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

Xiaodong Lai a,b, Xiaoyong Yang a,⇑, Yulong Liu c, Zhiqiang Yan d

a CAS Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China, Hefei 230026, China
b School of Earth Sciences, East China University of Technology, Nanchang 330013, China
c Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
d No. 108 Geologic Party, Liaoning Bureau of Nonferrous Metal Geology, Shenyang 110013, China

A R T I C L E   I N F O

Article history:
Received 28 October 2015
Received in revised form 20 January 2016
Accepted 27 January 2016
Available online 28 January 2016

Keywords:
Fe–REE–Nb deposit
Pb–Pb age
Microanalysis
Dolomite
Bayan Obo
North China Craton

A B S T R A C T

The Bayan Obo Fe–REE–Nb deposit is a world-largest REE deposit in Inner Mongolia, North China Craton. It also contains large Fe and Nb reserves. The REE ore body is hosted in H8 dolomite of the Bayan Obo Group. Depositional time and genesis of H8 dolomite are still controversial in addressing the genesis of the REE deposit. In this study, Pb–Pb age and geochemical features of carbonate minerals in H8 dolomite have been studied, providing constraints to genesis of H8 dolomite and the REE deposit. Results of Pb–Pb dating from unmetamorphosed and non-mineralized domains of the H8 dolomite well constrain the depositional age as 1619 ± 150 Ma, which is earlier than both REE ore and carbonatite dykes in the Bayan Obo region. This indicates that REE mineralization has characteristics of epigenetic origin. Geochemical data of carbonate minerals in H8 dolomite have low REE contents, distinctly distinguished from those carbonatitic dykes. However, the fine-grained H8 dolomite whole rocks have high REE contents, similar to those carbonatic dykes. Mineral analysis suggests a close relationship between REE mineralization and calcite carbonatite dykes and related-derived fluids, which could transport a large amounts of REE. Integrated with these new geochronological and geochemical data, we draw conclusion that the Bayan Obo Group was a Proterozoic depositional succession, REE mineralization is as result of sedimentary carbonate rocks once being metasomatised by fluids derived from regional REE-rich calcite carbonatitic magma at depth.

1. Introduction

The Bayan Obo Fe–REE–Nb deposit in Inner Mongolia of China is a world-largest REE deposit, and it also contains a large Fe–Nb reserves (Drew et al., 1990; Bai et al., 1996; Chao et al., 1997; Kynicky et al., 2012). Many studies have been carried out with the deposit on aspects of mineralogy (Campbell and Henderson, 1997; Zhang et al., 1998), chronology (Campbell et al., 2014; Conrad and McKee, 1992; Hu et al., 2009; Lai et al., 2015; Liu et al., 2004, 2008; Nakai et al., 1989; Philpotts et al., 1991; Wang et al., 1994; Yang et al., 2011; Zhong et al., 2015; Zhu et al., 2015), and geochemistry (Chao et al., 1992; Institute of Geochemistry, 1988; Lai and Yang, 2013; Lai et al., 2012; Le Bas et al., 2007; Ling et al., 2013; Smith et al., 2000; Sun et al., 2013; Wang et al., 1973; Yang and Le Bas, 2004; Yang et al., 2009; Yuan et al., 1992). However, there are still remarkable disagreements about its genesis, especially the REE mineralization process. REE mineralization is largely concentrated in a dolomite (H8 unit of the Bayan Obo Group), thus it is critical to the interpretation of the mineralization. However, the genesis of the H8 dolomite has long been disputed, because of its sedimentary characteristics (Qiao et al., 1997; Zhang et al., 2005, 2012) and igneous geochemical features (Cao et al., 1994; Institute of Geochemistry, 1988; Le Bas et al., 1997; Meng and Drew, 1992; Ren et al., 1994; Smith, 2007; Xu et al., 2012; Yang et al., 2000; Zhang et al., 2003). Furthermore, many carbonate dykes intruded into the Bayan Obo Group (Fan et al., 2014; Tao et al., 1998; Wang et al., 2002a), and geochemical studies suggest an important role of carbonatitic magma for the REE mineralization (Fan et al., 2006; Qin et al., 2007; Yang et al., 2003). In addition, REE-mineralized dolomite and carbonatite have nearly the similar Sm–Nd isochron ages, thus it has been regarded as igneous origin (Fan et al., 2014; Le Bas et al., 1997, 2007; Sun et al., 2013; Yang et al., 2003, 2011;
Yang and Le Bas, 2004; Yuan et al., 1992). However, recent studies show that the REE mineralization was formed in several stages, rather than in a single stage related to carbonatitic magmatism (Campbell et al., 2014; Lai et al., 2015; Ling et al., 2013; Smith et al., 2015; Xu et al., 2008, 2012).

Determination of the depositional age of the H8 unit enables us to understand the REE mineralization process better. Nevertheless, the age of Bayan Obo Group remains difficult to constrain due to the overprinting events. Contrasting views include Mesoproterozoic (Conrad and McKee, 1992; Gao et al., 1995; Liu et al., 2001), or Cambrian–Ordovician (Sun, 1992; Zhang et al., 2008, 2012) ages.

The REE mineralized H8 dolomite has been divided into two categories based on their texture, coarse-grained dolomite and fine-grained dolomite, introduced additional complexities in the interpretation of ore genesis. Previous studies were mostly focused on the REE mineralized dolomite whole rock, only fewer had been carried out on the non-mineralized H8 dolomite. In this contribution, the age of H8 formation without any mineralization is directly determined, as well as in-situ composition analysis of carbonate minerals from REE mineralized H8 dolomite and carbonatite dykes, providing constraints on the genesis of the deposit.

2. Geological setting

The Bayan Obo district is located in the northern margin of the North China Craton (NCC, Fig. 1a), bordering the Paleozoic Central Asian Orogenic Belt to the north (Xiao and Santosh, 2014). The basement in this area is represented by the Archean–Paleoproterozoic complex composed of gneiss, granulite, quartz schist, syenite, granodiorite and amphibolite with ages of ca. 2.50 Ga and 1.9–2.0 Ga (Fan et al., 2010; Wang et al., 2002b). The Bayan Obo Group unconformably overlies the basement and consists of low grade sandstones, siltstones, slate, limestones and dolomites (Bai et al., 1996; Drew et al., 1990; Institute of Geochemistry, 1988; Zhong et al., 2015). Magmatic activity within the region is represented by 1.3–1.4 Ga mafic dykes and coeval carbonatite dykes (the latter spatially associated with the REE–Nb–Fe deposit) (Fan et al., 2014; Wang et al., 2010; Yang et al., 2011; Yuan et al., 1992; Zhang et al., 2003), and by late Paleozoic dioritic–granitic intrusions (Fan et al., 2009; Ling et al., 2014).

The REE mineralization, represented by monazite(Ce), bastnaesite(Ce) and huanghoite (Le Bas et al., 1992; Philpotts et al., 1991; Zhang et al., 1998), occurs only within the H8 dolomite south of the Kuangou fault (Fig. 1b), which is a prominent structure in Bayan Obo and a tectonically active region with several fault zones. The H8 dolomite north of the Kuangou fault zone is devoid of any mineralization. The REE–Nb–Fe ores south of the Kuangou fault are divided into banded, massive, dolomite, riebeckite, biotite and aegirine types (Fig. 1c). The paragenetic sequence of the REE mineralization is very complex, at least five stages have been recognized based on pressure, temperature and characteristic minerals (Smith et al., 2000).

The Bayan Obo Fe–REE–Nb deposit is hosted in sedimental rocks of the Bayan Obo Group. Locally, this group has been divided into two parts, a lower regressive series (H1–H10) and an upper transgressive series (H11–H18), which comprises six formations, i.e., Dulahala Formation (H1–H3); Jianshan Formation (H4–H5); Halahuoqite Formation (H6–H8); Bilute Formation (H9–H10); Baiyinbaolage Formation (H11–H12); and Hujiertu Formation (H13–H18) (Bai et al., 1996; Institute of Geochemistry, 1988).

Fig. 2 summarizes comprehensive stratigraphy of the Bayan Obo Group.

There are two facies of REE mineralized H8 dolomite in the Bayan Obo deposit, weakly mineralized coarse-grained dolomite

Fig. 1. (a) Tectonic setting and location of the Bayan Obo deposit in the North China Craton (modified from Jahn et al. (2000)); (b) geological sketch map of Bayan Obo ore deposit, Inner Mongolia, China (modified from Le Bas et al. (1992)); (c) distribution of different types of REE ores of the Main Orebody and Eastern Orebody (modified from Institute of Geochemistry (1988)).
and ore-bearing fine-grained dolomite (Lai et al., 2012; Yang and Le Bas, 2004). The coarse-grained dolomite is irregularly distributed along the northern limb of the Bayan Obo syncline (Fig. 1a), it is defined by a grain size greater than 1 mm, and composed predominantly of coarse-grained euhedral–subhedral dolomite (Fig. 3a). The fine-grained dolomite constituting the major REE ore-hosting rock is continuously distributed along the Bayan Obo syncline (Fig. 1a), and it is composed mainly of dolomite and ankerite (Fig. 3b), which is mostly fine-grained, ranging from 0.05 mm to 0.1 mm in diameter.

In addition to mineralized H8 dolomite, there are many carbonatite dykes distributed in the Bayan Obo deposit, usually with 0.5–4.0 m wide and 6–200 m long (Fan et al., 2014; Tao et al., 1998; Wang et al., 2002a). These carbonatite dykes

<table>
<thead>
<tr>
<th>Formation</th>
<th>Layer column</th>
<th>Member (Thickness)</th>
<th>Brief lithological description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huijirtu Formation</td>
<td>H18 (882m)</td>
<td>slate or inequigranular sandstone intercalating limestone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H17 (406m)</td>
<td>Upper: sandy limestone Lower: calcareous sandstone intercalating inequigranular quartz sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H16 (410m)</td>
<td>quartz stone or limestone intercalating silty</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H15 (280-335m)</td>
<td>quartzite intercalating epidosite or actinolite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H14 (45-256m)</td>
<td>Slate or limestone</td>
<td></td>
</tr>
<tr>
<td>Baiyinbaolage</td>
<td>H13 (473m)</td>
<td>Upper: quartz sandstone or sandy slate Lower: coarse-grained pebbly sandstone</td>
<td></td>
</tr>
<tr>
<td>Formation</td>
<td>H12 (1584m)</td>
<td>metasandstone interbedding silicic slate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H11 (109m)</td>
<td>fine-grained quartzite</td>
<td></td>
</tr>
<tr>
<td>Bilute Formation</td>
<td>H10 (2340-2387m)</td>
<td>Metasiltstone, silicic limestone or olistolite intercalating spotted slate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H9 (161-428m)</td>
<td>Slate intercalating sandstone and siltstone</td>
<td></td>
</tr>
<tr>
<td>Halahuoyite</td>
<td>H8 (272-593m)</td>
<td>limestone predominating, dolomite appearing on the</td>
<td></td>
</tr>
<tr>
<td>Formation</td>
<td>H7 (406-453m)</td>
<td>calcareous slate intercalating medium-coarse grained metasandstone and silty limestone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H6 (141-308m)</td>
<td>slate or silty limestone intercalating medium-coarse grained metasandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H5 (178-1155m)</td>
<td>quartz sandstone or limestone intercalating slate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H4 (168-193m)</td>
<td>silty slate intercalating inequigranular quartz sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H3 (233-291m)</td>
<td>slate interbedding carboniferous sandstone and limestone</td>
<td></td>
</tr>
<tr>
<td>Jianshan Formation</td>
<td>H2 (391-483m)</td>
<td>metasiltstone intercalating fine-grained quartzite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H1 (295m)</td>
<td>pebbly sandstone and pebbly quartzite</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. A comprehensive stratigraphy of the Bayan Obo Group (modified after Lai et al., 1996 and Zhong et al., 2015).
intrude metamorphic basement rocks and the Bayan Obo Group near the ore body. Carbonatite dykes based on mineralogical compositions, include: dolomite and calcite types (Fig. 3c and d). The geochemistry of the ore-bearing dolomite marbles is similar to those of carbonatite dykes (Le Bas et al., 1992; Yang et al., 2003, 2000).

Un-mineralized sedimentary carbonate rocks show weak deformation and low-grade metamorphism (Fig. 3e and f), and occur together with quartz sandstone, sandstone and shale to the north of the Kuangou fault. The rocks to the northern and southern parts of the Kuangou fault are equivalent in stratigraphy and lithology (Guo et al., 1982; Institute of Geochemistry, 1988). The thick-layered dolomite of the Sailinhudong Group, about 25 km southeast of the Bayan Obo town (not shown in Fig. 1), shows typical sedimentary strata, yielding Pb–Pb ages of 1.2–1.4 Ga (Gao et al., 1995), and has been proposed to be stratigraphically comparable with the Bayan Obo Group (Ma et al., 2014; Pan, 1997).

3. Sampling and analytical methods

3.1. Pb–Pb isotope analysis

As mentioned above, a correlation has been established between the rocks of the Bayan Obo Group in both sides of the Kuangou fault (Guo et al., 1982; Institute of Geochemistry, 1988). The sedimentary carbonate samples studied here were collected from the H8 unit to the north of the Kuangou fault (Figs. 1b and 4a). For comparison, dolomite samples from the non-mineralized Sailinhudong Group at Heinaobao were also
studied (Fig. 4b). Sedimentary carbonate rocks samples in thinly layered units were formed under homogeneous physico-chemical conditions, and the Pb isotope system in these rocks have been shown to remain relatively closed since deposition (Babinski et al., 1999; Fölling et al., 2000; Jahn and Cuvellier, 1994). All the samples for Pb–Pb analysis were taken from the same thin layer to ensure similar conditions of deposition.

Nineteen samples of sedimentary carbonate rocks in the Bayan Obo were collected along the same layer (dotted line in Fig. 3e). The sedimentary carbonate rocks are fine-grained and well bedded (Fig. 3e), containing minor argillite beds (Fig. 3f). Most of the carbonates consist of minute rhombs and their near-euhedral shapes suggest diagenetic origin. Samples from Heinaobao consist of relatively fine-grained carbonate and silty argillite mixed in variable proportions, which are also of diagenetic in origin.

Fresh sample chips without weathering or alteration were carefully picked out from crushed whole-rock samples and washed with distilled water at room temperature. The rock chips without any fractures or veins were selected under the binoculars. The chips were then powdered to less than 200 mesh size with an agate mill, and dried for chemical analyses. About 100–150 mg sample powder was completely digested in Savillex Teflon screw-cap beakers by HCl at 200°C. The solution was heated until incipient dryness and was then converted to a 6 M HCl + 0.7 M HBr solution. The solution was then centrifuged for separation and purification, and Pb was purified by conventional anion-exchange method (AG1-X8, 200–400 resin). After cleaning the AG1-X8 column using HCl and water, HBr was used to condition the column. Pb was extracted from HBr onto the resin and finally collected by 6 M HCl. A second purification of Pb was conducted before it was measured by mass spectrometry. The Pb isotopes were measured using thermal ionization mass spectrometry method (TIMS) at the Laboratory for Isotope Geology, Tianjin Institute of Geology and Mineral Resources. The whole procedure blank for Pb is 0.05–0.1 ng. Fractionation of Pb isotopes during mass spectrometer analysis was calibrated against standard NBS981, which yielded 206Pb/204Pb = 16.940 ± 0.010, 207Pb/204Pb = 15.498 ± 0.009, and 208Pb/204Pb = 36.716 ± 0.023, respectively, during the course of this study. The precision for Pb isotope data on the mass spectrometer is better than 0.1%. Data regression of isochron age calculation was performed with isoplot v3.0 software (Ludwing, 2003).

3.2. Microanalysis of H8 dolomite

Coarse-grained and fine-grained dolomite samples, and carbonatite samples were collected from Eastern ore body and the famous Wu-dyke, respectively (Fig. 1b). In situ trace element concentration of carbonate minerals of the H8 dolomite and carbonatite were determined at the Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China, Chinese Academy of Sciences, using an Arf excimer laser ablation system (GeoLas Pro, 193 nm wavelength) coupled to a quadrupole ICP-MS (PerkinElmer Elan DRCII). Helium was applied as a carrier gas, argon was used as the make-up gas and mixed with the carrier gas before entering the ICP. Carbonate mineral analyses were carried out on polished thin sections, with spot size of 60 µm, rep rate of 20 Hz and laser energy of 200 mJ. Each analysis incorporated a background acquisition of approximately 30s (gas blank) followed by 40s data acquisition form the sample. The internal standard concentration was assumed as the theoretical value. The precision and accuracy estimated in this study are better than 10% according to the NIST-612 glass standard analysis.

4. Results

4.1. Pb–Pb dating

Results of Pb isotope analyses are listed in Table 1. 206Pb/204Pb values of the Bayan Obo sedimentary H8 limestone samples range from 19.292 to 26.270. The eighteen samples (sample XK-04 with a large error is excluded) from Bayan Obo in this study yield a whole rock Pb–Pb isochron age of 1619 ± 150 Ma (Fig. 5a, MSWD = 4.5). The Pb–Pb age of non-mineralized limestone from Bayan Obo indicates that the H8 Formation of Bayan Obo Group was deposited in the Mesoproterozoic. The error of Pb–Pb isochron is relative high in Heinaobao dolomite samples because of the very small range in Pb isotopes (Fig. 5b), and its average age of 1417 Ma is slightly
Results of Pb–Pb dating of dolomite from Bayan Obo and Heinaobao.

younger than the H8 formation, this suggests that the Sailinhudong Group at Heinaobao maybe stratigraphically comparable with the upper member of the Bayan Obo Group (Qiao et al., 1997).

4.2. Trace and REE elements of carbonate minerals

Previous studies have shown that, dolomite grains in the fine-grained dolomite have similar major element contents to carbonate minerals from carbonatite, while dolomite grains in the coarse-grained dolomite retain sedimentary carbonate mineral features in the core (Lai et al., 2012). Further microanalysis of those dolomite grains in this study shows that, trace and REE characteristics of dolomite grains in the fine-grained dolomite are similar to those from coarse-grained dolomite, both being different from those of carbonatite (Table 2).

The dolomite grains from both coarse- and fine-grained dolomites have very low U, Th and Hf contents, most of which are below the detection limits. In contrast, calcites in the calcite carbonatite dyke have much higher Th contents, resulting in high Th/U ratios (with an average of 313), which is consistent with the high Th/U ratio of the deposit (Campbell et al., 2014). REE abundances of dolomite grains from both coarse- and fine-grained dolomites are relatively low, the total REE contents ranging from 44.24 ppm to 146.2 ppm and 73.02 ppm to 135.3 ppm, with an average of 89.74 and 97.01 ppm, respectively (Table 2), which are close to continental crust average of 117 ppm (Rudnick and Gao, 2002). However, REE abundances in carbonate minerals of dolomite and calcite carbonatite are much higher (Table 2).

Primitive Mantle normalized trace elements diagrams for dolomite grains from both fine- and coarse-grained dolomite show nearly the same patterns (Fig. 6a, b) with positive anomolies of Ba, Pb, Sr, and negative anomalies of Zr, Ti and Nb. Spider diagrams of carbonate minerals from carbonatite are much different, in addition to their much higher trace element contents, they show weak negative anomalies of Pb and Sr (Fig. 6c, d). Differences are much clearer in their REE distribution patterns (Fig. 7), with dolomite grains from both fine- and coarse-grained dolomite showing low REE abundances and enrichment in MREE with a positive Eu anomalies (Fig. 7a, b). By contrast, carbonate minerals from carbonatite have much higher REE abundances and are enriched in LREE (Fig. 7c, d). Moreover, dolomite grains from fine-grained dolomite have lower (La/Yb)_N and (La/Sm)_N ratios than those from coarse-grained dolomite (Table 2), indicating dolomite grains are relatively enriched in MREE in the fine-grained dolomite.

5. Discussion

5.1. Age of the H8 formation

The age of the H8 formation is also disputed. For example, both H17 and H18 Formations of Bayan Obo Group were suggested a Middle Ordovician age, and other parts (H1–H16) proposed a Mesoproterozoic age (Bureau of Geology and Mineral Exploration of Inner Mongolia, 1991). Based on stratigraphic studies, some even proposed that the whole Bayan Obo Group formed in Cambrian–Ordovician (Sun, 1992; Zhang et al., 1993). However, the available isotope ages for these rocks indicate that they are all Mesoproterozoic (Conrad and McKee, 1992; Lai et al., 2015; Liu et al., 2001; Yang et al., 2011).

Since the first successful direct dating of sedimentary carbonates (Moorbath et al., 1987), the U–Pb or Pb–Pb method is considered to be an effective and applicable way to determine the depositional age or metamorphic age of carbonate rocks (Fairey et al., 2013; Gopalan et al., 2013; Jahn, 1988; Lafaye et al., 1996; Russell et al., 1996). There are three published Pb–Pb geochronological studies on the H8 dolomite, Pb–Pb isochron age of 1543 ± 380 Ma (Liu et al., 2001), Pb model ages of 1350–1265 Ma from the H8 ore-hosting dolomite (Institute of Geochemistry, 1988) and Pb–Pb isochron age of 1694 ± 45 Ma from sedimentary carbonate rocks (Yang et al., 2012). However, none of these ages can effectively reflect the depositional time of the H8 dolomite. The first two ages apply to the H8 ore-hosting dolomite, but their U–Pb system might have been influenced by the mineralizing process; the last one was derived from three sedimentary carbonate rock samples from three different locations, north of the Kuangou fault, south of the Kuangou fault and Heinaobao, and as such of questionable reliability.

The H8 limestone samples from the Bayan Obo Group used for Pb–Pb dating in this study were all collected from the same thin layer, north of the Kuangou fault, and they show typical sedimentary structures without any mineralization or metamorphism. Since the north and south strata of the Kuangou fault are stratigraphically and lithologically equivalent (Guo et al., 1982; Institute of Geochemistry, 1988), thus our new Pb–Pb isochron age of 1619 ± 150 Ma (Fig. 5a) can well constrain the period of deposition or diagenesis within unmetamorphosed H8 dolomite away from carbonatitic activity. This age is consistent with the inferred Mesoproterozoic geological and depositional history of the Bayan Obo Group. It is bracketed by the maximum deposition age (1710 ± 29 Ma) for this group, based on the youngest detrital zircon ages 1170 ± 29 Ma from this group, based on the youngest detrital zircon ages 1170 ± 29 Ma from this group, based on the youngest detrital zircon ages 1170 ± 29 Ma from this group, based on the youngest detrital zircon ages 1170 ± 29 Ma from this group, based on the youngest detrital zircon ages 1170 ± 29 Ma from this group, based on the youngest detrital zircon ages 1170 ± 29 Ma from this group, based on the youngest detrital zircon ages 1170 ± 29 Ma from this group, based on the youngest detrital zircon ages 1170 ± 29 Ma from this group, based on the youngest detrital zircon ages 1170 ± 29 Ma from this group, based on the youngest detrital zircon ages 1170 ± 29 Ma from this group, based on the youngest detrital zircon ages 1170 ± 29 Ma from this group, based on the youngest detrital zircon ages 1170 ± 29 Ma from this group, based on the youngest detrital zircon ages 1170 ± 29 Ma. Furthermore, initiation of the Zhaertai–Bayan Obo rift system has been placed at ~1.75 Ga (Li et al., 2007) and the H9
slate which overlies the H8 dolomite has been dated at \( \sim 1500 \) Ma (Lai et al., 2015; Liu et al., 2015; Zhang et al., 2003). This supports a depositional age of 1.6–1.5 Ga for the H8 dolomites, consistent with the Pb–Pb isochron age reported here.

The age of dolomite of the Sailinhudong Group from Heinaobao in this study is 1417 ± 490 Ma with a large error, the median age is similar to the age of 1283 ± 59 Ma and 1456 ± 69 Ma reported by Gao et al. (1995), and the average age is younger than the H8 dolomite, indicating that the Sailinhudong Group at Heinaobao is stratigraphically comparable with the Bayan Obo Group. By this dating, we suggest that the dolomite of Sailinhudong Group may correspond to the upper member of the Bayan Obo Group, which has been firstly proposed from stratigraphical contrast between Heinaobao and Bayan Obo by Qiao et al. (1997).

5.2. Genesis of the REE mineralization

The genesis of the Bayan Obo REE deposit has been long disputed. There are two main point views: (1) carbonatitic magma origin, which is based on the whole rock features and mineral major element characteristics of the ore-hosting H8 dolomite, especially the fine-grained REE-rich dolomite with geochemical similarity to the carbonatite (e.g., the Wu Dyke) (Yuan et al., 1992; Le Bas et al., 2007; Yang et al., 2011); (2) hydrothermal metasomatism, i.e., mineralizing fluids were derived from carbonatite magma, the fluids had formerly been defined being similar to those of carbonatitic/alkaline igneous related REE–Fe rich magmatic hydrothermal systems (e.g., Chao et al., 1992; Institute of Geochemistry, 1988; Lai et al., 2015; Yang et al., 2009; Smith and Henderson, 2000).

Fig. 5. Pb–Pb isochron diagrams of sedimentary carbonate rocks. (a) Limestone from northern part of the Kuangou fault in the Bayan Obo; (b) dolomite from Heinaobao.
Trace element results of carbonate minerals from dolomite in the Bayan Obo (ppm).

<table>
<thead>
<tr>
<th>Trace Element</th>
<th>Dolomite grains from coarse-grained dolomite</th>
<th>Dolomite grains from fine-grained dolomite</th>
<th>Carbonate grains from dolomite carbonatite</th>
<th>Carbonate grains from calcite carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb</td>
<td>0.03 155.0</td>
<td>0.03 98.4</td>
<td>0.01 148.6</td>
<td>0.02 448.6</td>
</tr>
<tr>
<td>Ba</td>
<td>0.17 145.7</td>
<td>0.11 101.5</td>
<td>0.17 119.9</td>
<td>0.06 2680</td>
</tr>
<tr>
<td>Sr</td>
<td>0.10 120.3</td>
<td>0.16 91.93</td>
<td>0.17 101.5</td>
<td>0.17 119.9</td>
</tr>
<tr>
<td>Nd</td>
<td>0.03 98.4</td>
<td>0.03 98.4</td>
<td>0.03 98.4</td>
<td>0.03 98.4</td>
</tr>
<tr>
<td>Eu</td>
<td>0.13 148.6</td>
<td>0.06 2680</td>
<td>0.06 2680</td>
<td>0.06 2680</td>
</tr>
<tr>
<td>Gd</td>
<td>0.03 98.4</td>
<td>0.03 98.4</td>
<td>0.03 98.4</td>
<td>0.03 98.4</td>
</tr>
<tr>
<td>Ce</td>
<td>0.17 119.9</td>
<td>0.17 119.9</td>
<td>0.17 119.9</td>
<td>0.17 119.9</td>
</tr>
<tr>
<td>Sm</td>
<td>0.03 98.4</td>
<td>0.03 98.4</td>
<td>0.03 98.4</td>
<td>0.03 98.4</td>
</tr>
<tr>
<td>Yb</td>
<td>0.13 148.6</td>
<td>0.06 2680</td>
<td>0.06 2680</td>
<td>0.06 2680</td>
</tr>
<tr>
<td>Lu</td>
<td>0.03 98.4</td>
<td>0.03 98.4</td>
<td>0.03 98.4</td>
<td>0.03 98.4</td>
</tr>
</tbody>
</table>

Dolomite grains from coarse-grained dolomite:
- Rb: 0.03 -
- Ba: 0.17 -
- Sr: 0.10 -
- Nd: 0.03 -
- Eu: 0.13 -
- Gd: 0.03 -
- Ce: 0.17 -
- Sm: 0.03 -
- Yb: 0.13 -
- Lu: 0.03 -

Dolomite grains from fine-grained dolomite:
- Rb: 0.03 -
- Ba: 0.17 -
- Sr: 0.10 -
- Nd: 0.03 -
- Eu: 0.13 -
- Gd: 0.03 -
- Ce: 0.17 -
- Sm: 0.03 -
- Yb: 0.13 -
- Lu: 0.03 -

Carbonate grains from dolomite carbonatite:
- Rb: 0.03 -
- Ba: 0.17 -
- Sr: 0.10 -
- Nd: 0.03 -
- Eu: 0.13 -
- Gd: 0.03 -
- Ce: 0.17 -
- Sm: 0.03 -
- Yb: 0.13 -
- Lu: 0.03 -

Calcite grains from calcite carbonate:
- Rb: 0.03 -
- Ba: 0.17 -
- Sr: 0.10 -
- Nd: 0.03 -
- Eu: 0.13 -
- Gd: 0.03 -
- Ce: 0.17 -
- Sm: 0.03 -
- Yb: 0.13 -
- Lu: 0.03 -
5.2.1. Evidence from depositional age of H8

The timing of mineralization in Bayan Obo has been debated for a long time. The Sm/Nd isochron ages of both carbonatite dyke and H8 ore-bearing dolomite are quite similar, ranging from 1223 to 1656 Ma (Le Bas et al., 2007; Ren et al., 1994; Yang et al., 2011; Zhang et al., 1994). The Sm–Nd whole rock isochron ages have been classified into two groups, 1.66–1.50 Ga and 1.35–1.22 Ga, which have been interpreted as reflecting two related periods of carbonatite magmatism (Le Bas, 2006). However, no other evidence for multi-stage carbonatitic magmatism is recorded at Bayan Obo, and all carbonatites intruded during 1.3–1.4 Ga (Lai et al., 2015; Yang et al., 2011; Zhang et al., 2003). Recent studies show that the main mineralization occurred at 1.2–1.3 Ga based on H8 whole-rock Sm–Nd analyses (Lai et al., 2015; Zhu et al., 2015). In contrast, Sm–Nd dating of REE veins, Th–Pb dating of REE minerals and Re–Os dating of pyrites yielded ages of 400–500 Ma (Hu et al., 2009; Liu et al., 2004; Wang et al., 1994), supporting the notion that there may be two main mineralization periods, one in the middle Proterozoic, and the other in the early Palaeozoic (Cao et al., 1994).

The ages of both mineralization processes are younger than the depositional age of H8 dolomite (1619 ± 150 Ma), thus there is no doubt that the REE mineralization was epigenetic. The main mineralization event is slightly younger than the carbonatite magmatism, indicating the mineralized fluids maybe related to carbonatites. The second mineralization period during the Caledonian was generated by remobilization of carbonatitic ore-forming materials (Lai et al., 2015; Zhu et al., 2015).

Besides, studies of ore-forming fluids on fluid inclusions indicated that fluids involving in the REE–Nb mineralization at Bayan Obo might be mainly of H2O–CO2–NaCl–REE–F system (Fan et al., 2004, 2006; Smith et al., 2000). Coexistence of brine inclusion and CO2-rich inclusion with similar homogenization temperatures give evidence that immiscibility was happened during REE mineralization, and the presence of REE-carbonates as an abundant solid in fluid inclusions shows that the original ore-forming fluids are very rich in REE. An unmixing of an original H2O–CO2–NaCl fluid with higher REE contents probably derived from carbonatite magma, and had the potential to produce economic REE ores at Bayan Obo (Fan et al., 2006).

All these suggest an epigenetic genetic process closely related to emplacement of carbonatitic magma, supporting the idea that the H8 dolomite is a sedimentary carbonate hydrothermally metasomatised by carbonatite associated fluids (Huang et al., 2015; Lai et al., 2015; Yang et al., 2009).

5.2.2. Evidence from in-situ analysis of carbonate minerals

Previous whole-rock studies showed that fine- and coarse-grained dolomites have significant geochemical differences. The fine-grained H8 dolomite has geochemical signatures similar to carbonatite, while coarse-grained dolomite has geochemical features that are similar to sedimentary carbonate rocks (Lai et al., 2015; Zhu et al., 2015).
Unlike their whole-rock, dolomite grains from both fine- and coarse-grained dolomites have nearly the same mineral geochemical characteristics (Figs. 6a, b and 7a, b), neither is similar to the carbonate minerals in carbonatite (Figs. 6c, d and 7c, d). In summary, the H8 dolomite has petrological and geochemical characteristics that are certainly not directly from carbonatitic magma.

REE abundances in the fine-grained H8 dolomite bulk rocks are extremely high, close to those that typify a carbonatite, and much higher than the coarse-grained dolomite (Lai et al., 2012). However, their REE contents in carbonate minerals are much different from whole-rock, dolomite grains from fine-grained dolomite have similar REE abundances to those from coarse-grained dolomite, both are much lower than carbonate minerals in carbonatite (Table 2, Fig.7), indicating that REE existed mainly in the form of accessory minerals, and that the mineralization process did not influence the REE content in dolomite grains. Though the H8 dolomite whole-rock may have geochemical features similar to carbonatite, they can be distinguished by their REE content of carbonate minerals.

Carbonate minerals of dolomite and calcite carbonatite in the Bayan Obo have high Yb/Ca ratio and low Yb/La ratio, which are characteristics of magmatic carbonate minerals (Møller and Morteani, 1983; Veksler and Keppler, 2000), in contrast, dolomite grains of both coarse- and fine-grained dolomites have relatively lower Yb/Ca ratio and higher Yb/La ratio (Fig. 8a), indicating these dolomite grains are not magmatic in origin. Carbonatitic whole rock displays a characteristic geochemistry featuring high (La/Yb)$_N$ and low Ti/Eu (Rudnick et al., 1993), this is consistent with the results shown in Fig. 8b, the dolomite grains of dolomite carbonatite show high (La/Yb)$_N$ and low Ti/Eu, whereas most dolomite grains from coarse- and fine-grained dolomite have lower (La/Yb)$_N$ and relatively higher Ti/Eu, which is characteristic of sedimentary carbonate rocks.

Carbonatitic magmas are potential sources for mineral deposits such as rare-earth elements (REE), U, Th and P (Censi et al., 1989; Cullers and Medaris, 1977; Ingrid, 1998; Samoilov, 1991; Walter et al., 1995; Williams et al., 2000; Wolff, 1994). Even at magmatic-hydrothermal stages, enrichment in CO$_2$ and F rich fluids, can still cause formation of REE ores and associated barite and fluorite minerals (Bau and Dulski, 1995; Bau and Møller, 1992; Hecht et al., 1999; Lottermoser, 1992; Subias and Fernandez, 1995). These enrichments are similar to the Bayan Obo deposit where barite and fluorine-bearing minerals are well developed (Institute of Geochemistry, 1988), indicating that carbonatitic magma and its derived fluids are likely sources for the REE mineralization in the Bayan Obo. This is supported by fluid inclusion studies, which show that fluids involved in REE mineralization are mainly within the H$_2$O–CO$_2$–NaCl–(F–REE) system, derived from carbonatitic magma (Fan et al., 2006, 2004; Qin et al., 2007; Smith and Henderson, 2000).

Calcite from calcite carbonatite have low (La/Yb)$_N$ and high Ti/Eu ratios similar to coarse- and fine-grained dolomites, especially the one who has the lowest REE content (Fig. 8b). This is different
from their whole-rock features (Lai et al., 2012), indicating dolomite grains from both coarse- and fine-grained dolomites may have been metasomatised by calcite carbonatite related fluids. This is also supported by that the calcite with lowest REE content from calcite carbonatite dykes has similar spider diagram to coarse- and fine-grained dolomite grains from both coarse-grained dolomite retain sedimentary characteristics, indicating they were metasomatised by carbonatitic related fluids. In summary, fine-grained dolomites have similar whole-rock geochemical characteristics to carbonatite dykes, coarse-grained dolomites have many features (petrological and geochemical) that are similar to sedimentary carbonate rocks. The dolomite grains from coarse-grained dolomite retain sedimentary characteristics in the core and mineralization occurs later than H8 dolomite deposition, leading us to propose that the H8 dolomite was the product of sedimentary carbonate hydrothermally metasomatised by associated fluids derived from calcite carbonatitic magma (soevite) at the depth in Bayan Obo.

6. Conclusions

(1) The Pb–Pb ages well constrain the depositional period of the H8 formation with ca. 1.6–1.5 Ga, indicating the Bayan Obo Group was a Proterozoic depositional succession.

(2) The geochemical signatures of fine-grained dolomite in H8 formation are comparable to those of coarse-grained dolomite, both are different from dolomite of carbonatites. The geochemical features of carbonate minerals can be used to constrain the genesis of the Bayan Obo deposit.

(3) The origin of H8 dolomite in the Bayan Obo deposit is a sedimentary carbonate rock, once being metasomatised by REE-rich calcite carbonatitic fluids in Meso-proterozoic, which is responsible for the massive REE mineralization.

Acknowledgments

This study was supported by State Key Basic Research Development Program of China (2012CB416602), Natural Science Foundation of China (41273055) and Research Fund of East China University of Technology (Grant No. DHBK2013209).

References


