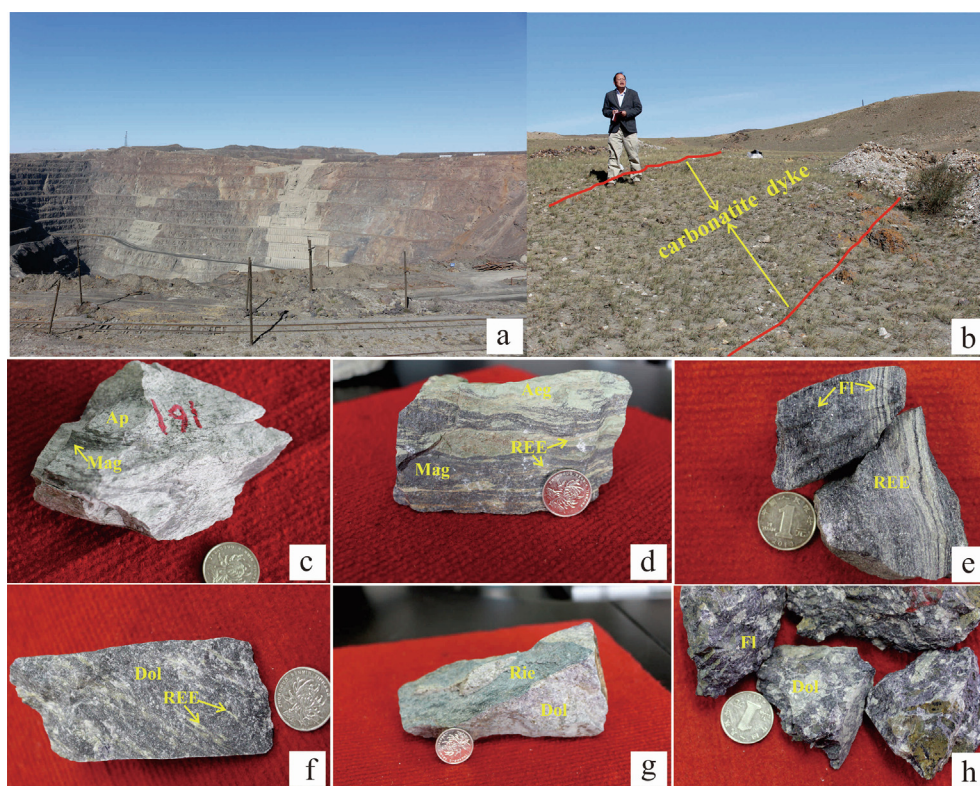


Fig. 2. Field photographs of East orebody, carbonatite dyke and major mineralization types from the Bayan Obo deposit. (a) Mining pit of the East orebody; (b) outcrop of the carbonatite dyke located in Jianshan; (c) apatite- REE (bastnaesite) – magnetite banded ore; (d) aegirine, magnetite and REE banded mineralization; (e) fluorite-REE-magnetite banded ores; (f) fine-grained dolomite with disseminated REE mineralization; (g) later riebeckite vein filling the joints in the H8 dolomite; (h) replacement of the host dolomite by fluorite. Ap – apatite; Mag – magnetite; Aeg – aegirine; Fl – fluorite; Dol – dolomite; Rie – riebeckite.

continuously distributed along the Bayan Obo syncline (Fig. 1b). It is composed mainly of dolomite and ankerite, with variable monazite, bastnaesite, magnetite, fluorite and barite. Compared to the coarse-grained dolomite marble, the fine-grained variety is far richer in REE, containing a great quantity of rare earth minerals. REE ores occur as massive, banded and disseminated mineralization (Fig. 2). Disseminated REE ores contain clusters of fine-grained monazite, with bastnaesite and magnetite grains filling micro fractures in dolomite (Fig. 2f). Banded REE-Nb-Fe ores are characterized by intervals of bands in very fine (mm-cm) scale, defined by concentrations of REE minerals (apatite, monazite and bastnaesite), magnetite, fluorite, riebeckite, aegirine and barite (Fig. 2c–e). Based on petrography, apatite formed earlier as fine aggregates, followed by the intimate intergrowth of bastnaesite and barite. The widespread replacements of the host dolomite by sodium metasomatism and fluorine metasomatism are represented by aegirine, riebeckite and fluorite bands. We observe the spatial interval distribution of aegirine, magnetite and REE in the ore rocks (Fig. 2d). Dark-purple fluorites occur as ribbons in fluorite-REE-magnetite banded ores (Fig. 2e) and in the form of disseminated veinlets in the dolomite type REE ores.

3. Analytical methods

3.1. Scanning electron microscope

The scanning electron microscope (SEM), cathodoluminescence observations and energy dispersive spectroscopy (EDS) analyses were made in the Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China, Chinese Academy of Sciences. A MIRA 3 LMH (FE-SEM) was used to take BSE images and equipped with EDAX GENESIS APEX to identify minerals and perform compositional X-ray maps of apatite. Apatite grains were separated from samples HNB52 (REE mineralized dolomite marble), 09BY161 (apatite, magnetite, rare-earth fluorocarbonate banded ore), BY09 (apatite-bearing coarse-grained dolomite marble), mounted in epoxy resin, polished down to near half sections, and then

photographed in reflected and transmitted light. Different chemical component zones and internal structure of mineral grains were observed using the back-scatter electron (BSE) and cathodoluminescence (CL) image technique. The samples were coated slightly with carbon to prevent charging before SEM analyses. The resolution of the electron microscopic image was 2.0 nm at 30 kV. All measurements were carried out using an accelerating voltage of 15 kV, a beam current of 20 nA on polished sections of samples in situ.

3.2. Electron microprobe analysis

Representative minerals from the H8 dolomite marble samples in polished sections were analyzed using an EPMA-1720H electron microprobe at the Key Laboratory of Nanjing Institute of Geology and mineral Resources. Appropriate matrix-specific standards and optimal instrumental conditions were carefully chosen with respect to different minerals. For the dolomite minerals, the standards are SrSO_4 for Sr, MnSiO_3 for Mn, BaSO_4 for Ba, apatite for P, quartz for Si, magnesite for Mg, siderite for Fe, cerussite for Pb and calcite for Ca. The measurements were performed using at 15 kV accelerating voltage and a 10 nA beam current, with an electron beam of 30 μm . As for apatite, the beam spot diameter was set at 1–2 μm . The accelerating voltage and beam current was 15 kV and 10 nA, respectively. The $\text{K}\alpha$ line was chosen for the analyses of Mg, F, Ca, Al, P, S, Cl, Fe, K, Na and Si. The $\text{L}\alpha$ line was chosen for As, Sr, La, Ce, Pr, Nd, Sm, Eu, Gd, Ba, Dy, Yb and Y. The $\text{M}\alpha$ line was chosen for Th, U and Pb. The standards utilized for analyzing the apatite minerals are SrSO_4 for S and Sr, K-feldspar for K, BaSO_4 for Ba, pyrope for Mg and Fe, FeAsS for As, jade for Na and Al, synthetic Yb for Yb, LaF_3 for F, monazite for Th, U, Pb, synthetic REE oxides, REEF_3 for REE, jade for Si, apatite for P and diopside for Ca. Raw data were corrected using standard ZAF correction procedures.

3.3. In-situ trace element analysis by LA-ICP-MS

Apatites were separated from intensively REE-mineralized H8 dolomite and weakly REE-mineralized H8 dolomite samples. Major and

trace element concentrations in apatite were measured in situ on polished epoxy resin by Laser Ablation Inductively-Coupled Plasma Mass Spectrometry (LA-ICP-MS) at the In situ Mineral Geochemistry Lab, Ore deposit and Exploration Centre (ODEC), Hefei University of Technology, China. The analyses were carried out on an Agilent 7900 Quadrupole ICP-MS coupled to a Photon Machines Analyte HE 193-nm ArF Excimer Laser Ablation system. Helium was applied as a carrier gas. Argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP. The following basic set of isotopes for apatite were monitored: ^{23}Na , ^{31}P , ^{43}Ca , ^{55}Mn , ^{85}Rb , ^{88}Sr , ^{89}Y , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu , ^{178}Hf , ^{208}Pb , ^{232}Th , ^{238}U . Each analysis was performed by a uniform spot size diameter of 25 μm at 8 Hz with energy of 12 mJ/cm^2 for 40 s after measuring the gas blank for 20 s. Standard reference materials BCR-29, glass standard NIST 610 and NIST 612 were used as external calibration standards. Every 10–15 sample analyses were followed by analyses of standard reference materials. The off-line data process was performed using LaTEcalc software (Hou Zhenhui, personal communication) with calcium as the internal standard element obtained by EPMA. The preferred values of element concentrations for the USGS reference glasses are from the GeoReM database (Jochum and Nohl, 2008).

4. Petrography

4.1. Dolomite

Two types of the dolomite marble are identified based on structural and textural features. Coarse-grained dolomite marble is intermittently distributed along the south of the Kuangou fault, the northern limb of the Bayan Obo syncline. Sample BY09 was collected near the fault and has an orientation paralleling the lineation of sheared dolomite (Fig. 3a, c). The dolomite mineral is up to 1.2 $\text{mm} \times 0.4 \text{ mm}$ in size. Euhedral, prismatic apatite is distributed along the dolomite layers. It is commonly observed that fine-grained dolomite marble is metasomatized to aggregates of fluorite $\pm$ monazite $\pm$ bastnaesite $\pm$ magnetite (Fig. 3b, d). Fine-grained dolomite marble samples BY19, HNB20,

HNB23, HNB28 were analyzed to find the distinctions in chemistry of dolomite mineral from that of coarse-grained type of H8 marble.

Marginal metasomatic texture and metasomatic perforation texture are universal phenomena, which are the results of newly added hydrothermal fluids interacting with the original dolomites along the margin or the crack/cleavage of dolomite (Fig. 4). Disseminated, vein-like monazites fill in fractures and grain boundaries in dolomite marble, implying that the dolomite was earliest phase. Intensely mineralized fine-grained dolomite is rich in metasomatic fluorite. The fluorite occurs as veins accompanied by abundant bastnaesite or as tiny droplets distributing within the dolomite minerals. Large dolomite grains are surrounded or replaced by numerous smaller dolomite grains and fine-grained REE minerals (Fig. 4a, b, d). We observe that magnetite and riebeckite encompass the coarse grained dolomite relic which retains relatively completed cleavage reflecting monomineral crystal structure (Fig. 4c, f). Large relict pods of dolomite are retained in intensely fluorine metasomatic rock in which a relative abundance of rare earth minerals are distributed along the contact zones between the dolomite and fluorite (Fig. 4e).

4.2. REE-Bearing minerals

Apatite, monazite and bastnaesite are representative REE minerals in the Bayan Obo deposit. In general, three types of fluorapatite are identified based on occurrences, associated minerals and internal structures under SEM and cathodoluminescent imaging. Type I and Type II fluorapatite are from fine-grained intensively mineralized dolomite marble samples. Type I fluorapatite has few REE mineral inclusions. Type II fluorapatite hosts abundant tiny REE mineral inclusions. Type III fluorapatite is from the coarse-grained weakly mineralized dolomite marble with an orientation paralleling the lineation of sheared dolomite.

Type I fluorapatite is mainly from apatite- REE (bastnaesite) - magnetite banded ore (sample 09BY161) which is the product of strong REE mineralization, constituted by 60% to 80% fluorapatite and REE-bearing minerals (Fig. 5a, b). Type I fluorapatite is typically anhedral granular and has sizes of 30–50 μm . As these microscope photos reveal,

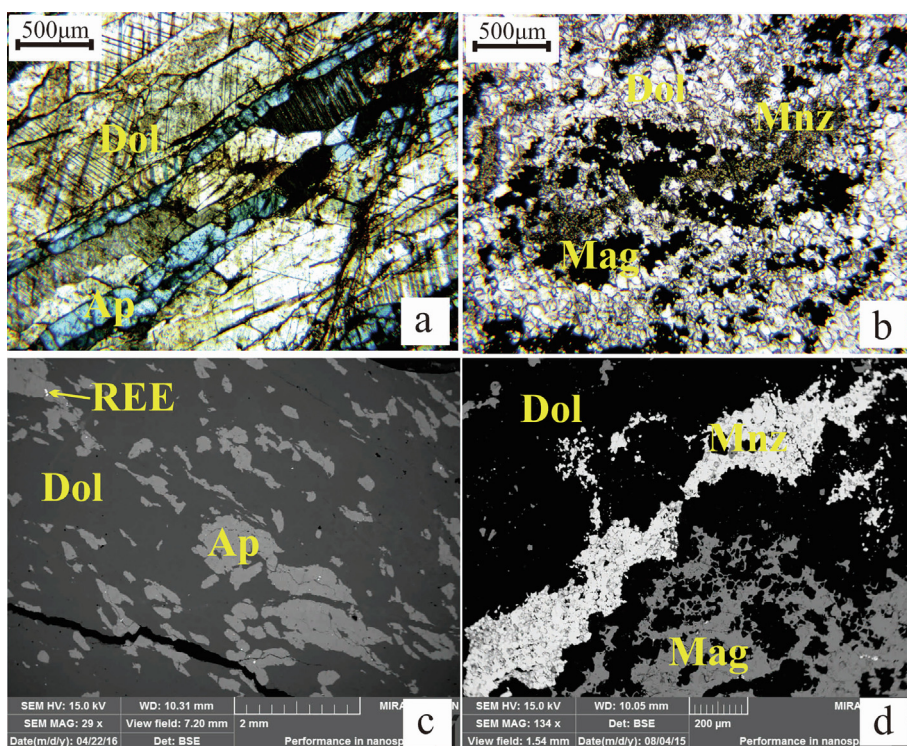


Fig. 3. (a) Photomicrograph of Bayan Obo coarse-grained dolomite marble near the south of Kuangou fault, cross-polarized light, strongly deformed; (b) Photomicrograph of Bayan Obo fine-grained dolomite marble containing clusters of monazite and magnetite, cross-polarized light; (c) back-scattered-electron image of coarse-grained dolomite marble with weak mineralization; (d) back-scattered-electron image of fine-grained dolomite marble. Dol – dolomite; Ap – apatite; Mag – magnetite; Mnz – monazite.

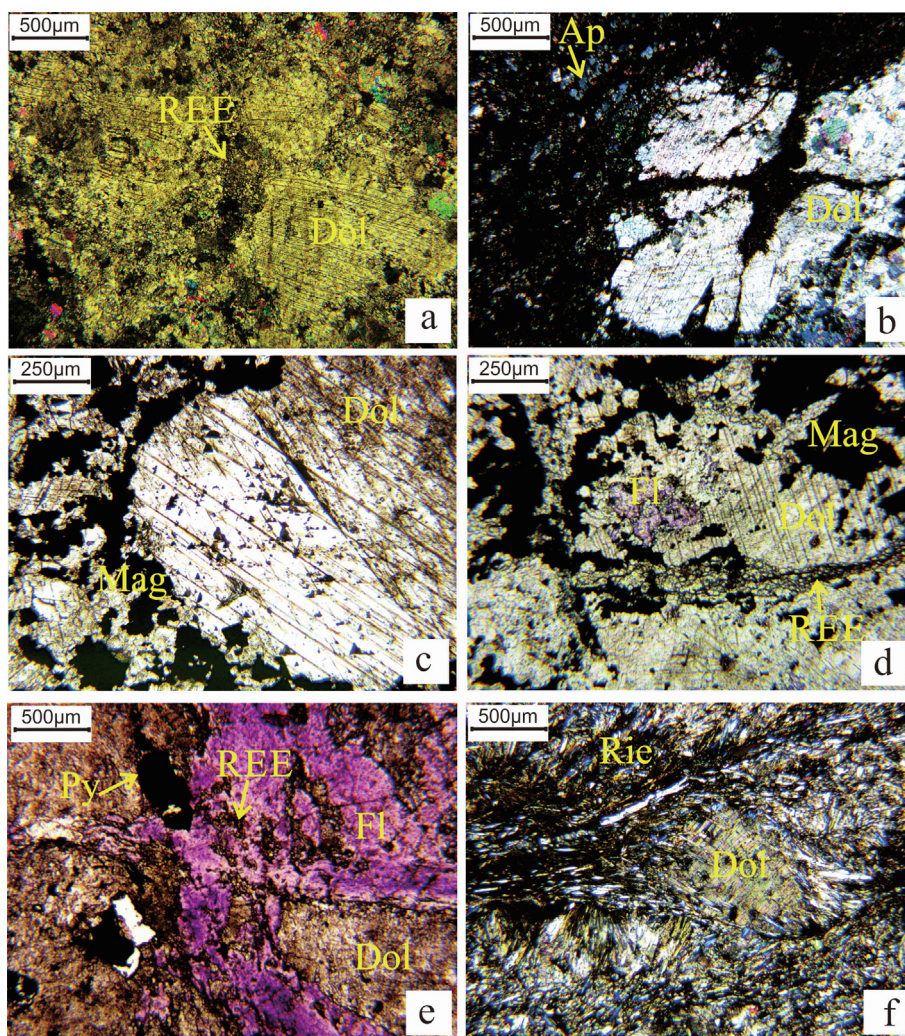


Fig. 4. Photomicrographs of metasomatic textures. (a) Clusters of REE minerals filling in fractures and grain boundaries in dolomite; (b) the superposition of hematization on early REE mineralization and pre-existing dolomite; (c) magnetite encompassing the coarse grain dolomite relic; (d) fluorite droplets distributing within the dolomite mineral which retains relatively completed cleavage, REE veins filling the cracks in dolomite; (e) Large relict pods of dolomite retained in intensely fluorine metasomatic rock; (f) coarse grain dolomite remained in riebeckite vein. Dol – dolomite; Ap – apatite; Mag – magnetite; Fl – fluorite; Py – pyrite; Rie – riebeckite.

bastnaesite associated with barite occurs as veins or bands crosscutting the Type I fluorapatite and infilling the fractures of magnetite grains, which indicates that apatite and magnetite formed earlier than the bastnaesite and barite (Fig. 6a). Type I fluorapatite has several notable features as follows:

- 1) Its chemical composition is heterogeneous even in the same fluorapatite under BSE imaging, the BSE-bright and BSE-dark regions occur in the same apatite crystal. Some dark zones occur as polygonal to irregular patches which are closely related to micro-cracks in the interior of apatite crystal and show sharp contact with the BSE-bright areas (Fig. 6b). The BSE-dark rims along the apatite grain are also observed and may show slightly variable thicknesses, displaying blurred boundary with the bright area.
- 2) There are numbers of grains displaying etch pits and pores, somewhere with very small floccules on crystal surface in the analysis of SEM. It is a symbol of dissolution texture, which demonstrates that the Type I fluorapatite grains have undergone latter hydrothermal alteration.
- 3) Few REE mineral inclusions are observed in the interior of the Type I fluorapatite, only some REE mineral (bastnaesite and monazite) grains (10–20 μm) filling the gaps and clearances between the fluorapatite particles.

Type II fluorapatite is mainly from apatite-monzonite mineralized dolomite marble (sample HNB52). Based on the petrology, apatite shows as fine-grained assemblages with most crystals < 40 μm.

Monazite has at least two different textural forms in the ore sample HNB52, corresponding to two different generations. The first generation is monomineral veinlets or bandlets, distributed along fractures and grain boundaries in the dolomite, with most monazite grains of 75–100 μm, prismatic (Fig. 5c). Another generation of monazite occurs as solid inclusions (5–30 μm long) dispersedly distributed inside the Type II fluorapatite aggregates (Fig. 5d). The small monazites are intimately connected with the BSE-dark areas in the Type II fluorapatite (Fig. 6c, d). Type II fluorapatites consist of a high proportion of severely REE-depleted altered zones and show different levels of darkness and irregular zoning patterns under BSE imaging, indicating that they have undergone strong fluid reaction. Different levels of brightness are derived from variable degrees of hydrothermal metasomatism. The slight dark regions occur as irregular net veins or veinlets, meandering through the fluorapatite grain. The deeper dark areas appear as patches (20–40 μm long), sometimes occupying the whole fluorapatite mineral. The most important feature of the Type II fluorapatite is that they host abundant tiny REE mineral inclusions within the leached areas. Those inclusions commonly appear as subhedral to anhedral grains, most 5–10 μm long, some up to 30 μm, having close genetic connection with the BSE-dark apatite (Fig. 6c, d). The distribution of BSE-dark regions and associated REE (small monazite inclusions) minerals (most < 30 μm) tend to correlate with the routes for fluids, namely along grain rims, brittle fractures or micro-cracks in apatite. The density of tiny monazite inclusions is basically proportional to the area ratio of the BSE-dark regions. Occasionally, hematite occurs as tiny veins filling in the fractures between grains (Fig. 6d).

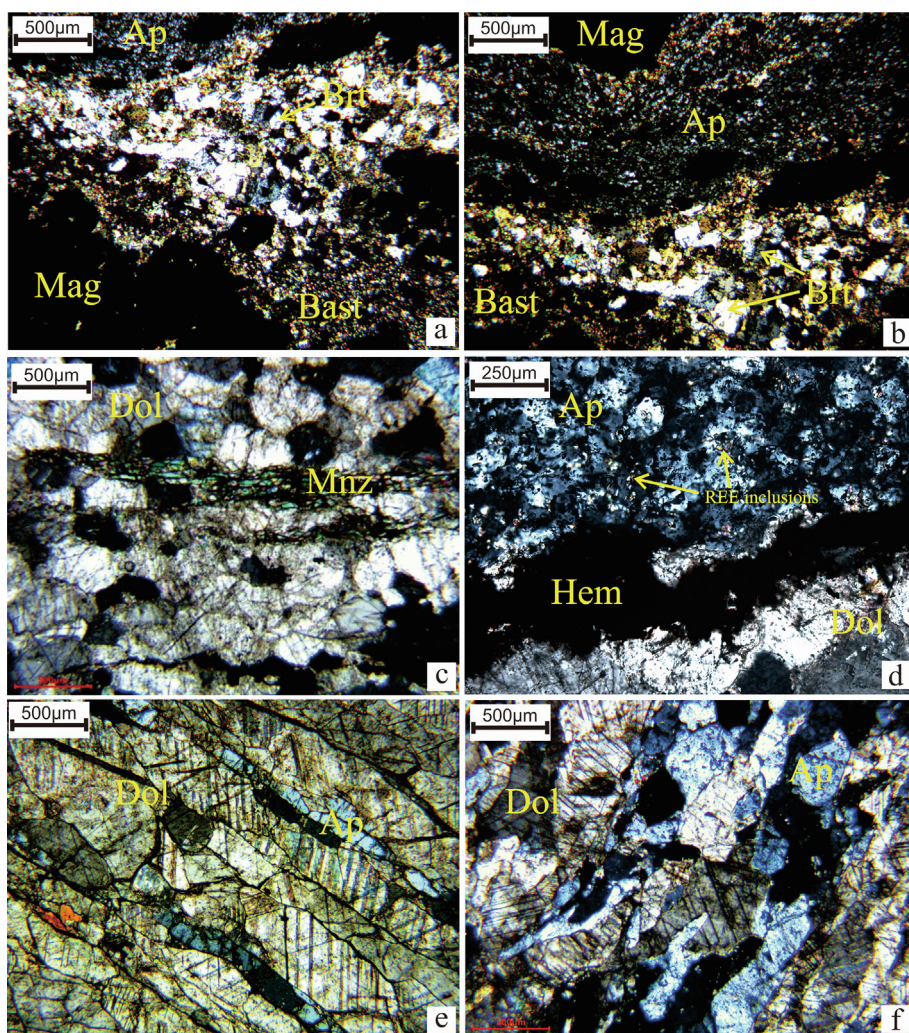


Fig. 5. Thin section photomicrographs of three types of apatites. (a) Type I fluorapatite from apatite – REE (bastnaesite) – magnetite banded ore (sample 09BY161), crosscut by bastnaesite + barite vein; (b) Type I fluorapatite occurring as fine-grained aggregates; (c) apatite–monazite mineralized dolomite marble (sample HNB52) with the first generation of monazite occurring as monomineral veinlets or bandlets; (d) Type II fluorapatite aggregates with abundant monazite inclusions, accompanied by the hematitization; (e) Type III apatite from the coarse-grained dolomite marble (sample BY09) having an orientation paralleling the lineation of sheared dolomite; (f) large-grained subprismatic to elongate Type III apatite with rare REE minerals. Dol – dolomite; Ap – apatite; Mag – magnetite; Brt – barite; Bast – bastnaesite; Mnz – monazite; Hem – hematite.

The Type III apatite derived from the coarse-grained dolomite marble (sample BY09) is subprismatic to elongate, having an orientation paralleling the lineation of sheared dolomites (Fig. 5e, f). This lineation may result from strongly deformation interpreted to be related to the regional thrusting and folding. Apatite is the dominant REE mineral with most crystal sizes of 200 µm (Fig. 6e, f). Occasionally, minor monazite occurs as tiny inclusions (10 µm). The representative character of the Type III fluorapatite is abnormal large monocrystal with elongated orientation with respect to the c-axis of fluorapatite. Cracks can always be associated with the BSE-dark regions due to the fluid infiltration. The paths of fluids following irregular cracks and microfractures of the apatite, occur as dark-veins of different levels of brightness overprinting the bright regions. Faintly visible BSE-dark veinlets intersect and form tangled and disordered nets in the slightly altered regions (Fig. 6f).

High resolution maps of trace elements in three distinct types of apatite minerals are shown in Figs. 7–9. In Type I fluorapatite, the BSE-bright areas are obviously richer in Ce and Nd elements, slightly richer in Na, slightly depleted in Ca compared with the dark areas appearing as patches under BSE imaging (Fig. 7). In Type II fluorapatite, element mapping reveals severe depletion of Ce, Nd and Sm contemporaneously with significant Na loss in altered areas (Fig. 8). The degree of these losses is positively correlated to the level of brightness in BSE image. Variations of Ca and P show their reverse trends with REE. The alteration-related areas in Type II fluorapatite, occurring as irregular veinlets and deeper dark patches under BSE, have elevated contents of Ca and P. Other elements such as Y, Sr, Th and Pb show no differences

in BSE-bright and BSE-dark regions because the contents are nearly equal or below the detection line in both areas. As shown in the mapping of elements (Fig. 9), Type III apatites are abnormally large monocystals cut by Sr, Si-rich veinlets. The slightly dark areas have a little lower concentrations of Na, Ce and Nd. The contents of P, F, Sm, Ba, S, Th and Pb in faintly visible BSE-dark veinlets and irregular BSE-dark regions are basically same as other areas in single apatite.

Cathodoluminescent images of different types of apatite from Bayan Obo deposit are shown in Fig. 10. Although the color of three types of apatite are nearly same, glow blue to grey, the internal textures of three Types of apatite are quite different. In Type I fluorapatite (Fig. 10a, b), grey-blue luminescent anhedral apatites show grey patches which mark alteration of the primary apatite grains. Gray areas under CL correspond to areas with Na and LREE depletion shown in the mapping of trace elements. The tremendously complex inner structure is the typical characteristic of Type II fluorapatite (Fig. 10c, d). In Type II fluorapatite, unaltered apatites fluoresce grey-blue and have been replaced by a variety of blue-luminescent apatites (brighter color under CL), producing a “messy” texture (Fig. 10d), which is the evidence of pervasive fluids alteration. The blue-luminescent altered apatites correspond to the dark areas under BSE imaging and are close related to the non-luminescent REE mineral inclusions (Fig. 10c). Type III apatite prisms fluoresce grey-blue and are fractured by irregular light grey, dark grey-fluorescent veins (Fig. 10e, f). The REE mineral inclusions are non-luminescent.

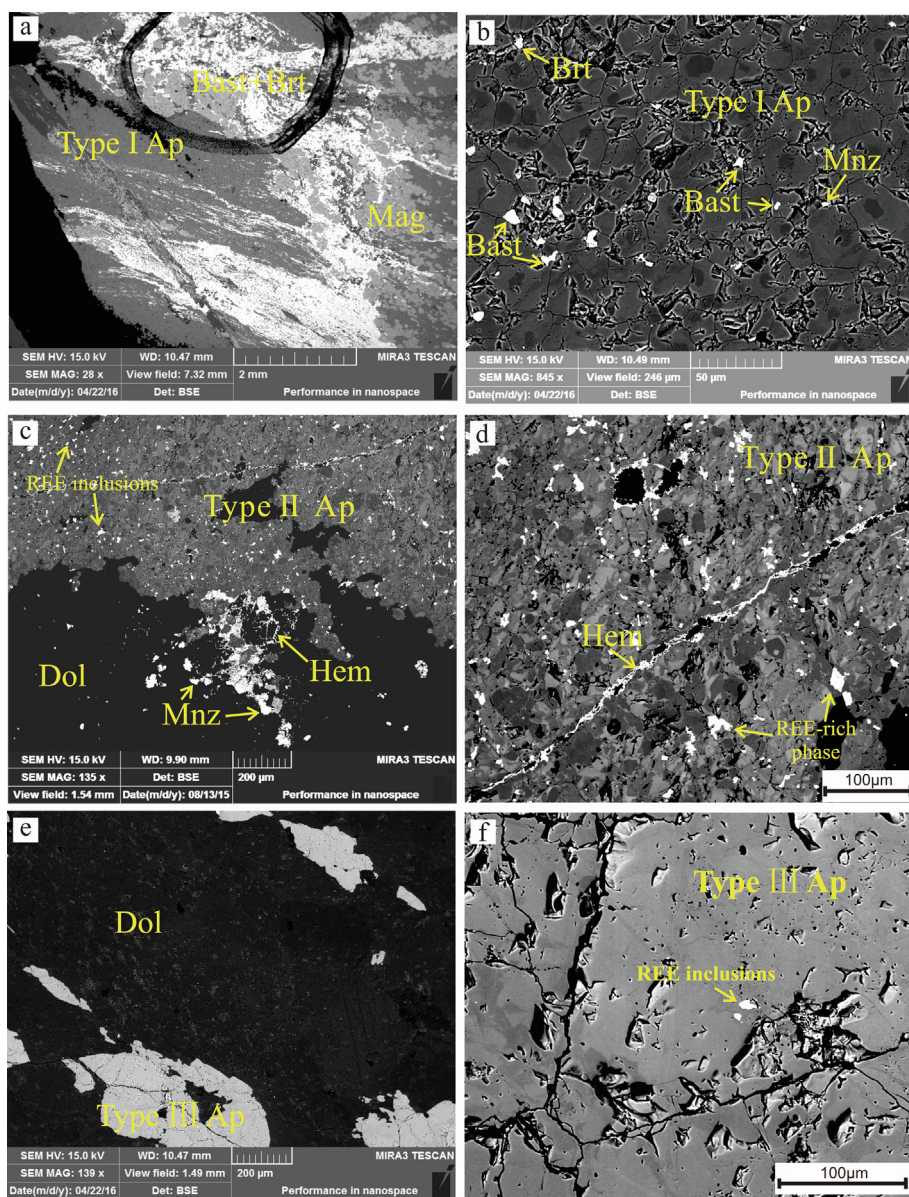


Fig. 6. Back-scattered-electron images of three types of apatites. (a) bastnaesite associated with barite occurring as veins or bands crosscutting the Type I fluorapatite and infilling the fractures of magnetite grains; (b) chemical heterogeneous composition zones in Type I fluorapatite with a few tiny REE minerals in the etch pits and pores; (c) Type II fluorapatite hosting abundant tiny REE mineral inclusions; (d) Type II fluorapatite showing different levels of darkness and irregular zoning patterns with hematite occurring as tiny veins filling in the fractures between grains; (e) Type III apatite as the dominant REE-bearing mineral in the coarse-grained dolomite marble; (f) occasionally minor tiny monazite inclusions within Type III apatite. Ap - apatite; Mag - magnetite; Brt - barite; Bast - bastnaesite; Mnz - monazite; Dol - dolomite; Hem - hematite.

5. Results

Chemical compositions of dolomite and fluorapatite from Bayan Obo determined by electron-microprobe are shown in [Tables 1 and 2](#). Trace element results of fluorapatite analyzed by LA-ICP-MS are presented in [Table 3](#).

5.1. Dolomite

For coarse-grained dolomite marble (sample BY09), we analyzed the chemical compositions of dolomite minerals from the rim to the core. Wide variations of the SrO contents were observed across the profile in dolomite mineral from coarse-grained dolomite marble. Two profiles are shown in [Fig. 11](#), where the SrO contents in the margin of the dolomite mineral reach up to 1.04 wt%, while SrO contents in the core as low as 0.16 wt% (one point low to 0.04 wt%), similar to the SrO contents of the sedimentary carbonates. The MnO contents across the profile of the individual dolomite mineral are relatively homogeneous. The MnO contents from several profiles of the coarse-grained dolomite mineral are from 0.24 wt% to 0.45 wt% and the majority of MnO contents are round 0.3 wt% – 0.4 wt%. The FeO contents of the coarse-

grained dolomite mineral are from 2.27 wt% to 3.42 wt% without significant changes from the rim to the core of the single dolomite mineral grain ([Table 1](#)).

Due to the limit of the beam spot diameter (30 μm) and the grain size of the dolomite from fine-grained dolomite marble, the whole dolomite grain was detected. The SrO contents of the dolomite minerals of fine-grained dolomite marble are below 0.28 wt%, mainly concentrating on the range of 0.1 wt% – 0.2 wt%, which are obviously different from those of dolomite minerals from the coarse-grained dolomite. The dolomite minerals from the fine-grained dolomite marble contain high levels of Mn (0.84 wt% – 3.32 wt% MnO), compared with those from coarse-grained dolomite marble ([Fig. 12a](#)). The FeO contents of the dolomite minerals from the samples HNB28, HNB23, HNB20 and BY19 are 3.59 wt% – 4.59 wt%, 9.42 wt% – 10.59 wt%, 4.29 wt% – 12.16 wt% and 6.75 wt% – 9.78 wt% respectively ([Table 1](#)), dramatically higher than those from the coarse-grained dolomite. The fine-grained dolomite contains higher REE, Mn and Fe compared to the coarse-grained dolomite. The dolomite grains from the coarse-grained dolomite display distinctively larger variations of Sr contents than those from the fine-grained dolomite ([Fig. 12b](#)).

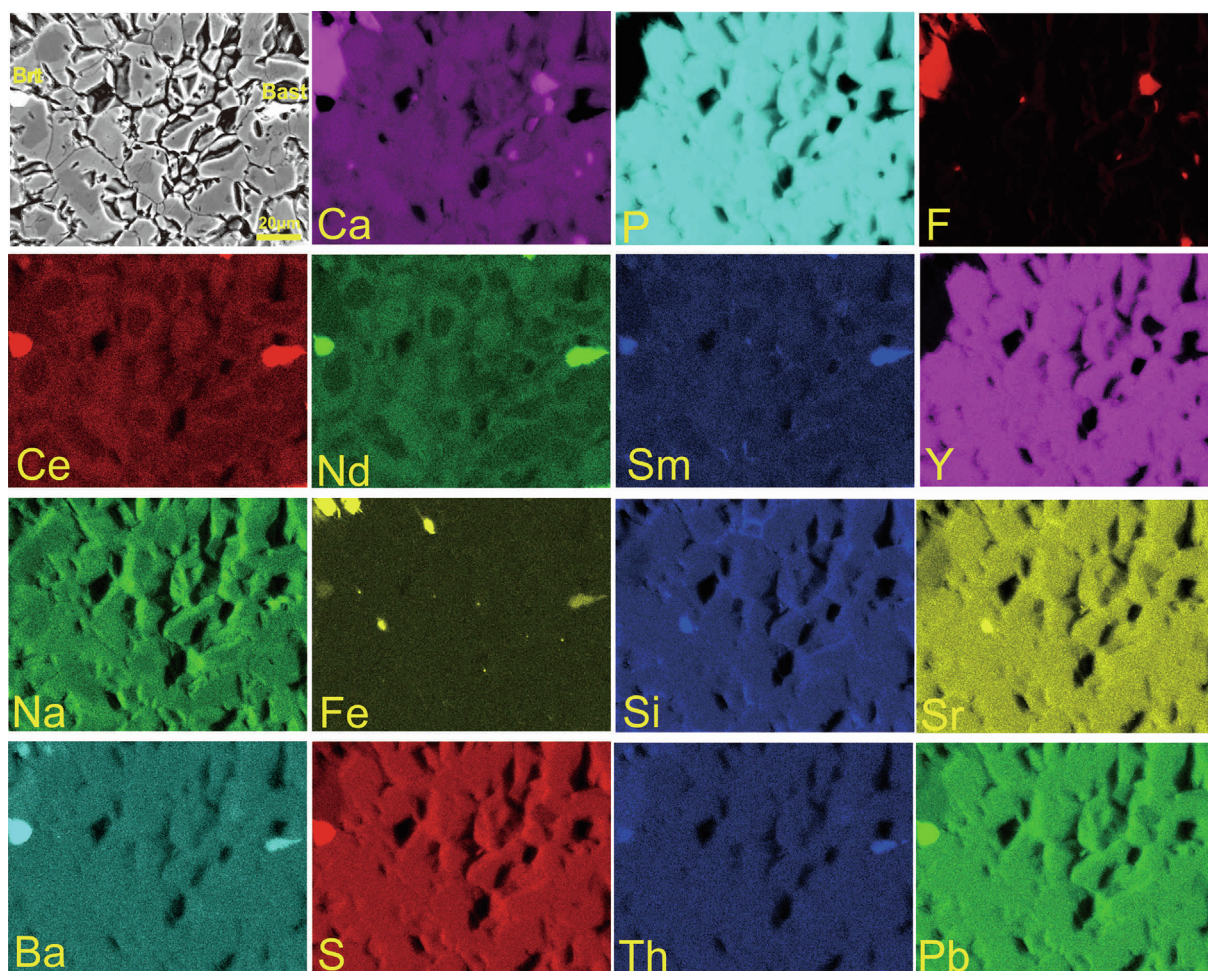


Fig. 7. High resolution mapping for Type I fluorapatite. The bright areas under BSE imaging are obviously richer in Ce and Nd elements, slightly richer in Na, slightly depleted in Ca compared with the dark areas appearing as patches. Bast - bastnaesite; Brt - barite.

5.2. Apatite

The unaltered regions of Type I and Type II fluorapatite from fine-grained dolomite marble samples (HNB52, 09BY161) contain high levels of F (4.18–6.47 wt%), Na_2O (0.15–1.48 wt%) and REE_2O_3 (0.73–7.17 wt%), with moderate amounts of SrO (0.21–0.88 wt%). In contrast, the apatite from the coarse-grained dolomite marble sample (BY09) contains slightly lower F (3.75–5.21 wt%), much lower REE_2O_3 (0.24–0.85 wt%) and Na_2O (0.02–0.20 wt%) and exceptionally high level of SrO (0.24–1.29 wt%, most of data in the range of 0.95–1.29 wt%) (Table 2).

Results of LA-ICP-MS analyses (Table 3) show that the unaltered fluorapatites from fine-grained dolomite marble samples (Type I and Type II fluorapatite) and the apatites from the coarse-grained dolomite marble samples (Type III fluorapatite) have obviously different REE distribution patterns (Fig. 13). These three types of apatite can also be discriminated by the plot of Y vs. Sr (Fig. 14e). The unaltered fluorapatites from fine-grained dolomite marbles have high REE and Y concentrations (total REE = 17470–77090 ppm) without obvious Eu anomalies. The unaltered regions of Type I fluorapatite show slightly high Na (2023–3407 ppm), moderate Sr (2126–2984 ppm) and high REE contents (total REE = 17470–25639 ppm, Y = 714–1482 ppm), displaying LREE-rich patterns ($(\text{La}/\text{Yb})_{\text{CN}} = 45$ to 93) (Fig. 13a) with slightly positive Ce anomalies ($\delta\text{Ce} = 1.20$ – 1.31) and negative Eu anomalies ($\delta\text{Eu} = 0.78$ – 0.96). The BSE-bright areas in Type II apatite are characterized by the highest Na, REE abundances (Na = 6073–10258 ppm, total REE = 38746–77090 ppm,

Y = 4428–8162 ppm) and strong enrichments in the light REE ($(\text{La}/\text{Yb})_{\text{CN}} = 36$ to 82), with no anomalies of Eu ($\delta\text{Eu} = 0.97$ – 1.02) and slightly positive Ce anomalies ($\delta\text{Ce} = 1.05$ – 1.12) (Fig. 13b). The unaltered regions in Type II apatite contain high level of Na (6073–10258 ppm) and relatively high amounts of Sr (4421–6422 ppm) compared to the unaltered areas in Type I fluorapatite (Fig. 14c, e).

Type III fluorapatite is abnormally large monocrystals with elongated orientation with respect to the c-axis of fluorapatite, occurring as colorless prisms. Values of total REE and Y cover a range of 2452–7496 ppm and 157–285 ppm respectively. The REE + Y and Na (496–1464 ppm) compositions of the Type III fluorapatite are one magnitude lower than those of the unaltered regions in Type I and Type II fluorapatite (Figs. 13c, 14c). The Type III fluorapatite is relatively lower in Th and Pb, 0.76–8.19 ppm and 1.39–4.28 ppm respectively (Fig. 14f). The contents of U in the apatite are below the LA-ICPMS detection limits. Nevertheless, the concentrations of Sr (6878–9949 ppm) surpass those of the other two Types of fluorapatite (Fig. 14e). The chondrite-normalized REE patterns exhibit variably LREE-rich patterns ($(\text{La}/\text{Yb})_{\text{CN}} = 13$ – 155) (Fig. 13c) with slightly negative Eu anomalies (0.89–1.03) and weakly positive Ce anomalies (1.01–1.16).

Type I and Type II fluorapatite have undergone hydrothermal alteration, having bright and dark regions under BSE imaging. In both Type I and Type II fluorapatite, Na, REEs contents in bright domains are noticeably higher than those of dark areas (Figs. 13, 14c, d). In contrast, the BSE-dark regions are richer in CaO , P_2O_5 versus the unaltered BSE-bright regions (Table 2). The leaching of REE was also accompanied by

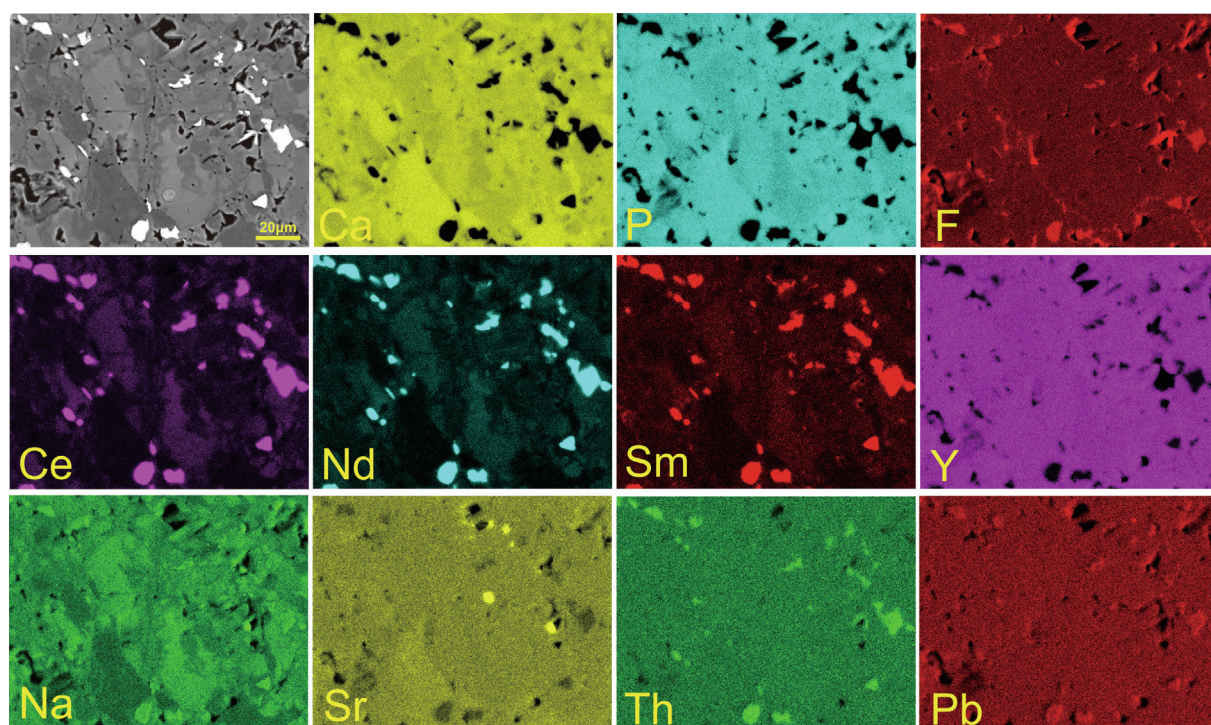


Fig. 8. High resolution mapping for Type II fluorapatite. Severe depletions of Ce, Nd and Sm are accompanied by significant Na loss in BSE-dark areas. The BSE-dark areas occur as irregular veinlets and deeper dark patches and have elevated contents of Ca and P.

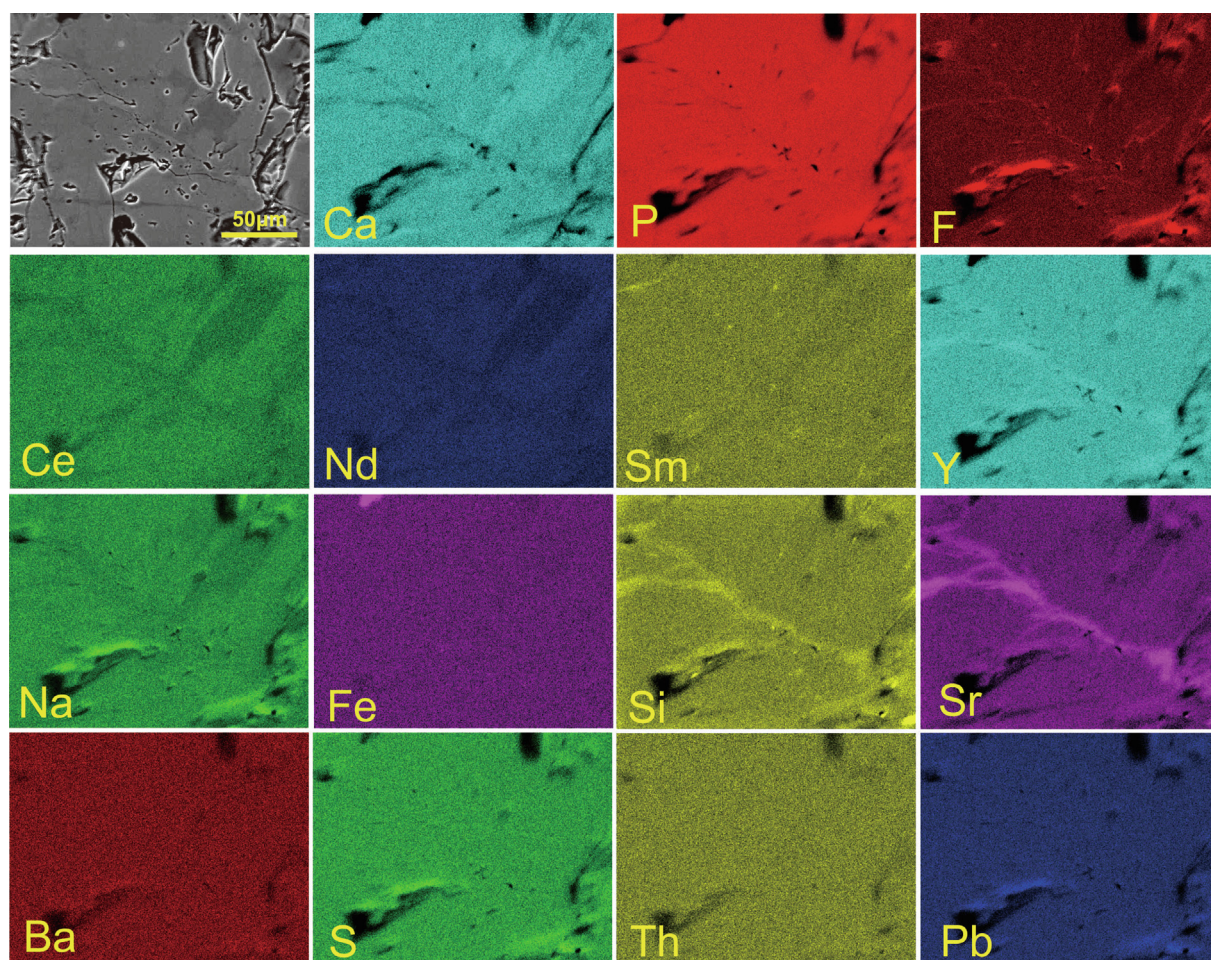


Fig. 9. High resolution mapping for Type III apatite. Type III apatites are abnormally large monocrystals and are cut by Sr, Si-rich veinlets.

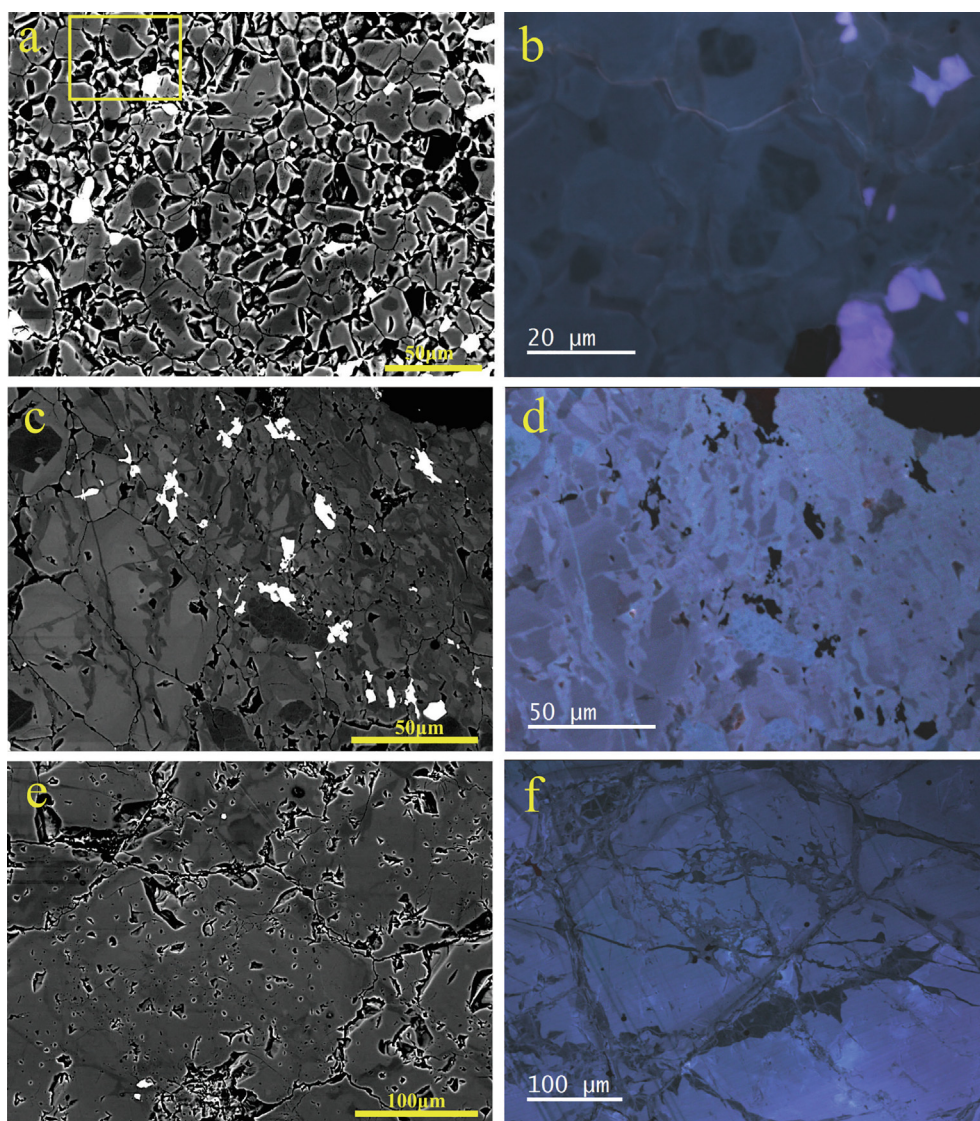


Fig. 10. Cathodoluminescent and BSE images of three types of apatite from Bayan Obo deposit. (a) Chemical heterogeneous composition zones in Type I fluorapatite under BSE; (b) in Type I fluorapatite, grey-blue luminescent anhedral apatites displaying grey patches under CL; (c) altered areas in Type II fluorapatite occurring as irregular veinlets and dark grey patches under BSE; (d) in cathodoluminescent image of Type II fluorapatite, grey-blue luminescent unaltered apatite replaced by a variety of blue-apatite, producing a “messy” texture; (e) BSE image of Type III apatite; (f) grey-blue luminescent Type III apatite prism fractured by irregular light grey, dark grey-luminescent veins. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the removal of Th and Pb (Fig. 14f). In Type II fluorapatite, the linear decrease of Th, Pb was observed from unaltered regions to altered regions in apatite.

In Type I fluorapatite, the Na₂O contents are reduced from 0.15 to 0.44 wt% in the bright areas to 0.01–0.09 wt% in the dark areas. Conversely, the BSE-dark regions in Type I fluorapatite have elevated CaO, P₂O₅ and BaO (Table 2). The contents of BaO in the bright areas of apatite are particularly low, below microprobe detection limits, while the values reach up to 0.05 wt% in the BSE-dark areas. The LA-ICPMS data (Table 3) of Type I fluorapatite are in good agreement with the microprobe data. BSE-dark areas also show variable degrees of depletion in LREE in the chondrite-normalized REE patterns, with total REE contents of 2481–20300 ppm, Y = 442–2069 ppm, (La/Nd)_{CN} = 6–46 (Fig. 13a). The altered regions show no obvious Eu anomalies (0.94–1.03) and varied positive Ce anomalies (1.02–1.56). The altered regions have similar concentrations of Sr (most in the range of 2277–2674 ppm) to the unaltered regions (Sr contents: 2126–2984 ppm) in Type I fluorapatite. The most obvious attribute of Type I fluorapatite is that the contents of Pb are relatively high, 92.5–109 ppm in BSE-bright areas and 62.7–98.8 ppm in BSE-dark areas. However, Type I fluorapatite has low Th contents of 2.12–6.34 ppm in BSE-bright areas and most of 1.65–4.5 ppm in BSE-dark areas, respectively (Table 3). The contents of U in the apatite are below the LA-ICP-MS detection limits, consistent with the fact that the

whole deposit is extremely depleted in U element.

Type II fluorapatite hosts abundant tiny REE mineral inclusions which are associated with the BSE-dark apatite. Values of Na₂O and SrO cover a range of 0.10–0.71 wt% and 0.54–1.06 wt% in the dark areas, and 0.89–1.48 wt% and 0.35–0.62 wt% in bright areas. The clear covariation between Na and REEs indicates that apatite incorporates rare earth elements and Y mainly via the coupled substitution $Na^{+} + (REE + Y)^{3+} = 2Ca^{2+}$ (Fig. 14a). The altered (BSE-dark) regions contain significantly lower Na₂O, REE, slightly lower Y (3161–5464 ppm) and higher CaO, P₂O₅, SiO₂, FeO and SrO contents than the unaltered (BSE-bright) regions in Type II fluorapatite. CaO and P₂O₅ in the dark areas increase by 4 wt% and 1–2 wt% respectively (Table 2). The BSE-bright apatite is Th, Pb-rich over the BSE-dark apatite in Type II fluorapatite (Fig. 14f). The Th contents are reduced from 8.48 to 30.5 ppm in the bright areas to 0.10–9.67 ppm in the dark areas. The Pb abundances decrease from 26.6 to 60.7 ppm in the bright areas to 2.27–22.3 ppm in the dark areas. Results of LA-ICPMS analyses show that BSE-dark regions exhibit intense LREE depletion with convex upward shaped REE patterns (Fig. 13b) (total REE = 9135–32949 ppm, (La/Nd)_{CN} = 2–37). The Type II fluorapatites in BSE-dark regions have δEu of 0.94–1.20 and δCe of 0.84–1.24, respectively.

The SrO contents of the altered regions in Type II fluorapatite vary from 0.54 to 1.06 wt%, which are dramatically higher than those of the altered regions in Type I fluorapatite (0.20–0.65 wt%, most between

Table 1
Electron microprobe analyses (wt. %) of dolomite from coarse-grained dolomite and fine-grained dolomite.

Coarse-grained dolomite																
MgO	19.61	19.04	19.06	19.45	19.20	19.50	19.53	19.8	19.96	19.00	19.65	18.96	19.17	19.19	18.93	
CaO	27.57	27.55	27.56	27.42	27.19	27.38	27.27	27.33	27.57	27.30	27.18	27.35	27.3	27.06	27.18	
SiO ₂	0.00	0.03	0.04	0.01	0.00	0.00	0.00	0.03	0.03	0.00	0.00	0.01	0.00	0.01	0.00	
P ₂ O ₅	0.42	0.38	0.38	0.27	0.35	0.39	0.42	0.44	0.44	0.33	0.44	0.33	0.42	0.28	0.36	
SrO	0.36	0.46	0.46	0.66	0.17	0.79	0.51	0.58	0.32	0.45	0.34	0.21	0.51	0.40	0.56	
MnO	0.34	0.39	0.38	0.29	0.40	0.38	0.41	0.41	0.31	0.39	0.41	0.44	0.40	0.34	0.36	
FeO	2.54	2.54	2.62	2.39	2.29	2.52	2.74	2.48	2.71	2.86	2.29	3.42	2.27	2.72	2.46	
PbO ₂	0.36	0.07	0.23	0.00	0.16	0.00	0.00	0.00	0.12	0.00	0.13	0.00	0.15	0.00	0.00	
BaO	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.05	0.00	0.00	0.00	0.00	0.03	
Total	51.20	50.45	50.73	50.51	49.76	50.96	50.92	51.05	51.48	50.38	50.44	50.71	50.22	50.01	49.90	
Coarse-grained dolomite																
MgO	19.05	18.98	19.10	18.44	19.48	19.33	19.22	19.19	19.05	19.14	18.02	19.09	19.17	18.95	19.12	
CaO	27.04	27.30	27.12	27.24	27.19	27.44	27.10	27.2	27.16	27.04	27.10	27.19	26.9	27.06	27.04	
SiO ₂	0.00	0.02	0.00	0.03	0.01	0.03	0.00	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.08	
P ₂ O ₅	0.44	0.33	0.28	0.41	0.39	0.46	0.42	0.40	0.45	0.43	0.48	0.39	0.49	0.50	0.45	
SrO	0.16	0.46	0.31	1.04	0.35	0.30	0.41	0.42	0.52	0.27	0.43	0.38	0.04	0.40	0.40	
MnO	0.41	0.38	0.35	0.44	0.24	0.37	0.30	0.32	0.41	0.42	0.39	0.35	0.37	0.44	0.37	
FeO	2.27	2.58	2.47	2.78	2.55	2.50	2.58	2.40	2.51	2.58	2.61	2.31	2.82	2.52	2.52	
PbO ₂	0.00	0.00	0.10	0.00	0.03	0.08	0.00	0.00	0.13	0.00	0.00	0.00	0.05	0.00	0.15	
BaO	0.06	0.03	0.05	0.00	0.01	0.00	0.03	0.00	0.04	0.00	0.03	0.02	0.00	0.00	0.01	
Total	49.44	50.09	49.77	50.38	50.25	50.50	50.06	49.94	50.28	49.89	49.08	49.74	49.80	49.88	50.14	
Fine-grained dolomite																
MgO	18.15	17.86	18.00	16.71	17.29	17.58	14.83	14.84	14.92	15.07	15.72	14.90	13.43	15.48	12.29	16.20
CaO	29.27	29.13	29.22	29.31	29.12	29.44	28.87	28.72	28.83	28.67	28.93	28.79	28.81	29.32	28.95	29.24
SiO ₂	0.02	0.00	0.02	0.06	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.04	0.00	0.03
P ₂ O ₅	0.40	0.52	0.44	0.36	0.40	0.42	0.44	0.44	0.47	0.37	0.27	0.29	0.00	0.43	0.50	0.51
SrO	0.17	0.18	0.16	0.08	0.11	0.05	0.04	0.11	0.20	0.03	0.11	0.02	0.19	0.06	0.06	0.06
MnO	1.77	1.32	2.05	1.89	2.53	2.13	1.10	0.84	1.10	1.00	1.11	1.14	1.15	3.32	1.90	2.63
FeO	4.33	3.59	3.97	4.35	4.58	3.95	10.59	10.30	10.35	9.75	10.43	9.91	10.17	7.59	12.16	7.75
PbO ₂	0.25	0.00	0.16	0.00	0.00	0.10	0.00	0.01	0.32	0.00	0.00	0.03	0.19	0.01	0.06	0.00
BaO	0.00	0.00	0.04	0.05	0.03	0.00	0.02	0.01	0.00	0.00	0.04	0.00	0.03	0.01	0.00	0.02
Total	54.35	52.61	54.05	53.52	54.01	53.66	55.95	55.37	56.03	55.13	55.81	55.23	56.18	54.84	56.65	54.71
Fine-grained dolomite																
MgO	17.09	16.56	16.36	15.98	17.28	15.67	15.67	15.67	15.59	15.91	15.82	15.69	16.25	14.48	14.28	16.13
CaO	29.44	29.48	29.18	29.40	29.35	29.56	29.28	29.28	29.32	29.39	29.45	29.12	29.10	29.16	29.34	29.24
SiO ₂	0.00	0.03	0.00	0.04	0.00	0.02	0.01	0.00	0.04	0.00	0.04	0.03	0.00	0.01	0.00	0.00
P ₂ O ₅	0.48	0.34	0.42	0.46	0.43	0.34	0.44	0.44	0.40	0.46	0.44	0.33	0.48	0.44	0.34	0.38
SrO	0.00	0.17	0.26	0.06	0.18	0.16	0.16	0.00	0.00	0.22	0.28	0.20	0.16	0.10	0.18	0.18
MnO	1.30	1.11	1.10	1.22	1.99	1.01	1.43	1.32	1.50	1.32	1.64	1.50	1.51	2.37	1.68	1.58
FeO	5.75	6.87	7.17	6.14	5.33	7.18	7.16	7.07	6.93	7.20	7.84	7.55	7.34	9.78	8.80	6.90
PbO ₂	0.00	0.00	0.00	0.08	0.21	0.00	0.00	0.14	0.00	0.19	0.00	0.12	0.01	0.08	0.00	0.00
BaO	0.00	0.00	0.00	0.01	0.04	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Total	54.07	54.56	54.50	54.17	54.19	54.32	54.20	53.92	53.79	54.69	55.53	54.56	54.85	55.04	54.62	54.43

Table 2
Electron microprobe analyses (wt. %) of three types of fluorapatite from Bayan Obo deposit.

Type I fluorapatite(bright domain)																			Type I fluorapatite(dark domain)																		
F	5.85	5.94	5.81	6.34	5.13	5.89	5.43	6.01	6.03	5.86	5.80	5.98	5.85	6.24	6.03	6.03	6.03	6.03																			
Cl	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.01	0.02	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00																			
CaO	49.14	49.50	49.29	49.14	51.76	50.92	50.60	50.24	50.68	51.12	52.30	52.01	51.09	51.15	52.80	52.36	52.36	52.36																			
P ₂ O ₅	40.00	39.83	39.82	39.58	40.97	40.81	40.59	40.18	39.92	41.10	40.34	40.80	40.64	40.38	40.77	41.01	41.01	41.01																			
Na ₂ O	0.44	0.24	0.36	0.39	0.15	0.19	0.32	0.06	0.09	0.09	0.04	0.01	0.05	0.04	0.04	0.03	0.03	0.03																			
SiO ₂	0.33	0.88	0.35	0.23	0.31	0.21	0.32	0.29	0.65	0.20	0.31	0.38	0.24	0.38	0.29	0.24	0.24	0.24																			
SiO ₂	0.33	0.88	0.35	0.23	0.31	0.21	0.32	0.29	0.65	0.20	0.31	0.38	0.24	0.38	0.29	0.24	0.24	0.24																			
Y ₂ O ₃	0.21	0.08	0.12	0.16	0.07	0.11	0.13	0.16	0.04	0.08	0.04	0.10	0.03	0.08	0.03	0.03	0.03	0.03																			
Al ₂ O ₃	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.02	0.00	0.01	0.01	0.01	0.01	0.01																			
MgO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01																			
As ₂ O ₃	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.01	0.01	0.03	0.03	0.02	0.03	0.03	0.06	0.06	0.06																			
SO ₃	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01																			
K ₂ O	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01																			
FeO	0.29	0.12	0.12	0.00	0.04	0.01	0.21	0.41	0.08	0.16	0.13	0.31	0.03	0.19	0.20	0.09	0.09	0.09																			
BaO	0.07	0.07	0.07	0.06	0.04	0.04	0.05	0.05	0.08	0.07	0.05	0.13	0.04	0.01	0.01	0.01	0.01	0.01																			
La ₂ O ₃	0.68	0.40	0.58	0.56	0.27	0.27	0.55	0.05	0.08	0.19	0.12	0.13	0.04	0.02	0.02	0.02	0.02	0.02																			
Ce ₂ O ₃	1.01	0.45	0.64	0.71	0.24	0.30	0.39	0.11	0.18	0.12	0.15	0.15	0.04	0.05	0.05	0.03	0.03	0.03																			
Pr ₂ O ₃	0.03	0.18	0.28	0.16	0.05	0.15	0.22	0.07	0.07	0.07	0.07	0.15	0.04	0.05	0.05	0.03	0.03	0.03																			
Nd ₂ O ₃	0.19	0.05	0.06	0.14	0.08	0.20	0.17	0.03	0.02	0.01	0.08	0.02	0.00	0.03	0.04	0.13	0.13	0.13																			
Gd ₂ O ₃	0.09	0.04	0.21	0.02	0.01	0.09	0.13	0.03	0.02	0.10	0.08	0.02	0.06	0.21	0.02	0.04	0.04	0.04																			
Dy ₂ O ₃	0.05	0.15	0.13	0.02	0.05	0.09	0.13	0.12	0.22	0.02	0.04	0.01	0.10	0.07	0.02	0.02	0.02	0.02																			
Yb ₂ O ₃	0.01	0.01	0.02	0.01	0.01	0.01	0.00	0.01	0.03	0.01	0.01	0.01	0.02	0.03	0.03	0.03	0.03	0.03																			
UO ₂	0.01	0.01	0.02	0.01	0.01	0.01	0.00	0.01	0.03	0.01	0.01	0.01	0.04	0.03	0.03	0.03	0.03	0.03																			
ThO ₂	0.04	0.05	0.05	0.00	0.00	0.02	0.00	0.06	0.03	0.02	0.10	0.09	0.09	0.03	0.12	0.23	0.23	0.23																			
PhO ₂	2.12	1.26	2.03	1.65	0.73	1.04	1.54	0.28	0.67	0.72	0.44	0.32	0.23	0.37	0.12	0.12	0.12	0.12																			
REE ₂ O ₃	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46																			
O = F, Cl	96.05	95.51	95.48	94.88	97.04	96.76	96.90	95.23	95.76	96.93	97.20	97.50	95.88	96.36	97.79	97.63	97.63	97.63																			
Total	6.47	6.23	6.23	6.23	6.23	6.23	6.23	6.23	6.23	6.23	6.23	6.23	6.23	6.23	6.23	6.23	6.23	6.23																			
Type II fluorapatite(bright domains)																																					
Type II fluorapatite(dark domains)																																					
F	6.47	6.23	5.27	4.18	4.76	4.57	5.73	4.55	4.78	7.44	5.48	6.75	4.72	4.19	4.41	5.22	5.22	5.22																			
Cl	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00																			
CaO	48.26	48.61	44.65	47.39	47.33	46.71	49.11	49.50	48.96	48.54	49.93	49.30	49.56	52.45	52.70	52.35	52.35	52.35																			
P ₂ O ₅	39.31	39.33	38.91	39.85	39.90	40.02	40.27	40.54	40.70	40.08	40.33	39.88	40.95	41.48	42.00	41.67	41.67	41.67																			
Na ₂ O	0.89	0.92	1.48	1.15	1.07	1.15	0.62	0.67	0.71	0.70	0.59	0.67	0.68	0.18	0.14	0.10	0.10	0.10																			
SiO ₂	0.62	0.53	0.51	0.60	0.59	0.35	0.61	0.60	0.54	0.66	0.63	0.59	0.62	0.69	1.06	0.64	0.64	0.64																			
SiO ₂	0.62	0.53	0.51	0.60	0.59	0.35	0.61	0.60	0.54	0.66	0.63	0.59	0.62	0.69	1.06	0.64	0.64	0.64																			
Y ₂ O ₃	0.44	0.40	0.81	0.50	0.60	0.48	0.46	0.52	0.56	0.50	0.60	0.44	0.66	0.14	0.16	0.12	0.12	0.12																			
Al ₂ O ₃	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01																			
MgO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01																			
As ₂ O ₃	0.01	0.02	0.03	0.03	0.03	0.01	0.03	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01																			
SO ₃	0.01	0.03	0.05	0.00	0.00	0.00	0.03	0.04	0.02	0.00	0.04	0.04	0.04	0.01	0.01	0.01	0.01	0.01																			
K ₂ O	0.01	0.01	0.01	0.00	0.00	0.00	0.07	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01																			
FeO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01																			
BaO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01																			
La ₂ O ₃	0.12	0.19	0.09	0.36	0.08	0.22	0.10	0.09	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01																			
Ce ₂ O ₃	1.43	1.79	2.64	2.08	1.87	2.26	0.82	0.89	0.88	0.93	0.73	0.92	0.83	0.32	0.27	0.26	0.26	0.26																			
Pr ₂ O ₃	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01																			
Nd ₂ O ₃	1.53	1.71	2.47	1.84	1.69	2.00	1.25	1.24	1.18	1.46	1.27	1.45	1.46	0.33	0.09	0.27	0.27	0.27																			
Sm ₂ O ₃	0.43	0.36	0.61	0.45	0.38	0.50	0.23	0.48	0.34	0.39	0.31	0.44	0.49	0.06	0.05	0.05	0.05	0.05																			
Eu ₂ O ₃	0.13	0.11	0.28	0.15	0.10	0.21	0.10	0.16	0.11	0.06	0.16	0.12	0.11	0.00	0.00	0.02	0.02	0.02																			
(continued on next page)																																					

(continued on next page)

Table 2 (continued)

	Type II fluorapatite (bright domains)										Type II fluorapatite (dark domains)									
	52	46	84	60	40	59	38	40	49	45	28	37	43	02	09	10	03	03	03	03
Gd ₂ O ₃	0.52	0.46	0.84	0.60	0.40	0.59	0.38	0.40	0.49	0.45	0.28	0.37	0.43	0.02	0.09	0.10	0.03	0.03	0.03	0.03
Dy ₂ O ₃	0.22	0.12	0.15	–	0.20	–	0.10	0.08	0.28	0.14	0.17	0.17	0.05	0.10	0.10	–	–	–	–	–
Yb ₂ O ₃	0.20	0.04	0.10	0.09	–	0.01	0.10	–	0.16	0.06	0.07	–	0.02	–	–	0.12	–	–	–	–
UO ₂	0.01	0.00	–	0.00	–	0.02	0.02	–	0.01	0.01	–	0.01	–	–	0.04	–	–	–	–	–
ThO ₂	–	–	–	0.06	–	0.00	–	–	–	0.04	–	0.02	–	–	–	–	0.03	–	–	–
PbO ₂	0.06	0.04	0.06	0.04	0.161	0.15	–	–	–	0.06	–	–	–	0.11	–	–	–	–	–	–
REE ₂ O ₃	4.58	4.78	7.17	5.56	4.72	5.79	3.08	3.34	3.45	3.49	2.98	3.47	3.38	0.83	0.59	0.83	0.83	0.83	0.83	0.83
O = F, Cl	–2.72	–2.62	–2.21	–1.75	–2.00	–1.93	–2.41	–1.91	–2.01	–3.13	–2.30	–2.84	–1.98	–1.76	–1.85	–2.19	–1.85	–2.19	–1.85	–2.19
Total	97.94	98.31	96.74	97.61	97.15	97.36	97.62	97.86	97.77	98.42	98.25	98.39	98.67	98.37	99.34	98.86	99.34	98.86	99.34	98.86

	Type III fluorapatite										Type III fluorapatite									
	3.75	3.86	3.89	5.21	3.75	4.06	4.51	3.91	4.14	4.05	3.75	4.06	4.51	3.91	4.14	4.05	3.75	4.06	4.51	3.91
F	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Cl	0.02	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00
CaO	52.66	52.78	52.73	51.73	52.34	53.79	53.28	53.59	53.79	53.79	53.28	53.59	53.59	53.59	54.01	54.32	53.59	53.79	53.28	53.59
P ₂ O ₅	42.36	42.32	42.26	41.90	41.96	42.50	42.44	41.87	42.50	42.50	42.44	41.87	41.87	42.58	42.58	42.67	41.87	42.50	42.44	41.87
Na ₂ O	0.20	0.16	0.16	0.15	0.14	0.04	0.02	0.05	0.04	0.04	0.02	0.05	0.05	–	–	0.02	0.05	0.04	0.02	0.05
SrO	1.29	1.24	1.12	1.06	1.20	1.16	0.99	0.95	1.16	1.16	0.99	0.95	0.95	0.24	0.24	0.33	0.95	1.16	0.99	0.95
SiO ₂	–	–	–	0.04	–	–	0.02	–	–	–	0.02	–	–	–	–	0.02	–	–	0.02	–
Y ₂ O ₃	–	–	0.10	–	0.05	0.11	0.08	0.03	0.11	0.11	0.08	0.03	0.03	0.03	0.03	–	0.03	0.11	0.08	0.03
Al ₂ O ₃	–	–	–	–	0.00	0.00	–	–	0.00	0.00	–	–	–	0.01	0.01	–	–	0.00	–	–
MgO	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	–	–	–	0.00	0.00	–	–	0.01	0.01	–
As ₂ O ₃	–	–	–	0.01	0.01	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
SO ₃	–	–	–	0.00	0.01	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
K ₂ O	0	0.00	–	–	–	–	–	–	–	0.01	–	–	0.03	0.02	–	–	–	0.01	–	–
FeO	0	0.09	–	–	0.01	–	–	–	–	0.01	–	–	0.01	0.02	–	–	–	0.01	–	–
BaO	0.02	0.00	–	–	–	–	–	–	–	0.04	–	–	0.03	0.02	–	–	–	0.03	0.02	–
La ₂ O ₃	0.04	0.13	–	–	0.10	0.13	0.01	0.10	0.10	0.02	0.01	0.01	0.03	0.01	–	0.02	0.03	0.01	0.01	–
Ce ₂ O ₃	0.40	0.36	0.35	0.44	0.32	–	–	0.32	0.32	–	–	–	–	–	–	0.06	0.02	–	–	–
Pr ₂ O ₃	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.03	0.03	–	–	–
Nd ₂ O ₃	0.21	0.06	0.24	0.15	0.20	0.03	0.10	0.20	0.20	0.03	0.10	0.03	0.05	0.01	0.19	0.19	0.03	0.03	0.03	0.03
Sm ₂ O ₃	–	0.05	0.01	–	–	–	–	–	–	–	–	–	–	0.00	–	–	–	0.00	–	–
Eu ₂ O ₃	0.09	–	0.05	–	–	0.01	0.02	–	–	0.01	0.02	0.02	0.05	–	–	0.06	–	–	–	–
Gd ₂ O ₃	0.07	0.09	–	0.12	0.14	–	0.06	0.14	–	–	0.06	0.06	0.02	0.02	0.09	0.09	0.02	0.02	0.02	0.02
Dy ₂ O ₃	–	–	0.02	0.00	0.11	0.13	0.00	0.11	–	0.13	0.01	0.01	0.12	0.10	–	–	–	–	–	–
Yb ₂ O ₃	–	0.00	0.11	–	–	0.09	–	–	–	0.09	0.07	–	–	–	–	0.02	–	–	–	–
UO ₂	0.02	0.02	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
ThO ₂	–	–	0.03	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
PbO ₂	–	–	–	0.09	–	–	0.09	–	–	0.03	0.03	0.03	0.01	–	–	–	–	–	–	–
REE ₂ O ₃	0.82	0.69	0.78	0.77	0.85	0.38	0.26	0.85	–	0.03	0.03	0.03	0.46	0.24	0.48	0.48	0.46	0.24	0.48	0.48
O = F, Cl	–1.58	–1.62	–1.64	–2.19	–1.57	–1.71	–1.90	–1.57	–	–	–	–	–	–	–	–	–	–	–	–
Total	99.57	99.57	99.46	98.77	98.76	100.44	99.77	98.76	100.44	99.77	99.77	99.77	99.34	99.55	99.55	100.21	99.34	99.55	99.77	100.21

–, below the detection limit.

Table 3
LA-ICPMS analyses (ppm) of apatite from Bayan Obo Fe-REE-Nb deposit.

Sample	Unaltered region in Type I fluorapatite							Altered region in Type I fluorapatite						
	No.1	No.2	No.4	No.5	No.6	No.7	No.8	No.9	No.3	No.10	No.11	No.12	No.13	
Na	2723	2213	2759	2023	2886	3407	2420	1358	956	2145	431	691	2768	
Mn	590	519	469	391	409	514	334	240	281	481	451	493	711	
Rb	-	0.02	0.11	0.05	0.01	-	0.13	0.04	0.02	0.07	2.08	0.23	0.13	
Sr	2984	2540	2543	2292	2126	2764	2423	2326	2277	2561	2349	2674	7183	
Y	1093	921	1248	820	745	1482	714	935	557	1041	442	650	2069	
La	2239	2626	2136	2312	3097	2031	2774	1300	1153	2160	157	455	1228	
Ce	8330	8469	9100	8320	9800	8845	8554	4633	3762	8118	608	1522	8623	
Pr	1185	1026	1044	1285	1044	1399	1074	613	412	992	122	269	1220	
Nd	6516	4656	7819	4555	6353	8427	5591	3258	1832	4750	788	1479	5583	
Sm	1258	606	1551	442	1053	1956	886	629	291	759	226	371	1132	
Eu	325	165	418	116	239	541	184	174	89	214	76	117	348	
Gd	853	410	1070	280	580	1460	472	469	226	548	216	325	964	
Tb	92.1	53.5	112	39.0	63.2	152	53.3	58.1	30.1	70.6	31.4	45.9	140	
Dy	383	253	455	211	277	598	233	273	153	327	158	216	700	
Ho	50.9	39.4	60.8	34.1	38.3	75.0	33.0	40.9	23.1	47.8	24.1	33.4	108	
Er	84.2	71.1	96.8	71.8	64.9	110	61.0	77.5	43.8	84.9	48.8	63.9	185	
Tm	6.59	6.37	7.40	7.40	6.01	8.51	5.51	7.18	4.38	8.27	4.39	6.21	14.2	
Yb	26.5	25.7	29.5	33.4	23.8	32.0	24.5	31.1	19.0	33.5	19.0	24.9	47.8	
Lu	2.33	2.70	2.76	3.42	2.37	3.18	2.45	2.73	1.92	3.28	1.52	2.38	4.13	
Hf	0.57	-	-	0.43	-	-	-	-	0.15	0.03	5.28	-	0.02	
Pb	99.5	96.5	106	92.5	109	108	103	64.5	82.3	98.8	74.1	82.9	62.7	
Th	4.95	3.64	4.31	2.86	5.64	2.12	6.34	1.65	3.00	2.46	4.50	3.45	17.4	
U	-	-	-	0.01	-	-	0.07	-	0.01	-	-	-	-	
ΣREE	21,353	18,410	24,212	17,470	22,881	25,639	19,949	11,567	8042	18,116	2481	4931	20,300	
LREE	19,855	17,548	22,378	16,790	21,826	23,199	19,063	10,607	7540	16,992	1978	4213	18,136	
HREE	1498	862	1834	680	1055	2440	885	959	502	1124	503	718	2164	
LREE/HREE	13.25	20.35	12.20	24.69	20.69	9.51	21.53	11.05	15.03	15.12	3.93	5.87	8.38	
(La/Yb) _N	60.54	73.27	51.87	49.59	93.41	45.46	81.06	29.96	43.48	46.21	5.93	13.12	18.42	
8Eu	0.91	0.96	0.94	0.94	0.85	0.94	0.78	0.94	1.02	0.97	1.03	1.01	0.99	
8Ce	1.24	1.26	1.28	1.31	1.20	1.24	1.22	1.27	1.34	1.36	1.02	1.05	1.56	

Sample	Unaltered region in Type II fluorapatite																					
	No.3	No.8	No.10	No.11	No.12	No.13	No.15	No.16	No.17	No.23	No.24	No.25	No.26	No.27	No.28	No.31	No.32	No.33	No.36	No.37	No.39	No.40
Na	8974	6475	7901	7597	7422	8047	7578	10,258	10,155	6262	6073	7465	8997	8607	8398	7971	7635	7968	7371	9746	7863	7834
Mn	247	208	236	223	192	229	207	253	253	203	230	203	250	243	258	237	225	265	213	623	195	215
Rb	0.36	0.28	0.09	0.23	0.16	0.21	0.12	0.18	0.31	0.25	0.31	0.21	0.20	0.20	0.35	-	0.34	0.20	0.11	0.37	0.17	0.17
Sr	5211	5334	5257	5127	5458	5236	5191	6422	4421	5295	5324	5240	5265	5619	5409	5248	5292	5395	5032	5256	5213	4985
Y	5467	5403	5861	4854	4582	5472	5435	6342	8162	4714	4428	5261	5052	5092	5445	5487	5370	4892	5177	5932	5337	5396
La	7875	5282	5601	7031	6327	6879	7058	9856	6755	10,121	4029	6352	8768	8684	8526	6669	8185	7364	6412	7604	7000	7064
Ce	24,305	17,219	18,869	20,823	19,440	22,195	21,143	29,054	23,263	28,949	13,870	19,811	26,169	24,818	24,008	21,206	23,568	21,449	19,826	23,747	20,790	21,494
Pr	4050	2702	3128	3086	2975	3504	3265	4618	4145	4220	2233	3165	3999	3796	3539	3281	3645	3192	3153	3809	3334	3240
Nd	20,519	14,167	17,371	15,351	15,358	17,153	16,558	23,297	23,617	19,304	11,587	16,092	18,874	18,437	17,208	16,792	17,516	15,636	19,370	17,337	16,266	16,266
Sm	3553	2670	3185	2652	2819	3162	2977	3782	4778	2974	2322	2988	3190	3021	3113	3042	3046	2896	2931	3558	3131	3083
Eu	1067	858	987	791	824	962	903	1087	1487	865	730	901	926	895	917	911	898	851	875	1122	929	957
Gd	2835	2379	2683	2193	2188	2542	2429	2811	4177	2234	1945	2435	2493	2348	2495	2457	2424	2291	2459	2984	2568	2565
Tb	345	302	341	278	272	326	312	351	520	275	260	315	307	296	326	317	308	296	308	373	324	328
Dy	1500	1375	1540	1295	1267	1482	1417	1492	2247	1232	1185	1428	1391	1352	1495	1446	1402	1381	1406	1652	1464	1524
Ho	212	202	214	189	179	208	201	219	316	178	172	201	195	197	213	208	199	193	199	232	207	215
Er	351	340	365	317	301	356	338	376	500	303	290	333	333	329	357	354	350	341	342	382	353	358
Tm	29.0	28.6	29.1	26.7	24.9	29.5	28.4	31.9	37.6	25.0	25.1	27.4	27.9	26.6	29.7	29.4	28.2	27.9	27.9	31.0	29.7	28.9

(Continued on next page)

(continued on next page)

Table 3 (continued)

Unaltered region in Type II fluorapatite																							
Sample	No.3	No.8	No.10	No.11	No.12	No.13	No.15	No.16	No.17	No.23	No.24	No.25	No.26	No.27	No.28	No.31	No.32	No.33	No.36	No.37	No.39	No.40	
Yb	103	99.9	107	91.2	88.7	99.0	97.8	107	133	89.0	90.2	100	102	93.2	107	106	103	97.0	98.3	103	102	107	
Lu	8.29	8.18	8.32	7.36	7.19	8.03	7.73	8.87	10.3	7.20	7.28	7.76	8.13	7.62	8.12	8.61	8.12	7.90	7.55	8.68	8.46	8.19	
Hf	0.04	0.05	0.14	0.03	0.05	0.19	2.44	0.20	0.05	0.05	74.50	0.10	-	0.08	0.02	0.04	0.06	0.95	0.04	-	0.89	0.48	
Pb	46.5	27.3	36.8	34.3	26.6	37.2	27.1	52.8	42.6	31.6	51.4	28.8	45.7	43.3	46.7	35.5	37.9	42.9	35.6	60.7	31.6	35.1	
Th	19.6	16.3	12.5	18.8	13.2	16.0	20.0	26.8	21.1	30.4	8.48	15.2	24.9	24.1	21.2	16.7	21.5	21.3	17.6	17.3	21.8	21.6	
U	-	-	0.01	-	-	-	-	-	-	-	0.03	-	-	0.02	-	-	-	-	-	-	-	-	
ΣREE	66,751	47,631	54,428	54,132	52,070	58,906	56,736	77,090	71,987	70,778	38,746	54,156	66,784	64,300	62,342	56,828	61,679	56,257	53,678	64,976	57,577	57,238	
LREE	61,368	42,897	49,140	49,734	47,743	53,855	51,904	71,693	64,045	66,433	34,771	49,310	61,927	59,651	57,312	51,901	56,859	51,623	48,832	59,210	52,522	52,103	
HREE	5383	4734	5288	4399	4327	5050	4831	5397	7941	4344	3975	4846	4857	4649	5031	4927	4821	4634	4846	5767	5055	5134	
LREE/LREE/																							
HREE	11.40	9.06	9.29	11.31	11.03	10.66	10.74	13.28	8.07	15.29	8.75	10.17	12.75	12.83	11.39	10.53	11.80	11.14	10.08	10.27	10.39	10.15	
(La/Yb) _N	54.89	37.92	37.70	55.28	51.18	49.86	51.77	66.19	36.47	81.62	32.04	45.57	61.37	66.84	56.99	45.01	57.24	54.45	46.80	52.76	49.10	47.15	
8Eu	0.99	1.02	1.00	0.97	0.98	1.00	1.00	0.98	0.99	0.98	1.02	0.99	0.97	0.99	0.97	0.99	0.98	0.98	0.97	1.02	0.97	1.01	
8Ce	1.05	1.11	1.09	1.09	1.10	1.10	1.08	1.05	1.05	1.09	1.12	1.08	1.08	1.06	1.07	1.11	1.06	1.08	1.08	1.08	1.05	1.10	

Altered region in Type II fluorapatite

Sample	No.1	No.2	No.4	No.5	No.6	No.7	No.9	No.14	No.18	No.19	No.20	No.21	No.22	No.30	No.34	No.35
Na	2669	3874	1818	3713	2232	2227	3547	2185	1967	2811	2824	2088	4686	1607	3505	1868
Mn	271	285	248	224	124	156	253	118	225	264	187	169	204	219	190	230
Rb	0.09	0.42	0.18	0.07	0.20	0.13	0.22	0.10	0.10	0.32	0.20	0.18	0.46	0.27	0.22	0.15
Sr	3913	4560	5640	5793	5588	6124	5932	15,194	5971	5976	5828	5456	6209	5936	6062	5967
Y	4557	4492	3432	4824	5047	5464	3864	3314	3438	4245	3946	4985	4516	3161	5190	3177
La	954	693	363	1438	382	1427	233	863	425	3685	1449	457	2359	308	1014	561
Ce	4078	3449	1868	7106	2208	1396	6881	3684	2250	10,849	5810	2452	10,462	1473	6074	2895
Pr	748	707	461	1199	562	421	1154	661	503	1852	878	571	1691	357	1113	587
Nd	5030	5098	3536	7892	4329	3609	7218	4273	3760	9889	5323	4242	10,277	2796	7354	4041
Sm	1730	1778	1321	2110	1671	1818	1795	1317	1242	2193	1545	1556	2359	1079	2103	1276
Eu	624	728	437	686	636	741	566	463	422	691	521	570	746	377	699	444
Gd	1946	1898	1513	1933	1930	2465	1592	1439	1353	1861	1556	1852	2108	1291	1995	1346
Tb	275	275	209	269	280	367	214	209	195	246	223	265	282	188	278	185
Dy	1334	1291	973	1296	1357	1702	1021	1030	912	1149	1083	1316	1313	881	1306	895
Ho	190	185	130	190	209	229	148	146	125	164	154	195	188	122	198	128
Er	313	299	204	330	356	338	255	244	197	272	256	323	310	195	347	220
Tm	25.3	23.9	14.5	27.6	28.8	24.0	21.3	19.2	14.3	21.2	20.2	26.4	24.9	14.7	28.5	17.8
Yb	87.3	82.3	46.7	101	99.8	71.6	75.3	64.1	47.4	71.3	68.8	90.4	91.1	47.3	107	60.4
Lu	6.74	6.78	3.55	7.71	7.73	5.08	6.21	4.97	3.80	5.59	5.64	6.82	7.78	3.87	8.20	5.25
Hf	0.02	0.14	0.07	0.06	-	0.06	0.56	0.01	0.03	0.14	0.09	0.16	0.10	0.03	0.01	0.09
Pb	17.0	16.7	5.41	12.8	2.27	7.88	22.3	8.22	12.9	17.4	10.8	8.79	20.5	7.08	5.54	13.7
Th	1.67	1.24	0.38	3.67	0.25	0.10	2.37	2.09	0.34	9.67	4.36	0.46	5.23	0.65	0.91	1.11
U	-	-	-	-	0.01	-	-	-	-	0.04	-	-	-	-	-	-
ΣREE	17,341	16,514	11,079	24,586	14,057	13,420	22,373	14,417	11,449	32,949	18,893	13,923	32,219	9135	22,624	12,660
LREE	13,164	12,452	7985	20,431	9788	8218	19,040	11,261	8602	29,160	15,526	9848	27,895	6391	18,357	9804
HREE	4176	4062	3094	4155	4268	5202	3333	3156	2848	3789	3367	4074	4325	2743	4267	2857
LREE/HREE	3.15	3.07	2.58	4.92	2.29	1.58	5.71	3.57	3.02	7.70	4.61	2.42	6.45	2.33	4.30	3.43
(La/Yb) _N	7.84	6.04	5.57	10.19	2.74	2.33	13.59	9.66	6.43	37.06	15.12	3.63	18.58	4.67	6.81	6.66
8Eu	1.04	1.20	0.94	1.02	1.08	1.07	1.00	1.02	0.99	1.02	1.02	1.03	1.00	0.98	1.03	1.03
8Ce	1.12	1.09	0.96	1.24	0.96	0.84	1.24	1.14	1.04	1.01	1.24	1.01	1.23	0.95	1.24	1.11

Type III fluorapatite

Sample	No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9	No.10	No.11	No.12	No.13	No.14	No.15
No.1	No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9	No.10	No.11	No.12	No.13	No.14	No.15
No.2	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9	No.10	No.11	No.12	No.13	No.14	No.15	
No.3	No.3	No.4	No.5	No.6	No.7	No.8	No.9	No.10	No.11	No.12	No.13	No.14	No.15		
No.4	No.4	No.5	No.6	No.7	No.8	No.9	No.10	No.11	No.12	No.13	No.14	No.15			
No.5	No.5	No.6	No.7	No.8	No.9	No.10	No.11	No.12	No.13	No.14	No.15				
No.6	No.6	No.7	No.8	No.9	No.10	No.11	No.12	No.13	No.14	No.15					
No.7	No.7	No.8	No.9	No.10	No.11	No.12	No.13	No.14	No.15						
No.8	No.8	No.9	No.10	No.11	No.12	No.13	No.14	No.15							
No.9	No.9	No.10	No.11	No.12	No.13	No.14	No.15								
No.10	No.10	No.11	No.12	No.13	No.14	No.15									
No.11	No.11	No.12	No.13	No.14	No.15										
No.12	No.12	No.13	No.14	No.15											
No.13	No.13	No.14	No.15												
No.14	No.14	No.15													
No.15	No.15														

(continued on next page)

(continued on next page)

Table 3 (continued)

Sample	Type III fluorapatite														
	No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9	No.10	No.11	No.12	No.13	No.14	No.15
Na	1302	740	896	1457	1315	819	1271	1255	496	772	1080	536	956	1343	768
Mn	81.7	82.6	88.9	140	101	61	112	122	87.8	60.6	94.5	81.8	68.6	101	81.2
Rb	–	–	–	–	–	–	–	–	1.47	–	1.27	–	–	–	2.77
Sr	9501	8503	9018	8840	9246	9949	8905	8700	8188	9358	8964	6878	8606	8921	8209
Y	265	226	215	185	186	234	190	179	166	204	190	157	198	191	170
La	1112	591	828	1232	1334	637	1348	1186	353	481	1153	500	985	1398	755
Ce	3102	1766	2018	2817	2927	2099	2905	2665	1077	1611	2626	1188	2401	2995	1757
Pr	406	255	262	330	344	313	353	320	149	239	312	153	301	354	218
Nd	1767	1137	1143	1365	1396	1374	1439	1302	706	1104	1284	690	1243	1423	962
Sm	281	212	191	207	200	234	216	201	141	200	192	122	194	220	162
Eu	81.1	59.1	56.0	54.1	57.6	63.0	57.4	51.0	37.8	57.1	52.2	35.3	52.7	56.4	42.4
Gd	194	154	142	135	141	166	141	129	108	140	133	95.5	134	145	121
Tb	21.3	16.5	14.9	14.3	14.3	16.6	14.5	12.1	14.6	14.0	13.7	10.8	14.0	15.0	11.8
Dy	87.4	70.0	61.9	61.0	59.7	70.7	62.1	55.9	49.5	64.2	60.8	48.7	61.9	65.2	49.4
Ho	11.7	10.4	9.48	8.54	8.73	9.94	8.47	7.71	7.36	9.03	8.96	6.77	8.90	8.88	6.91
Er	24.3	19.6	18.2	15.6	16.5	19.7	15.0	16.4	13.8	16.8	15.5	14.8	17.7	17.6	14.2
Tm	2.10	1.87	1.78	1.64	1.45	1.77	1.73	1.35	1.35	1.59	1.39	1.13	1.83	1.60	1.47
Yb	9.55	9.96	7.71	5.99	7.33	11.4	8.64	7.48	6.04	8.18	7.57	4.86	6.46	6.45	5.45
Lu	1.10	0.93	0.83	0.87	0.95	0.99	0.77	0.57	0.69	0.77	0.70	0.60	0.79	1.00	0.51
Hf	–	–	–	–	–	–	–	–	–	–	–	–	0.07	–	–
Pb	3.23	2.77	2.62	3.35	3.70	1.39	3.60	3.35	3.90	1.86	3.71	3.51	2.16	4.28	2.03
Th	6.63	3.19	3.75	5.50	6.92	3.01	5.41	4.63	3.37	2.61	5.40	3.50	4.09	7.49	2.85
U	–	0.01	–	–	–	–	0.01	–	0.02	–	–	–	–	–	–
ΣREE	7101	4303	4755	6248	6509	5016	6569	5957	2662	3948	5860	2872	5422	6707	4106
LREE	6749	4020	4497	6005	6259	4719	6317	5724	2463	3693	5618	2688	5176	6446	3896
HREE	351	283	257	243	250	297	252	233	198	255	242	183	245	261	210
LREE/HREE	19.21	14.20	17.49	24.72	25.04	15.90	25.04	24.57	12.41	14.49	23.25	14.68	21.10	24.70	18.53
(La/Yb) _N	83.56	42.58	76.98	147.53	130.63	40.22	111.92	113.63	41.88	42.22	109.26	73.78	109.37	155.36	99.27
8Eu	1.01	0.96	1.00	0.93	1.00	0.93	0.94	0.91	0.90	0.99	0.95	0.97	0.95	0.91	0.89
8Ce	1.13	1.11	1.06	1.06	1.03	1.15	1.01	1.04	1.15	1.16	1.05	1.04	1.07	1.02	1.05

Sample	Type III fluorapatite														
	No.16	No.17	No.18	No.19	No.20	No.21	No.22	No.23	No.24	No.25	No.26	No.27	No.28	No.29	No.30
Na	1166	1058	861	1091	501	1090	1199	1203	1045	1464	1130	1330	1253	850	935
Mn	92.7	105	83.7	76.4	63.0	115	121	89.3	85.1	91.4	93.2	82.1	125	103	104
Rb	–	1.31	2.09	–	–	–	4.61	1.26	–	–	–	1.05	–	–	0.86
Sr	9523	8602	8658	9360	8840	8379	8701	9103	9063	8852	9140	9594	8755	8380	7845
Y	214	185	225	206	285	180	181	198	214	220	211	228	189	181	165
La	1290	1067	581	1167	189	1029	1166	1374	878	1562	1177	1427	1132	770	802
Ce	2882	2511	1872	2620	780	2351	2618	3007	2308	3362	2767	3251	2551	1817	1897
Pr	368	295	267	324	143	287	316	362	306	406	347	394	317	231	239
Nd	1524	1242	1260	1280	749	1188	1300	1447	1286	1577	1438	1600	1317	975	1016
Sm	223	196	220	205	202	179	192	212	218	239	212	241	193	169	164
Eu	62.0	51.2	59.3	54.2	64.0	50.1	50.6	57.7	61.9	64.3	60.2	65.2	51.8	46.3	46.4
Gd	154	136	155	134	171	121	131	149	152	158	154	165	136	119	117
Tb	16.7	13.7	16.3	14.3	19.0	12.6	12.7	15.7	16.0	16.1	15.5	16.7	14.3	12.5	12.6
Dy	73.7	58.7	69.4	62.5	86.8	52.6	57.4	65.9	68.7	69.5	66.8	71.0	60.1	55.5	52.5
Ho	9.94	8.32	9.90	8.85	12.5	7.57	7.96	9.02	9.41	9.72	9.43	10.9	8.40	7.64	7.56
Er	18.3	16.2	20.2	16.9	22.5	15.5	17.2	17.2	16.7	20.1	18.9	18.4	16.0	14.8	14.0
Tm	1.73	1.48	1.81	1.58	2.47	1.40	1.33	1.84	1.73	1.68	1.68	2.01	1.51	1.54	1.30
Yb	8.34	8.02	10.3	7.19	10.7	8.08	7.67	8.37	6.52	8.23	9.19	8.13	7.59	5.67	7.92

(continued on next page)

Table 3 (continued)

Sample	Type III fluorapatite														No.30
	No.16	No.17	No.18	No.19	No.20	No.21	No.22	No.23	No.24	No.25	No.26	No.27	No.28	No.29	
Lu	0.87	1.11	0.82	0.79	1.24	0.90	0.83	0.87	0.80	0.96	0.88	1.05	0.93	0.92	0.71
Hf	—	—	—	—	—	—	0.02	—	—	—	—	—	—	0.69	—
Pb	4.13	3.96	3.35	3.58	1.54	3.37	3.15	3.53	2.42	3.97	3.96	3.38	2.82	3.01	3.00
Th	6.09	5.77	4.00	4.86	0.76	4.36	5.00	5.98	3.62	8.19	5.57	6.32	5.22	3.28	4.16
U	—	—	—	—	—	—	—	—	—	—	—	—	0.02	0.01	—
ΣREE	6632	5605	4541	5895	2452	5303	5878	6728	5332	7496	6278	7271	5806	4226	4378
LREE	6349	5362	4258	5649	2126	5084	5643	6461	5058	7211	6002	6978	5562	4009	4164
HREE	284	243	283	246	326	219	234	268	274	285	276	293	245	218	213
LREE/HREE	22.37	22.03	15.02	23.00	6.52	23.20	24.07	24.14	18.49	25.32	21.74	23.82	22.74	18.43	19.52
(La/Yb) _N	110.98	95.43	40.27	116.43	12.72	91.32	109.07	117.77	96.54	136.14	91.87	125.94	106.97	97.52	72.65
8Eu	0.97	0.91	0.93	0.94	1.03	0.99	0.92	0.94	0.99	0.95	0.97	0.94	0.93	0.95	0.98
8Ce	1.01	1.08	1.16	1.03	1.11	1.04	1.04	1.02	1.09	1.01	1.05	1.05	1.03	—	—

—, below the detection limit.

0.20 and 0.38 wt%). The altered regions in Type I and Type II fluorapatite also have differences in the BaO, SO₃, SiO₂ and FeO contents. Altered (BSE-dark) regions in Type I fluorapatite contain higher BaO and slightly higher SO₃ than the altered (BSE-dark) regions in Type II fluorapatite.

6. Discussion

6.1. Coarse-grained dolomite (H8_c) and fine-grained dolomite (H8_f)

Contrasting the major elements of dolomite minerals from the coarse-grained dolomite (H8_c) and fine-grained dolomite (H8_f), we discover that dolomite from H8_f contains higher REE, Mn, Fe, lower Sr, compared to that from the H8_c. In the H8_c, SrO contents in the rim of the dolomite minerals reach up to 1.04 wt%, while SrO contents in the core as low as 0.16 wt% (one point low to 0.04 wt%). Yang and Le Bas (2004) suggested that SrO and MnO contents of carbonate minerals can be used as important parameters to distinguish sedimentary carbonate and carbonatite. Carbonate minerals from carbonatites typically contain both SrO and MnO higher than 0.15 wt%. However, the dolomite from H8_c possesses abnormally low SrO contents in the core, maybe retaining the feature of the sedimentary carbonates. Yang et al. (2011) proposed that major element contents of the whole rock of coarse-grained dolomite marble are comparable to those of the calcite-dolomite carbonatite dykes and interpreted the high Sr of the coarse-grained H8 as a primary magmatic signature. Petrological observation and experimental studies prove that carbonate minerals crystallized from primitive carbonatite magma may have higher SrO than those from evolved carbonatite magma, while Mn, REE, U, Th, F and Ba increase in the residual melt (Wyllie et al., 1996; Le Bas et al., 1997; Le Bas and Srivastava, 1989). The hypothesis of igneous carbonatite origin of coarse-grained H8 is inconsistent with the fact that abrupt rise in SrO contents in the rim and abnormally low SrO contents in the core. The high SrO contents in the margin of dolomite from H8_c can be interpreted as the result of sedimentary original dolomite marble being undergone the fluid metasomatism (Smith et al., 2015). Newly formed Sr-rich apatite shows elongated orientation paralleling the lineation of sheared coarse-grained dolomite (Fig. 5e), implying that the apatite was generated during deformation and metamorphism processes. The rim of dolomite grains may be exposed to Sr-rich and REE-depleted metamorphic fluid alteration. Lai et al. (2016) demonstrated that the geochemical signatures of the dolomite minerals in the fine-grained dolomite are similar to those in the coarse-grained dolomite, enriched in MREE, both different from dolomite minerals from carbonatite dykes, which are characterized by enriched in light REE. The carbon and oxygen isotopes of dolomite from ore body host H8 marble are distinctively different from those from mantle-derived carbonatite (Yang et al., 2009). Paradoxes exist based on the facts that the whole rock geochemistry of fine-grained dolomites (H8_f) has the extremely high REE geochemical characteristics, while a considerable proportion of individual fine-grained dolomite minerals with low SrO, REE contents are quite different from those of dolomite minerals from carbonatite dykes (Lai et al., 2016). The very high REE contents of the fine-grained mineralized dolomite bulk rocks can be explained by the enrichment of accessory phases, such as apatite, monazite and bastnaesite. Metasomatic textures exhibiting that coarse-grained dolomite relics are surrounded by the REE minerals and gangue minerals, which are ubiquitous in the REE mineralized dolomite. Therefore, both coarse-grained dolomite (H8_c) and fine-grained dolomite (H8_f) are probably sedimentary carbonate, weakly mineralized H8_c being altered by SrO-rich, REE-relatively depleted metamorphic fluid and intensively mineralized H8_f related to REE, Fe-rich hydrothermal solution may derived from carbonatite.

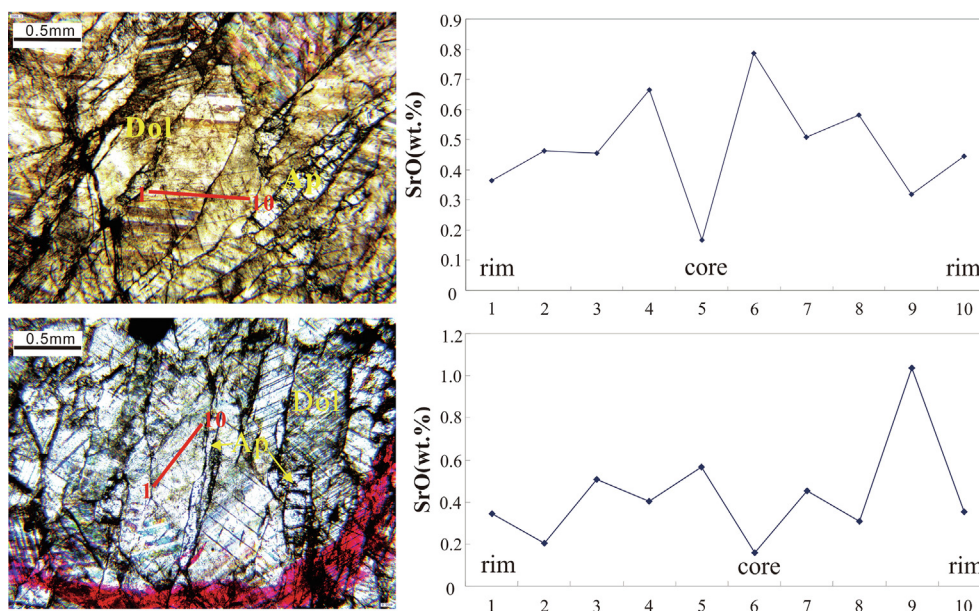


Fig. 11. SrO compositional variation from the rim to the core in dolomite mineral from coarse-grained dolomite. The data of dolomites were obtained by EPMA.

6.2. Types of apatite

Apatite serves as one of the main carriers of REE elements for Bayan Obo deposit, as well as concentrating high contents of Sr, Th, U and Pb. Apatite is a superb mineral as a geochemical tracer of metasomatic fluids because it can be chemically altered by aqueous brines, pure H₂O, and aqueous fluids containing CO₂, HCl, H₂SO₄, and/or F (Harlov, 2015). Apatite can fingerprint the existence, nature and evolution of mineralizing hydrothermal fluids utilizing cathodoluminescence and trace element geochemistry. Zirner et al. (2015) proposed that oscillatory zonation, overgrowth and conversion textures in the apatite from Ilimaussaq complex rock under back-scattered electron (BSE) are related to magmatic differentiation, hydrothermal metasomatic overprint, respectively. Li and Zhou (2015) studied the Yinachang Fe-Cu (REE) deposit in Southwestern China, identifying two types of fluorapatite which display the altered zonation under BSE imaging. Bouzari et al. (2016) once used the cathodoluminescent and textural characteristics to identify specific types of hydrothermal alteration related to porphyry copper deposits. These above examples demonstrated that REE can be mobilized during multiple stages of hydrothermal activity. We separated the apatite into three groups based on detailed mineralogical observations under microscope, scanning electron microscope and cathodoluminescence. Distinct internal structures and chemical compositions of three types of apatite and different types of metasomatic alteration observed in BSE-dark areas provide useful tools to restrict sources of hydrothermal and metasomatic fluids.

Although displaying similar gray/glow blue luminescence contributed to the Eu²⁺ activation, the three types of apatite display different inner structures (Fig. 10). Under CL, altered areas are relative to gray blue-luminescent apatites in Type I apatite. On the contrary, altered areas are corresponding to the bright color-luminescent apatites in Type II apatite. Type III fluorapatite prisms are cut by gray/dark-luminescent veinlets. The wide range of colors and different textures of apatite under CL are caused by concentrations and types of activators, depending on its origin and affected by associated alteration processes (Bouzari et al., 2016). Le Bas et al. (1992) reported the grey/blue CL in apatites from the carbonatite dykes to the north of East orebodies and in coarse-grained H8 marble at Bayan Obo. Campbell and Henderson (1997) observed that apatite related to the main period of REE mineralization is pink/cream/grey under CL. In our study, three types of apatite display glow blue /gray CL, which is quite similar to the

descriptions in Le Bas et al. (1992). Marshall (1988) and Ting (1994) suggested that the blue luminescence of Eu²⁺ containing, or vacancy-activated is a typical feature of apatite from carbonatite. However, apatites from some metamorphic rocks also display blue/grey CL (Deng, 1980; Xu et al., 2006). The main activators controlling CL properties of apatite are Mn²⁺, Dy³⁺, Eu³⁺, Sm³⁺, Eu²⁺, producing CL peaks in the visible yellow green, yellow, red, orange, blue part of the spectrum respectively (Deng, 1980; Marshall, 1988; Liu and Hua, 2003).

In-situ micro-analyses on chemical compositions by EPMA and LA-ICP-MS techniques verify the correctness of categorizations. REE, Na-rich primary apatites display similar phenomena that concentrations of Na and LREE are reduced in the altered zones in Type I and Type II apatite. Altered areas are relative regular patches in Type I apatite, complex shapes and irregular veins in Type II apatite (Figs. 7,8,10). Type III apatite monocrystals are cut by Sr, Si-rich veinlets (Fig. 9). From the plot of Y vs. Sr (Fig. 14e), the plot of Na vs. REE + Y (Fig. 14c), and the plot of Pb vs. Th + U (Fig. 14f), these three types of apatite can be easily distinguished. Both the Type I and the Type II fluorapatite are obviously richer in REE and slightly higher in F content compared with Type III apatite, suggesting that the former two are intimately associated with igneous carbonatite. It is clear that carbonatite is an important source of REE in Bayan Obo. The mineralized hydrothermal fluids are rich in REE, demonstrated by the REE daughter minerals in fluid inclusions (Fan et al., 2003). Type III apatite possesses the highest Sr contents and the lowest REE + Y and Na contents, implying the different fluid source.

For REE-uptake in apatite, several charge-compensating coupled substitution mechanisms have been proposed (Roeder et al., 1987; Ronsbo, 1989; Pan and Fleet, 2002). The most important two mechanisms are:



The Y + REE (apfu) displays a clear positive covariance with Na (apfu) and no obvious correlation with Si (apfu) (Fig. 14a, b), indicating that Y³⁺ and REE³⁺ are charge-balanced through the following coupled substitution formula (1).

The plot of Y vs. Sr can sufficiently separate the three types of apatite and the Type II fluorapatite displays the distinctive enrichment in Y, followed by the Type I fluorapatite (Fig. 14e). Fluid inclusions in gangue and REE ore phases from the Bayan Obo Fe- REE-Nb deposit

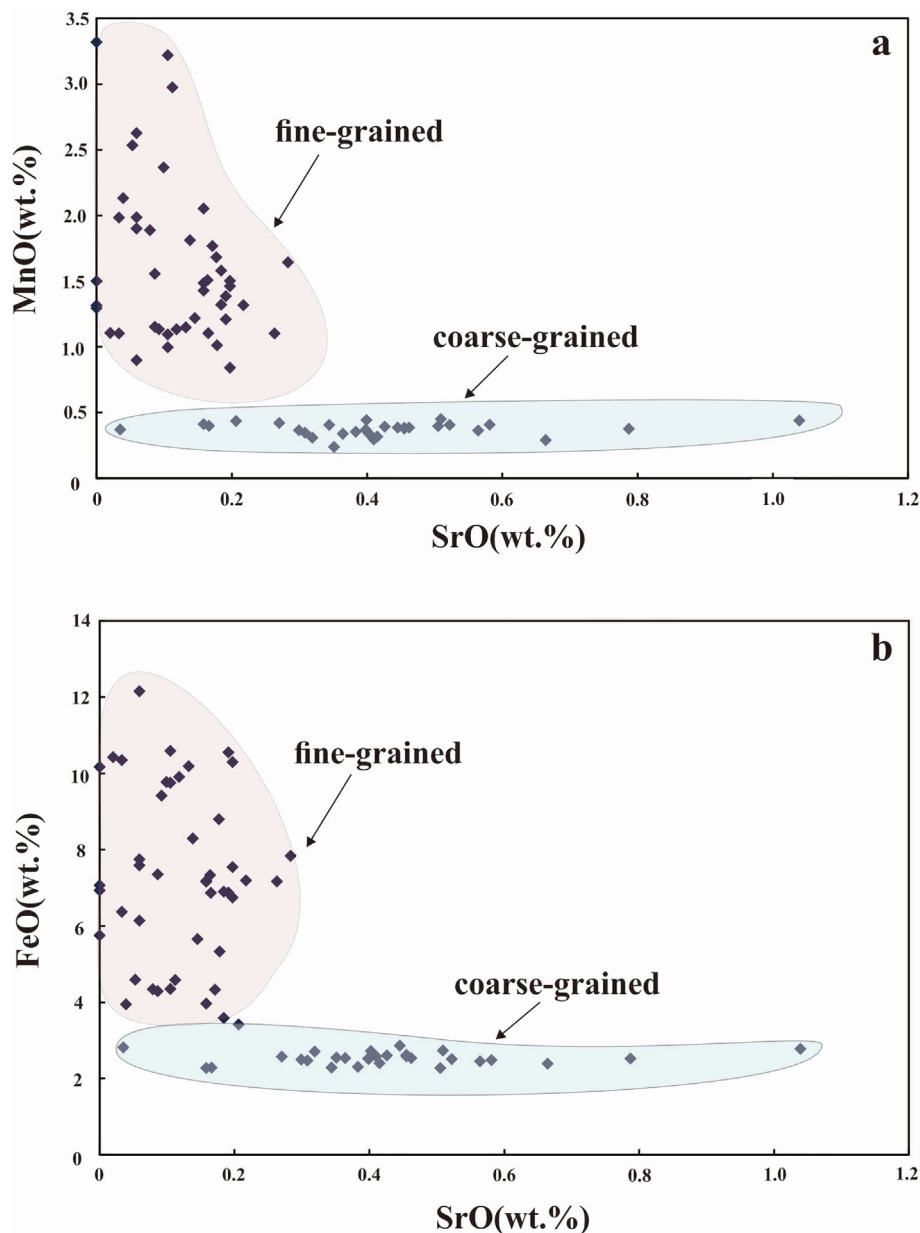


Fig. 12. Plot of MnO vs. SrO (a), FeO vs. SrO (b) for coarse-grained and fine-grained dolomite marble. The plotted data of dolomites were obtained by EPMA.

record a protracted history of fluid-rock interaction, with distinct fluid compositions related to distinct paragenetic stages in the mineralization, indicating significant REE mobility under a wide range of chemical and P-T conditions (Smith et al., 2000). The Y concentrations in the hydrothermal solution varied with the precipitated mineral associations in different paragenetic stages and the predominant complex ligands in the fluid (Broom-Fendley et al., 2017). Type II fluorapatite formed earlier than Type I fluorapatite which contemporaneously precipitated with fluorite or precipitated from a solution suffering the extraction of fluorite. A specific REY distribution with positive Y_N anomaly commonly occurred in hydrothermal fluorites. Y acts as a Lu-like heavy pseudolanthanide in fluorine-rich solutions and YF^{2+} may be more stable than any $REEF^{2+}$ (Bau and Dulski, 1995). In Bayan Obo, fluorite is characterized by LREE enrichment relative to MREE and HREE and contains different levels of Y positive anomaly, indicating F-complexation predominantly controlling the distribution of Y and REE (Xu et al., 2012). Large scale fluorite precipitation can lead to the Y depletion in the residual solution.

Despite that three types of apatites are entirely different in Th + U

and Pb compositions (Fig. 14f), they are all extremely U-depleted (< 0.07 ppm). Therefore, radiogenic Pb was primarily derived from the radiogenic decay of the Th. Low U abundance and high common lead contents are characteristics of the whole deposit, discouraging us to get the valid U-Pb age of mineralized time. The contents of Pb in Type I fluorapatite are dramatically high, ranging from 60 ppm to 110 ppm. Whereas, the amounts of Th in Type I fluorapatite are low and not enough to produce the radiogenic Pb abundance. Consequently, we conclude that the majority of Pb in Type I fluorapatite was added during precipitating from a migrated REE-rich hydrothermal solution, which contained a high amount of Pb. The great mobility of Pb, demonstrated by various hydrothermal experiments, facilitates its migration from the crystal structure into fluid. As the hydrothermal fluid continues to migrate, the Pb successively increases during the fluid interacting with the pre-existing Th-rich minerals and country rocks. Type I fluorapatite inherited the Pb enrichment from the evolved hydrothermal solution.

EPMA and LA-ICPMS data have demonstrated that the dark regions in the Type I and Type II fluorapatite are strongly depleted in the Na,

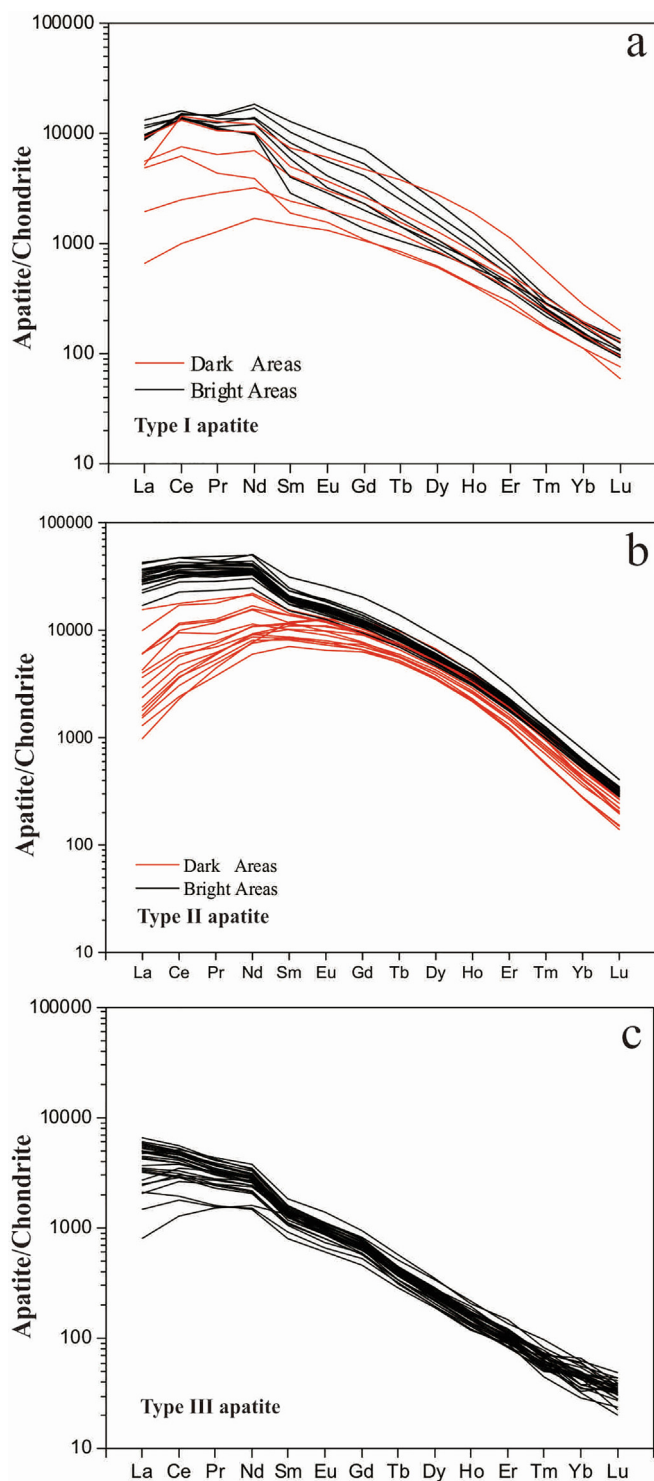


Fig. 13. Chondrite-normalized REE abundance diagrams for three types of apatites measured by LA-ICPMS. (a) Chondrite-normalized REE patterns for the bright and dark areas in Type I fluorapatite; (b) chondrite-normalized REE patterns for the bright and dark areas in Type II fluorapatite; (c) chondrite-normalized REE patterns for Type III fluorapatite. In (a) and (b), the black lines represent the unaltered regions in apatite and the red lines represent the altered regions. Normalization values from Sun and McDonough (1989). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

LREE and Pb. The mapping of elements also displays the loss of LREE and Na. Mobilization of the lanthanides from the apatite is interpreted as the product of interaction with fluids percolating through the rocks.

Experimental studies proved that the REE mobilization and redistribution in apatite may occur during hydrothermal overprinting by dissolution-reprecipitation processes (Harlov et al., 2003, 2005; Kusebauch et al., 2015; Putnis and Austrheim, 2010). In the Bayan Obo deposit, both apatite and amphibole show compositional variations that are consistent with multiple generations of fluid influx into the deposits, even within a single paragenetic stage (Campbell and Henderson, 1997; Smith, 2007; Liu et al., 2018a). Apatite textures and compositions are powerful tool in deciphering the REE mineralization as well as metasomatic processes (Broom-Fendley et al., 2016, 2017). Fluid compositions are the crucial factor controlling the style of REE transportation, deposition and remobilization in hydrothermal system.

6.2.1. REE-rich mesothermal hydrothermal fluid responsible for REE leaching in Type I fluorapatite

Chemical compositions are heterogeneous in Type I fluorapatite, BSE-bright and BSE-dark regions occurring in the same apatite crystal. Zoned granular apatite crystals (fine grained) from H8 dolomite were also described by Le Bas et al. (1992). Few REE mineral inclusions are observed in the interior of the Type I fluorapatite. One interpretation for the lack of monazite inclusions in the Type I fluorapatite could be that the fluid was enriched in Na and Ca. Previous experiments showed that Na- or Ca-rich fluids cannot induce the formation of REE mineral inclusions in apatite (Broman et al., 1999) as the Na and Ca can freely enter the apatite structure to maintain charge balance and to stabilize the LREE (Harlov and Förster, 2003; Harlov et al., 2005). Type I fluorapatite is mainly derived from apatite-REE (bastnaesite)-magnetite banded ore (sample 09BY161). Based on petrography, bastnaesite associated with barite occurs as veins or bands crosscutting the Type I fluorapatite and infilling the fractures of magnetite grains, suggesting that apatite and magnetite formed earlier than the bastnaesite-barite vein. Gieré (1996) proposed that phosphate ions are important complexing agents of the REE, especially at high temperatures. Migdisov et al. (2016) pointed out that phosphate complexes are unlikely to contribute significance to the mobility of REE due to the extremely low solubility of solid REE phosphates. Therefore, they act as depositional ligands rather than a transporting ligand in ore processes, precipitating from the fluid together with the REE at the early stage. The contents of BaO in the BSE-dark areas of Type I apatite reach up to 0.053 wt%, apparently higher than those in BSE-bright areas. The SrO contents maintain relatively invariable. The Type I fluorapatite may have been leached by the fluid with a high capability to dissolve LREEs. LREEs leached from the fluorapatite were migrated into the low pH, SO_4^{2-} -rich fluids, leaving behind a reprecipitated LREE-depleted fluorapatite. Sulfate ligand and the condition of low pH encourage REE mobility. Elevated concentrations of rare earth elements were presented in acid-sulfate and acid-sulfate-chlorite hydrothermal waters (70–93 °C) which interacted with their host rhyolitic volcanic in Yellowstone National Park (Lewis et al., 1998). As the SO_4/F increases in the fluid, sulfate complexes account for the majority of dissolved LREEs in the water. Decrease of pH leads to apatites dissolution, liberating LREEs into fluids or forming new minerals during hydrothermal alteration with high activity of SO_4^{2-} and low-pH condition (Hikov, 2011).

Sulfate ligand complexing with REE may have been related to the last stage of hydrothermal activity in the carbonatite complex (Enkhbayar et al., 2016). Hydrothermal metasomatic fluid in this stage is rich in SO_4^{2-} , Ba and REE verified by the fact that bastnaesite and barite are closely associated and that barite hosts high amounts of Ce, Nd, Sm and Pb observed in the compositional X-ray maps of Type I apatite. Contributions of sulfate species to the mass of dissolved Nd are very significant at high (> 300 °C) temperature expanding the range of pH over which Nd can be stabilized in F⁻ bearing solutions. Complexes involving sulfate ions could play a significant role in REE transportation by weakly acidic hydrothermal solution even in the presence of fluoride ions (Migdisov and Williams-Jones, 2008; Migdisov et al., 2016). The development of porosity is clear evidence of the dissolution reaction

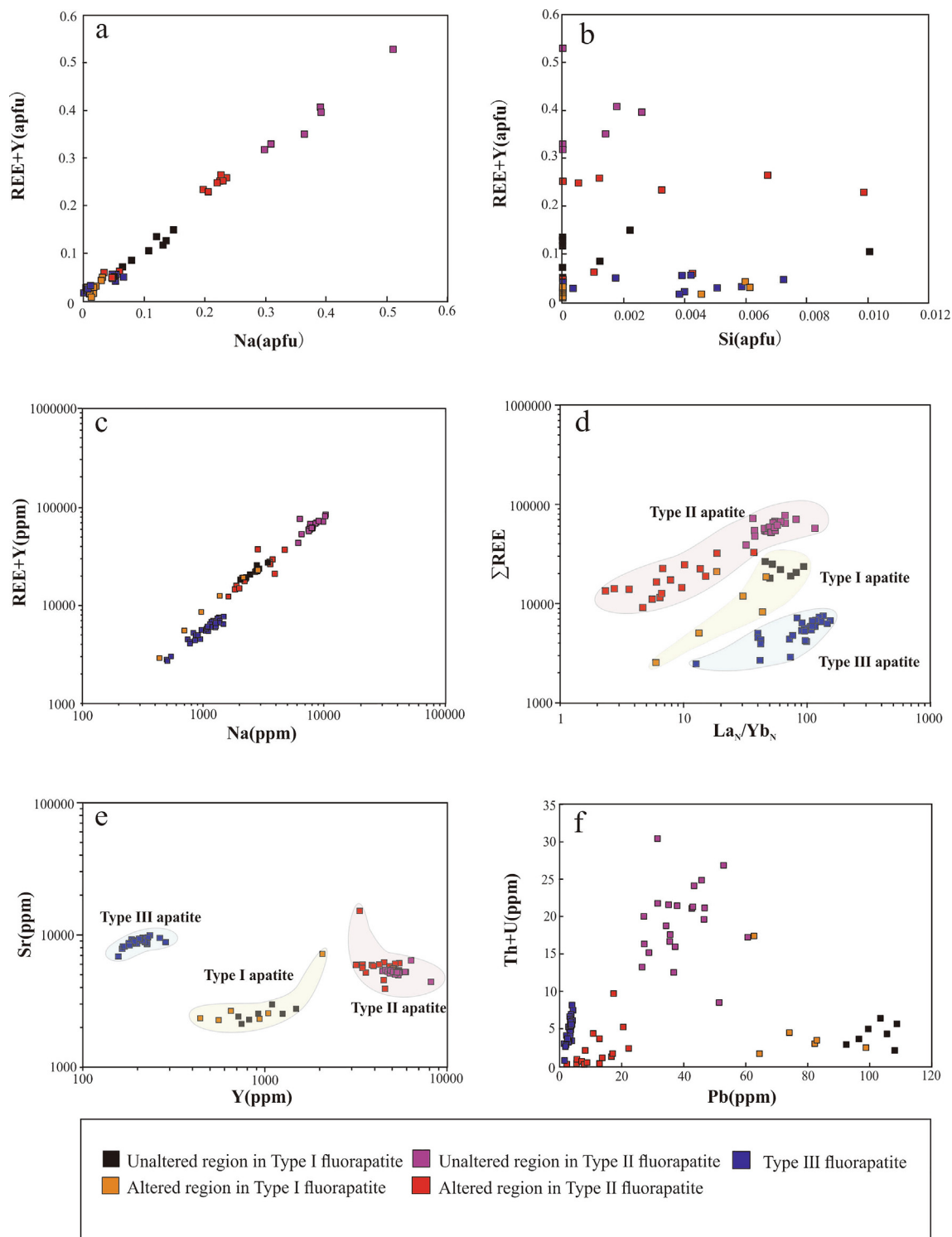
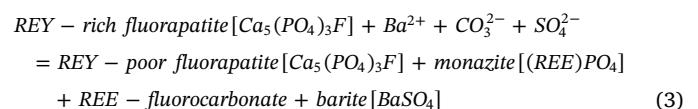


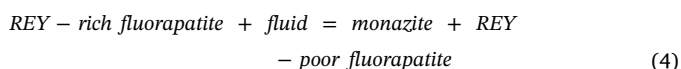
Fig. 14. Cationic plots of Na vs. (REE + Y) (a), Si vs. (REE + Y) (b) for different fluorapatite domains. The plotted data for different types of apatite were obtained by EPMA. (c) Plots of Na vs. (REE + Y) for different apatites obtained by LA-ICPMS as well as illustrate a positive, linear relationship between Na and LREE + Y. (d) Plots of $(La/Yb)_N$ vs. the total REE for different fluorapatite domains with the altered regions in Type I and Type II apatite both display the depletion in LREE. Plots of Y vs. Sr (e) and Pb vs. (Th + U) (f) for different apatite domains. The plotted data were obtained by LA-ICPMS.

due to the fluid infiltrating through apatite. The reprecipitated REE-depleted fluorapatite preserves the shape and crystalline orientation of the individual crystal. The distribution of altered apatite is associated with the cracks and micro-fractures, which facilitates the transfer of Na, REE, Pb, Th to the SO_4^{2-} , CO_2 -dominated mesothermal hydrothermal fluid. The dissolution-reprecipitation of the fluorapatite proceeded via a reaction:



6.2.2. Fluid-induced dissolution-precipitation causing internal redistribution within Type II fluorapatite

Previous studies of natural assemblages as well as experimental investigations implied that monazite associated with fluorapatite is a potential tracer of metasomatic processes (Bonyadi et al., 2011; Harlov et al., 2005; Li and Zhou, 2015; Zirner et al., 2015; Feng et al., 2016). In our study, REE-leached apatite, and monazite inclusions hosted within this apatite are probably the results of fluid-induced alteration of apatite via dissolution-precipitation processes, which have been widely recognized (Harlov et al., 2002, 2003, 2005, 2005; Torab and Lehmann, 2007; Bonyadi et al., 2011). Experimental studies of the reaction of REE-rich apatite with a range of solutes at a wide range of temperatures and pressures have proven that monazite inclusions form most readily from HCl, KCl or H₂SO₄ dominated fluids that are deficient in Na and Ca (Harlov and Förster, 2003; Harlov et al., 2005). The type II apatite displays different chemical composition zones, and the altered apatite displays the typical Na, REY losses. Removal of Na and Si, resulting in charge imbalance, frees the (Y + REE) to react with P to form monazite and/or xenotime, either as inclusions in the apatite or as grains on the surface of the apatite (Harlov et al., 2005). The monazite inclusions have close genetic connection with the BSE-dark apatite, proving that Type II apatite formed as a result of the metasomatic overprint. The SrO contents of the altered regions in type II fluorapatite are extremely high, demonstrating that overprinting fluid is rich in Sr. The coprecipitation of hematite and REE minerals in the micro-pores implies a relatively high oxidation state of the metasomatic fluid. The activity of Ca and Na of the fluid must have been low, otherwise the formation of monazite inclusions would be retarded. Oxidized, Sr-rich, Na-depleted, REE-poor metamorphic fluid is responsible for the metasomatic event. Removal of Na at high REE levels from the apatite results in the apatite breaking down to provide the material necessary REY, P for the nucleation and growth of the monazite. The chemical reaction can be simplified as:



Abundant micro-porosities and micro cracks in leached apatite are necessary to serve as the channels for fluid infiltration and as nucleation sites for monazite inclusions (Harlov and Förster, 2003). The leached apatite-growth of new monazite texture indicates a dissolution-precipitation process, implying later stage hydrothermal metasomatism and REE remobilization in the geological history. Heterogeneous compositional zones under BSE prove that apatite is susceptible to metamorphic-hydrothermal perturbation. The higher ⁸⁷Sr/⁸⁶Sr ratios in the recrystallized dolomite and apatite compared with the primary apatite and dolomite also demonstrate that carbonatite-original REE ores have undergone subsequent thermal perturbation induced by Sr-rich, but REE-poor, metamorphic fluid (Song et al., 2018).

6.2.3. Metamorphic fluid leading to the formation of Type III fluorapatite

Type III fluorapatite from coarse-grained dolomite (H8c) is sub-prismatic to elongate with an orientation paralleling the lineation of the dolomite. This lineation may result from strong deformation interpreted to be related to the regional thrusting and folding. Most apatite crystals are 400–600 μm long, with width of 200 μm. The REE + Y and Na compositions of Type III fluorapatite are one magnitude lower than those of the unaltered regions in Type I and Type II fluorapatite, whereas the Sr contents are abnormally higher than those of the unaltered regions in Type I and Type II apatite. Compositions of Sr, F, Th and Pb of Type III fluorapatite are comparable to those of the altered regions in Type II fluorapatite to a certain extent. Therefore, the Type III apatite is inferred to have crystallized from a different fluid source which is rich in Sr and depleted in REE. Deng et al. (2017) suggested that the Sr-rich metasomatic fluid affected the primary apatite and led to the LREE depletion and the elevated Sr contents. This metamorphic

fluid was derived from sedimentary rocks. Considering that the c-axes of Type III fluorapatite are parallel to the lineation of the dolomite which are resulted from regional thrusting and folding, the source of Type III fluorapatite may be the Sr-rich, but REE-poor, metamorphic fluid (Wang et al., 1994; de Jong et al., 2006; Ling et al., 2013; Lai et al., 2015).

6.2.4. Factors controlling the different styles of REE remobilization

The altered regions in Type I and Type II fluorapatite have differences in the SrO, BaO, SO₃, SiO₂ and FeO contents. CL features are significantly different between altered areas in Type I and Type II fluorapatite. Altered areas occur as grey-luminescent patches in Type I fluorapatite and display as complex bodies with a variety of blue-luminescent in Type II fluorapatite. The REE + Y and Na compositions of Type III fluorapatite are one magnitude lower than those of the unaltered regions in the Type I and Type II fluorapatite. These evidences prove that REE remobilization processes occur in different metasomatic events. Multi-phase, fluid-mineral interactions are ubiquitous in the Bayan Obo deposit (Campbell and Henderson, 1997; Deng et al., 2017; Smith et al., 2015). The large variations in fluid chemistry indicated by the evidences of fluids inclusions pointed to successive episodes of mineralization involving fluids of different compositions. Multistage histories of deposition and remobilization of REE existed in the Bayan Obo deposit (Smith et al., 2000, 2015; Kynicky et al., 2012). The different styles of REE remobilization may be mainly controlled by the components of the metasomatic fluids, e.g. the activity of Ca and Na.

In the main REE mineralization stage, the REE-rich fluorapatite formed together with monazite (Fig. 15a). The large grained monazites of the early generation in ores are proposed to be precipitated from the primary carbonatite-related hydrothermal fluid especially at higher temperature. The Type I fluorapatite formed later than Type II fluorapatite and also precipitated in the REE mineralization stage, intimately associated with REE-rich hydrothermal solution derived from igneous carbonatite. Subsequently, the altered regions in Type I fluorapatite were formed by the SO₄²⁻, CO₂-dominated mesothermal hydrothermal fluid metasomatism (Fig. 15b). The fluid enriched in Na, Ba, SO₄²⁻, interacted with REE-rich fluorapatite via dissolution-precipitation processes. Sulfate ligand and the condition of low pH encouraged the rare elements mobility, causing the leaching of REE from REE-rich fluorapatite precursor, leading to a significant amount of LREE depletion in altered fluorapatite. The metasomatic fluid was probably late-stage evolved hydrothermal solution derived from carbonatitic, alkaline igneous, or other igneous-related REE- and Fe-rich magmatic systems (Smith and Henderson, 2000). The leached apatite-monazite inclusion texture in Type II fluorapatite implies a much later hydrothermal overprinting event (Fig. 15c). The oxidized, Sr-rich, Na-depleted, REE-poor fluid interacted with the fluorapatite, leading to the LREE extreme depletion in BSE-dark fluorapatite, numerous REE mineral inclusions and a “mottled” texture under CL. Meanwhile, the Type III apatite in the coarse-grained dolomite crystallized from the Sr-rich, Na-depleted and REE-poor metamorphic fluid accompanied by extensional regional compressional deformation.

7. Conclusion

Based on results of the two types of dolomite marble and three types of fluorapatite, we draw the conclusions as follows:

- 1) The coarse-grained and fine-grained dolomite marble were formed by different geological processes. The dolomite from coarse-grained dolomite marble shows the parallel lineation and abnormally high SrO contents in the rim and significantly low SrO contents in the core. The dolomite from fine-grained dolomite marble hosting REE reserves contains high levels of Mn and Fe. Metasomatic textures are ubiquitous in fine-grained mineralized dolomite.
- 2) Three types of apatites show big differences in cathodoluminescent

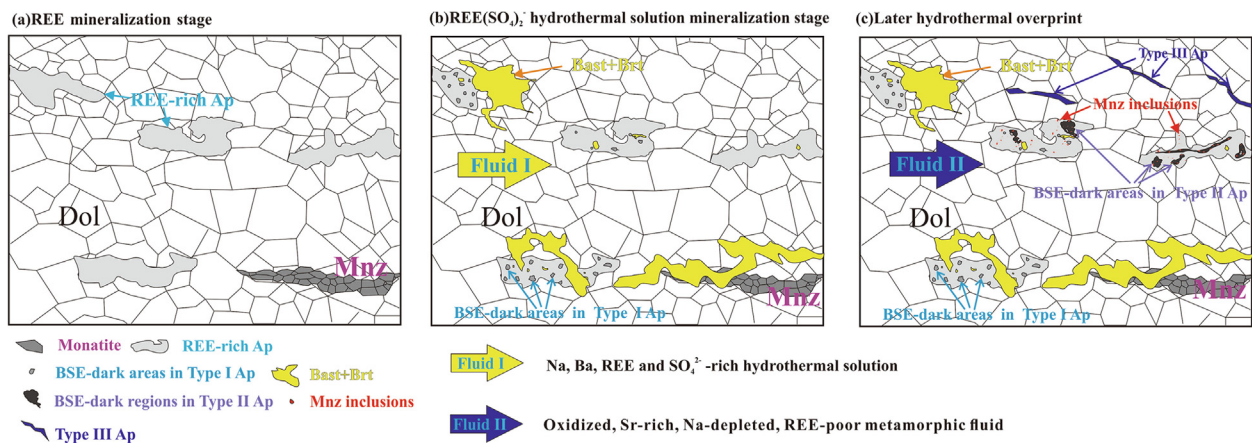


Fig. 15. Cartoons illustrating the REE mineralization and remobilization histories in the Bayan Obo deposit (the model revised from Li et al., 2015). (a) In REE mineralization stage, REE-rich fluorapatite formed together with monazite. (b) In the $\text{REE}(\text{SO}_4)_2$ hydrothermal solution mineralization stage, the fluid rich in Na, Ba, SO_4^{2-} , interacted with REE-rich fluorapatite. During this process a significant amount of REE, especially LREE, were leached out of the fluorapatite. (c) At Later hydrothermal overprint, oxidized, Sr-rich, Na-depleted, REE-poor metamorphic fluid interacted with the fluorapatite, leading to the formation of BSE-dark regions and numerous REE mineral inclusions in Type II fluorapatite. Meanwhile, coarse-grained dolomite marble was subjected to deformation and Type III apatite formed as the fluxing of the metamorphic fluid into the deposit.

signatures. Both Type I and Type II fluorapatite are heterogeneous in chemical compositions under BSE. The typical REE-rich feature of unaltered regions in Type I fluorapatite and Type II fluorapatite supports the primary REEs derived from a carbonatite source. The fluid responsible for the strong LREE depletion in Type I fluorapatite was rich in REE, Na, Ba, CO_3^{2-} and SO_4^{2-} , similar to carbonatite-related REE-rich mesothermal hydrothermal fluid. Whereas, the metamorphic fluids contributed to the internal REE redistribution in Type II fluorapatite and formation of the Type III fluorapatite.

3) The Bayan Obo deposit had experienced multistage hydrothermal metasomatism. Primary REEs were derived from a carbonatite source. The Sr-rich, Na-depleted and REE-poor metamorphic fluid flowed into the deposit and resulted in REE remobilization.

Acknowledgements

This study is supported by the National Key R & D Program of China (No. 2018YFC0604206) and the National Natural Science Foundation of China (No. 41502036). We thank Dr. Fangyue Wang for providing assistance in LA-ICPMS lab work. We are particularly grateful to two anonymous reviewers for their constructive comments that have helped to significantly improve the quality of the paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.oregeorev.2019.04.020>.

References

- Bai, G., Yuan, Z.X., 1985. Carbonatites and related mineral resources. *Bull. Inst. Miner. Deposit. Chin. Acad. Geol. Sci.* 13, 107–140.
- Bau, M., Dulski, P., 1995. Comparative study of yttrium and rare-earth element behaviors in fluorine-rich hydrothermal fluids. *Contrib. Miner. Petrol.* 119, 213–223.
- Belousova, E.A., Griffin, W.L., O'Reilly, S.Y., Fisher, N.L., 2002. Apatite as an indicator mineral for mineral exploration: trace-element compositions and their relationship to host rock type. *J. Geochem. Explor.* 76, 45–69.
- Bonyadi, Z., Davidson, G.J., Mehrabi, B., Meffre, S., Ghazban, F., 2011. Significance of apatite REE depletion and monazite inclusions in the brecciated Se-Chahun iron oxide-apatite deposit, Bafq district, Iran: Insights from paragenesis and geochemistry. *Chem. Geol.* 281, 253–269.
- Bouzari, F., Hart, C.J.R., Bissig, T., Barker, S., 2016. Hydrothermal alteration revealed by apatite luminescence and chemistry: a potential indicator mineral for exploring covered porphyry copper deposits. *Econo. Geol.* 111, 1397–1410.
- Broman, C., Nyström, J.O., Henríquez, F., Elfman, M., 1999. Fluid inclusions in magnetite-apatite ore from a cooling magmatic system at El Laco, Chile. *Geol. Foeren.*

- Stockholm Foerh. 1, 253–267.
- Broom-Fendley, S., Styles, M.T., Appleton, J.D., Gunn, G., Wall, F., 2016. Evidence for dissolution-precipitation of apatite and preferential LREE mobility in carbonatite-derived late-stage hydrothermal processes. *Am. Mineral.* 101, 596–611.
- Broom-Fendley, S., Brady, A.E., Wall, F., Gunn, G., Dawes, W., 2017. REE minerals at the Songwe Hill carbonatite, Malawi: HREE-enrichment in late-stage apatite. *Ore Geol. Rev.* 81, 23–41.
- Campbell, L.S., Compston, W., Sircombe, K.N., Wilkinson, C.C., 2014. Zircon from the East of the Bayan Obo Fe-Nb-REE deposit, China, and SHRIMP ages for carbonatite-related magmatism and REE mineralization events. *Contrib. Miner. Petrol.* 168, 1040–1062.
- Campbell, L.S., Henderson, P., 1997. Apatite paragenesis in the Bayan Obo REE-Nb-Fe ore deposit, Inner Mongolia, China. *Lithos* 42, 89–103.
- Cao, R.L., Zhu, S.H., Wang, J.W., 1994. Source materials for the Bayan Obo Fe-REE-Nb ore deposit and problems of the genetic theory. *Sci. China B* 24, 1298–1307.
- Chao, E.C.T., Back, J.M., Minkin, J.A., Ren, Y.C., 1992. Host-rock controlled epigenetic, hydrothermal metasomatic origin of the Bayan Obo REE-Fe-Nb ore deposit, Inner Mongolia, P.R. China. *Appl. Geochem.* 7, 443–458.
- Chao, E.C.T., Tatsumoto, M., Back, J.M., Minkin, J.A., McKee, E.H., Ren, Y.C., 1995. Multiple lines of evidence for establishing the mineral paragenetic sequence of the Bayan Obo rare earth ore deposit of Inner Mongolia, China. In: Maurice, Y.T. (Ed.), *Proceedings of the International Association on the Geology of Ore Deposits, 8th Symposium volume*, pp. 53–73.
- Chao, E.C.T., Back, J.M., Minkin, J.A., Tatsumoto, M., Wang, J.W., Conrad, J.E., McKee, E.H., Hou, Z.L., Meng, Q.R., Hang, S.G., 1997. The sedimentary carbonate-hosted giant Bayan Obo REE-Fe-Nb ore deposit of Inner Mongolia, China: a cornerstone example for giant polymetallic ore deposits of hydrothermal origin. *USGS Bull.* 2143, 65.
- de Jong, K., Xiao, W.J., Windley, B.F., Masago, H., Hualo, C., 2006. Ordovician ⁴⁰Ar/³⁹Ar phengite ages from the blueschist-facies Ondor Sum subduction-accretion complex (Inner Mongolia) and implications for the early Paleozoic history of continental blocks in China and adjacent areas. *Am. J. Sci.* 306, 799–845.
- Deng, H.X., 1980. Cathodoluminescence study of apatite. *Geochimica* 4, 368–374 (in Chinese with English abstract).
- Deng, M., Xu, C., Song, W.L., Tang, H.Y., Liu, Y., Zhang, Q., Zhou, Y., Feng, M., Wei, C.W., 2017. REE mineralization in the Bayan Obo deposit, China: evidence from mineral paragenesis. *Ore Geol. Rev.* 91, 100–109.
- Enkhbayar, D., Seo, G., Choi, S.G., Lee, Y.J., Batmunkh, E., 2016. Mineral chemistry of REE-rich apatite and sulfur-rich monazite from the Mushgai Khudag, alkaline volcanic-plutonic complex, South Mongolia. *Int. J. Geosci.* 7, 20–31.
- Fan, H.R., Tao, K.J., Xie, Y.H., Wang, K.Y., 2003. Laser Raman spectroscopy of typical rare-earth fluoro-carbonate minerals in Bayan Obo REE-Fe-Nb deposit and identification of rare-earth daughter minerals hosted in fluid inclusions. *Acta Petrol. Sin.* 19, 169–172 (in Chinese with English abstract).
- Fan, H.R., Hu, F.F., Yang, K.F., Pirajno, F., Liu, X., Wang, K.Y., 2014. Integrated U-Pb and Sm-Nd geochronology for a REE-rich carbonatite dyke at the giant Bayan Obo REE deposit, Northern China. *Ore Geol. Rev.* 63, 510–519.
- Fan, H.R., Yang, K.F., Hu, F.F., Liu, S., Wang, K.Y., 2016. The giant Bayan Obo REE-Nb-Fe deposit, China: controversy and ore genesis. *Geosci. Front.* 7, 335–344.
- Feng, M., Xu, C., Kynicky, J., Zeng, L., Song, W.L., 2016. Rare earth element enrichment in Palaeoproterozoic Fengzhen carbonatite from the North China block. *Int. Geol. Rev.* 58, 1940–1950.
- Gao, J.Y., Wang, Y.X., Qiu, Y.Z., Zhang, Q., 1999. Origin of the ore-bearing dolomite in Bayan Obo ore deposit. *Acta Sediment. Sin.* 17 (A12), 675–680 (in Chinese with English abstract).
- Giere, R., 1996. Formation of rare earth minerals in hydrothermal systems. In: Jones,

- A.P., Wall, F., Williams, C.T. (Eds.), Rare Earth Minerals. Chemistry, Origin and Ore Deposits. The Mineralogical Society Series, pp. 105–150.
- Harlov, D.E., 2015. Apatite: a fingerprint for metasomatic processes. *Elements* 11, 171–176.
- Harlov, D.E., Andersson, U.B., Förster, H.J., Nystrom, J.O., Dulski, P., Broman, C., 2002. Apatite-monzonite relations in the Kiirunavaara magnetite-apatite ore, northern Sweden. *Chem. Geol.* 191, 47–72.
- Harlov, D.E., Förster, H.J., Schmidt, C., 2003. High P-T experimental metasomatism of a fluorapatite with significant britholite and fluorellestadite components: implications for LREE mobility during granulite-facies metamorphism. *Mineral. Mag.* 67, 61–72.
- Harlov, D.E., Förster, H.J., 2003. Fluid-induced nucleation of (Y + REE)-phosphate minerals within apatite: nature and experiment. Part II. Fluorapatite. *Am. Mineral.* 88, 1209–1229.
- Harlov, D.E., Wirth, R., Förster, H.J., 2005. An experimental study of dissolution - reprecipitation in fluorapatite: fluid infiltration and the formation of monazite. *Contrib. Miner. Petrol.* 150, 268–286.
- Hikov, A., 2011. Rare earth element mobility during hydrothermal alteration in Asarel porphyry copper deposit, Central Srednogie. *Compt. Rend. Acad. Bulg. Sci.* 64, 1162–1170.
- Hu, F.F., Fan, H.R., Liu, S., Yang, K.F., Chen, F., 2009. Samarium-neodymium and rubidium-strontium isotopic dating of veined REE mineralization for the Bayan Obo REE-Nb-Fe deposit, Northern China. *Resour. Geol.* 59, 407–414.
- Institute of Geochemistry, Chinese Academy of Sciences (IGCAS), 1988. The Geochemistry of the Bayan Obo ore Deposit. Science Press, Beijing (in Chinese).
- Jochum, K.P., Nohl, U., 2008. Reference materials in geochemistry and environmental research and the GeoReM database. *Chem. Geol.* 253, 50–53.
- Kusebauch, C., John, T., Whitehouse, M.J., Klemme, S., Putnis, A., 2015. Distribution of halogens between fluid and apatite during fluid-mediated replacement processes. *Geochim. Cosmochim. Acta* 170, 225–246.
- Kynicky, J., Smith, M.P., Xu, C., 2012. Diversity of rare earth deposits: the key example of China. *Element* 8, 361–367.
- Lai, X.D., Yang, X.Y., 2013. Geochemical characteristics of the Bayan Obo giant REE-Nb-Fe deposit: constraints on its genesis. *J. S. Am. Earth Sci.* 41, 99–112.
- Lai, X.D., Yang, X.Y., Sun, W.D., 2012. Geochemical constraints on genesis of dolomite marble in the Bayan Obo REE-Nb-Fe deposit, Inner Mongolia: implications for REE mineralization. *J. Asian Earth Sci.* 57, 90–102.
- Lai, X.D., Yang, X.Y., Santosh, M., Liu, Y.L., Ling, M.X., 2015. New data of the Bayan Obo Fe-REE-Nb deposit, Inner Mongolia: implications for ore genesis. *Precamb. Res.* 263, 108–122.
- Lai, X.D., Yang, X.Y., Liu, Y.L., Yan, Z.Q., 2016. Genesis of the Bayan Obo Fe-REE-Nb deposit: evidences from Pb-Pb age and microanalysis of the H8 Formation in Inner Mongolia, North China Craton. *J. Asian Earth Sci.* 120, 87–99.
- Le Bas, M.J., Keller, J., Tao, K.J., Wall, F., Williams, C.T., Zhang, P.S., 1992. Carbonatite dykes at Bayan Obo, Inner-Mongolia. *China. Mineral. Petrol.* 46, 195–228.
- Le Bas, M.J., Spiro, B., Yang, X.M., 1997. Oxygen, carbon and strontium isotope study of the carbonatitic dolomite host of the Bayan Obo Fe-Nb-REE deposit, Inner Mongolia, N China. *Mineral. Mag.* 61, 531–541.
- Le Bas, M.J., Srivastava, R.K., 1989. The mineralogy and geochemistry of the Mundwara carbonatite dykes, Sirohi District, Rajasthan, India. *N J Mineral Abh.* 160, 207–227.
- Le Bas, M.J., Yang, X.M., Taylor, R.N., Spiro, B., Milton, J.A., Zhang, P.S., 2007. New evidence from a calcite-dolomite carbonatite dyke for the magmatic origin of the massive Bayan Obo ore-bearing dolomite marble, Inner Mongolia, China. *Mineral. Petrol.* 90, 223–248.
- Lewis, A.J., Komninou, A., Yardley, B.W.D., Palmer, M.R., 1998. Rare earth element speciation in geothermal fluids from Yellowstone National Park, Wyoming, USA. *Geochim. Cosmochim. Acta* 62, 657–663.
- Li, X.C., Zhou, M.F., 2015. Multiple stages of hydrothermal REE remobilization recorded in fluorapatite in the Paleoproterozoic Yinachang Fe-Cu-(REE) deposit, Southwest China. *Geochim. Cosmochim. Acta* 166, 53–73.
- Ling, M.X., Liu, Y.L., Williams, I.S., Teng, F.Z., Yang, X.Y., Ding, X., Wei, G.J., Xie, L.H., Deng, W.F., Sun, W.D., 2013. Formation of the world's largest REE deposit through protracted fluxing of carbonatite by subduction-derived fluids. *Sci. Rep.* 3, 1776–1783.
- Liu, Y.F., Bagas, L., Nie, F.J., Jiang, S.H., Li, C., 2016. Re-Os system of black schist from the Mesoproterozoic Bayan Obo Group, Central Inner Mongolia, China and its geological implications. *Lithos* 261, 296–306.
- Liu, Y.L., Chen, J.F., Li, H.M., Qian, H., Xiao, G.W., Zhang, T.R., 2005. Single-grain U-Th-Pb-Sm-Nd dating of monazite from dolomite type ores of the Bayan Obo deposit. *Acta Petrol. Sin.* 21, 881–888 (in Chinese with English abstract).
- Liu, S., Fan, H.R., Yang, K.F., Hu, F.F., Rusk, B., Liu, X., Li, X.C., Yang, Z.F., Wang, Q.W., Wang, K.Y., 2018a. Fertilization in the giant Bayan Obo REE-Nb-Fe deposit: implication for REE mineralization. *Ore Geol. Rev.* 94, 290–309.
- Liu, X.D., Hua, R.M., 2003. Cathodoluminescence study of apatite in gold-bearing quartz vein from Bitan Au-Ag-Cu deposit. *Acta Mineral. Sin.* 23, 129–135 (in Chinese with English abstract).
- Liu, Y.L., Yang, G., Chen, J.F., Du, A.D., Xie, Z., 2004. Re-Os dating of pyrite from Giant Bayan Obo REE-Nb-Fe deposit. *Chin. Sci. Bull.* 49, 2627–2631.
- Liu, Y.L., Ling, M.X., Williams, I.S., Yang, X.Y., Wang, C.Y., Sun, W.D., 2018b. The formation of the giant Bayan Obo REE-Nb-Fe deposit, North China, Mesoproterozoic carbonatite and overprinted Paleozoic dolomitization. *Ore Geol. Rev.* 92, 73–83.
- Liu, J.Y., Zhang, T.R., Guo, A.F., Zhang, Y.X., 2006. A discussion on the practicability of prospecting in the deep part of the east mine and kernel part of the Bayan syncline, Bayan Obo ore field. *Geol. Rev.* 52, 821–825 (in Chinese with English Abstract).
- Liu, C.H., Zhao, G.C., Liu, F.L., Shi, J.R., 2017. Detrital zircon U-Pb and Hf isotopic and whole-rock geochemical study of the Bayan Obo Group, northern margin of the North China Craton: implications for Rodinia reconstruction. *Precamb. Res.* 303, 372–391.
- Marshall, D.J., 1988. Cathodoluminescence of geological materials. *Unwin* pp.146.
- Migdisov, A.A., Williams-Jones, A.E., 2008. A spectrophotometric study of Nd(III), Sm(III) and Er(III) complexation in sulfate-bearing solutions at elevated temperatures. *Geochim. Cosmochim. Acta* 72, 5291–5303.
- Migdisov, A.A., Williams-Jones, A.E., Brugger, J., Caporuscio, F.A., 2016. Hydrothermal transport, deposition, and fractionation of the REE: experimental data and thermodynamic calculations. *Chem. Geol.* 439, 13–42.
- Pan, Y., Fleet, M.E., 2002. Composition of the apatite-group minerals: substitution mechanisms and controlling factors. In: Kohn, M.J., Rakovan, J., Hughes, J.M. (Eds.), *Phosphates: Geochemical, Geobiological, and Materials Importance*, pp. 13–49.
- Putnis, A., Austrheim, H., 2010. Fluid-induced processes: metasomatism and metamorphism. *Geofluids* 10, 254–269.
- Ren, Y., Zhang, Y., Zhang, Z., 1994. Study on heat events of ore-forming Bayan Obo deposit. *Acta Geosci. Sin.* 15, 95–101 (in Chinese with English abstract).
- Roeder, P.L., Macarthur, D., Ma, X.P., Palmer, G.R., Mariano, A.N., 1987. Cathodoluminescence and microprobe study of rare-earth elements in apatite. *Am. Mineral.* 72, 801–811.
- Ronsbo, J.G., 1989. Coupled substitutions involving REEs and Na and Si in apatites in alkaline rocks from the Ilmaussaq intrusion, South Greenland, and the petrological implications. *Am. Mineral.* 74, 896–901.
- Smith, M.P., 2007. Metasomatic silicate chemistry at the Bayan Obo Fe-REE-Nb deposit, Inner Mongolia, China: contrasting chemistry and evolution of fenitising and mineralising fluids. *Lithos* 93, 126–148.
- Smith, M.P., Henderson, P., Campbell, L.S., 2000. Fractionation of the REE during hydrothermal processes: constraints from the Bayan Obo Fe-REE-Nb deposit, Inner Mongolia, China. *Geochim. Cosmochim. Acta* 64, 3141–3160.
- Smith, M.P., Campbell, L.S., Kynicky, J., 2015. A review of the genesis of the world class Bayan Obo Fe-REE-Nb deposits, Inner Mongolia, China: multistage processes and outstanding questions. *Ore Geol. Rev.* 64, 459–476.
- Smith, M.P., Henderson, P., 2000. Preliminary fluid inclusion constraints on fluid evolution in the Bayan Obo Fe-REE-Nb deposit, Inner Mongolia, China. *Econ. Geol.* 95, 1371–1388.
- Song, W.L., Xu, C., Smith, M.P., Chakhmouradian, A.R., Brenna, M., Kynicky, 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, 323–326.
- Sun, J., Fang, N., Li, S.Z., Chen, Y.L., Zhu, X.K., 2012. Magnesium isotopic constraints on the genesis of Bayan Obo ore deposit. *Acta Petrol. Sin.* 28, 2890–2902 (in Chinese with English abstract).
- Sun, S.S., McDonough, W.F., 1989. Chemical and isotopic systematic of oceanic basalts: implications for mantle composition and processes. In: Saunders, A.D., Norry, M.J. (Eds.), *Magmatism in the Ocean Basins*. *Geol. Soc. Special Pub.* pp. 313–345.
- Sun, J., Zhu, X.K., Chen, Y.L., Fang, N., 2013. Iron isotopic constraints on the genesis of Bayan Obo ore deposit, Inner Mongolia, China. *Precambrian Res.* 235, 88–106.
- Ting, W., 1994. A fluid and solid inclusion study of the Sukulu Carbonatite Complex, Uganda. Unpubl. Ph.D. thesis. Kingston University, p. 254.
- Torab, F.M., Lehmann, B., 2007. Magnetite-apatite deposits of the Bafq district, Central Iran: apatite geochemistry and monazite geochronology. *Mineral. Mag.* 71, 347–363.
- Tu, G.Z., 1998. The unique nature in ore composition, geological background and metallogenetic mechanism of non-conventional super-large ore deposits: a preliminary discussion. *Sci. China (Ser. D Earth Sci.)* 41, 1–6.
- Wang, J.W., Tatsumoto, M., Li, X.B., Premo, W.R., Chao, E.C.T., 1994. A precise ^{232}Th - ^{208}Pb chronology of fine-grained monazite: age of the Bayan Obo REE-Fe-Nb ore deposit. *China. Geochim. Cosmochim. Acta* 58, 3155–3169.
- Waychunas, G.A., 2002. Apatite luminescence: Reviews in Mineralogy and Geochemistry 48, 710–742.
- Wyllie, P.J., Jones, A.P., Deng, J., 1996. Rare earth elements in carbonate-rich melts from mantle to crust. In: *Rare Earth Minerals: Chemistry, Origin and Ore Deposits*. Mineralogical Society Series. No.7. Chapman & Hall, London 103, pp. 77.
- Xie, Y.L., Hou, Z.Q., Goldfarb, R.J., Guo, X., Wang, L., 2016. Rare earth element deposits in China. *Econ. Geol.* 18, 115–136.
- 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, 12–24.
- Xu, H.F., Cui, J.G., Qiu, X.P., 2006. In: *Applications of Cathodoluminescence in Petrology and Mineral Deposits*. *Geology Press, Beijing*, pp. 5–10.
- Xu, C., Taylor, R.N., Li, W.B., Kynicky, J., Chakhmouradian, A.R., Song, W.L., 2012. Comparison of fluorite geochemistry from REE deposits in the Panxi region and Bayan Obo, China. *J. Asian Earth Sci.* 57, 76–89.
- Yang, K.F., Fan, H.R., Santosh, M., Hu, F.F., Wang, K.Y., 2011. Mesoproterozoic carbonatitic magmatism in the Bayan Obo deposit, Inner Mongolia, North China: constraints for the mechanism of super accumulation of rare earth elements. *Ore Geol. Rev.* 40, 122–131.
- Yang, X.M., Le Bas, M.J., 2004. Chemical compositions of carbonate minerals from Bayan Obo, Inner Mongolia, China: implications for petrogenesis. *Lithos* 72, 97–116.
- Yang, X.Y., Sun, W.D., Zhang, Y.X., Zheng, Y.F., 2009. Geochemical constraints on the genesis of the Bayan Obo Fe-Nb-REE deposit in Inner Mongolia. *China. Geochim. Cosmochim. Acta* 73, 1417–1435.
- Yang, X.Y., Lai, X.D., Franco, P., Liu, Y.L., Ling, M.X., Sun, W.D., 2017. Genesis of the Bayan Obo Fe-REE-Nb formation in Inner Mongolia, North China Craton: a perspective review. *Precamb. Res.* 288, 39–71.
- Yang, X.M., Yang, X.Y., Zheng, Y.F., Le Bas, M.J., 2003. A rare earth element-rich carbonatite dyke at Bayan Obo, Inner Mongolia, North China. *Mineral. Petrol.* 78, 93–110.
- Yuan, Z., Bai, G., Wu, C., Zhang, Z., Ye, X., 1992. Geological features and genesis of the Bayan Obo REE ore deposit, Inner Mongolia. *China. Appl. Geochem.* 7, 429–442.

- Zhang, Z.Q., Tang, S.H., Wang, J.H., Yuan, Z.X., Bai, G., 1994. New data for ore-forming age of the Bayan Obo REE deposit, Inner Mongolia. *Acta Geosci. Sin.* 1–2, 85–94 (in Chinese with English abstract).
- Zhang, Z.Q., Tang, S.H., Yuan, Z.X., Bai, G., Wang, J.H., 2001. The Sm-Nd and Rb-Sr isotopic systems of the dolomites in the Bayan Obo ore deposit, Inner Mongolia, China. *Acta Petrol. Sin.* 17, 637–642 (in Chinese with English abstract).
- Zhang, Z.Q., Yuan, Z.X., Tang, S.H., Bai, G., Wang, J.H., 2003. In: *Age and Geochemistry of the Bayan Obo Ore Deposit*. Geological Publishing House, pp. 1–205 (in Chinese with English Abstract).
- Zhang, S.H., Zhao, Y., Yang, Z.Y., He, Z.F., Wu, H., 2009. The 1.35Ga diabase sills from the northern North China Craton: implications for breakup of the Columbia (Nuna) supercontinent. *Earth Planet. Sci. Lett.* 288, 588–600.
- Zhang, S.H., Zhao, Y., Liu, Y.S., 2017. A precise zircon Th-Pb age of carbonatite sills from the world's largest Bayan Obo deposit: implications for timing and genesis of REE-Nb mineralization. *Precamb. Res.* 291, 202–219.
- Zhao, G.C., Sun, M., Wilde, S.A., Li, S.Z., 2003. Assembly, accretion and breakup of the paleo-mesoproterozoic columbia supercontinent: records in the North China Craton. *Gondwana Res.* 6, 417–434.
- Zhao, G.C., Sun, M., Wilde, S.A., Li, S.Z., 2004. A Paleo-Mesoproterozoic supercontinent: assembly, growth and breakup. *Earth Sci. Rev.* 67, 91–123.
- Zhong, Y., Zhai, M.G., Peng, P., Santosh, M., Ma, X.D., 2015. Detrital zircon U-Pb dating and whole-rock geochemistry from the clastic rocks in the northern marginal basin of the North China Craton: constraints on depositional age and provenance of the Bayan Obo Group. *Precamb. Res.* 258, 133–145.
- Zhu, X.K., Sun, J., Pan, C.X., 2015. Sm-Nd isotopic constraints on rare-earth mineralization in the Bayan Obo ore deposit, Inner Mongolia, China. *Ore Geol. Rev.* 64, 543–553.
- Zirner, A.L.K., Marks, M.A.W., Wenzel, T., Jacob, D.E., Markl, G., 2015. Rare earth elements in apatite as a monitor of magmatic and metasomatic processes: the Ilímaussaq complex, South Greenland. *Lithos* 228–229, 12–22.