



The formation of the ore-bearing dolomite marble from the giant Bayan Obo REE-Nb-Fe deposit, Inner Mongolia: insights from micron-scale geochemical data

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Abstract

The genesis of Earth's largest rare earth element (REE) deposit, Bayan Obo (China), has been intensely debated, in particular whether the host dolomite marble is of sedimentary or igneous origin. The protracted (Mesoproterozoic to Paleozoic) and intricate (magmatic to metasomatic) geological processes complicate geochemical interpretations. In this study, we present a comprehensive petrographic and in situ, high-spatial resolution Sr-Pb isotopic and geochemical investigation of the host dolomite from the Bayan Obo marble. Based on petrographic evidence, the dolomite marble is divided into three facies including coarse-grained (CM), fine-grained (FM), and heterogeneous marble (HM). All carbonates are ferroan dolomite with high SrO and MnO contents (> 0.15 wt.%), consistent with an igneous origin. Trace element compositions of these dolomites are highly variable both among and within individual samples, with CM dolomite displaying the strongest LREE enrichment. In situ $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of the dolomite are generally consistent with mantle values. However, initial $^{208}\text{Pb}/^{204}\text{Pb}$ ratios define a large range from 35.45 to 39.75, which may result from the incorporation of radiogenic Pb released from decomposition of monazite and/or bastnäsite during Early Paleozoic metasomatism. Moreover, in situ Sr isotope compositions of dolomite indicate a large range ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70292\text{--}0.71363$). CM dolomite is characterized by a relatively consistent, unradiogenic Sr isotope composition ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70295\text{--}0.70314$), which is typical for Mesoproterozoic mantle. The variation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios together with radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ signatures for dolomite within FM and HM possibly represents recrystallization during Early Paleozoic metasomatism with the contribution of radiogenic Sr and Pb from surrounding host rocks. Therefore, our in situ geochemical data support a Mesoproterozoic igneous origin for the ore-bearing dolomite marble in the Bayan Obo deposit, which subsequently underwent intensive metasomatism during the Early Paleozoic.

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Introduction

Bayan Obo is the Earth's largest rare earth element (REE) deposit and the main source of niobium and thorium in China. The genesis of this deposit has been intensely debated since its discovery in 1927. One of the main points of contention is whether the dolomitic host rock is of sedimentary or igneous origin. Several researchers consider the mineralized dolomite rock to be of sedimentary origin based on field observations, geochronology, and geochemistry (Meng 1982; Tu et al. 1985; Wang et al. 1994), whereas others suggest it represents a carbonatite intrusion based on field evidences, mineralogy, and geochemistry (Le Bas et al. 1997; Yang and Le Bas 2004; Yang et al. 2011; Sun et al. 2013; Campbell et al. 2014; Fan et al. 2016; Song et al. 2018). Of note, fenitization is common at the contacts between the dolomitic orebody and carbonatite dykes and surrounding country rocks, represented by K-rich slates, which supports the argument that the dolomitic rock is of igneous origin (Le Bas et al. 1997; Yang and Le Bas 2004; Yang et al. 2011). In addition, based on petrographic evidence, Wang et al. (2010) argued that the fine-grained dolomitic marble is part of a volcano-sedimentary sequence. More recent studies have proposed that (1) the source of REE for the Bayan Obo deposit is a mantle-derived carbonatite intrusion or from REE-enriched metasomatic fluids released from an unexposed carbonatite reservoir (Ling et al. 2013; Smith et al. 2015; Fan et al. 2016; Yang et al. 2017; Song et al. 2018); (2) at least two major magmatic/metasomatic events occurred at Bayan Obo (ca. ~ 1300 and ca. ~ 440 Ma), suggesting that Bayan Obo underwent complicated deformation and hydrothermal events that resulted in the complex REE mineralization (Campbell et al. 2014; Smith et al. 2015; Zhu et al. 2015; Fan et al. 2016; Yang et al. 2017; Zhang et al. 2017a). The dolomitic host rock to the REE-Nb-Fe orebodies is known as “H8 dolomite” in the published geological map (Drew and Meng 1990). The most widely used term for “H8 dolomite” is dolomite marble (e.g., Le Bas et al. 1997, 2007), and Le Bas et al. (1997) defined the marble as any carbonate rock that has been recrystallized by metamorphism regardless of its sedimentary or igneous origin. This study adopts this definition and hence describes the dolomitic host rock as marble.

The field relationships, mineralogy and geochemistry of the Bayan Obo marble, which is the host of the REE-Nb-Fe deposit, have been extensively investigated. Geochemical (major and trace), isotopic (C, O, Sr, Nd, Mg, and Fe), and geochronological (U-Th-Pb and Sm-Nd) data have been reported for the Bayan Obo marble and generally suggest mixed source signatures from both mantle carbonatite and sedimentary limestone (Smith et al. 2015; Fan et al. 2016; Yang et al.

2017). The carbonatite dykes and surrounding sedimentary limestones have also been investigated to help elucidate the origin of the Bayan Obo REE deposit (Le Bas et al. 1997, 2007; Yang et al. 2011). However, it is unlikely that these Mesoproterozoic carbonatite dykes and limestones still preserve their original geochemical signatures, which complicates deciphering the petrogenetic history of the Bayan Obo H8 dolomite marble. The complex deformation and hydrothermal events, especially the dominant Early Paleozoic metasomatism imparted on the marble, make it difficult to decipher the primary signature of the dolomite marble based on whole rock geochemistry (e.g., Smith et al. 2015).

It is also important to note that most of the bulk rock trace element geochemical signatures reported for the Bayan Obo marble are dominantly controlled by the presence of disseminated REE minerals. Thus, the bulk rock trace element data cannot be used to discriminate between the competing hypotheses cited above for the origin of the host dolomite marble at Bayan Obo. Hence, a geochemical investigation at the mineral or micron-scale is needed in order to help decipher the origin and evolution of this giant REE deposit (Smith et al. 2015). Analytical technologies, such as laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS), make it possible to investigate geochemical signatures within petrographic context. For example, Campbell et al. (2014) conducted a detailed chemical study on zircon from Bayan Obo, and their results suggest an igneous origin for core domains, whereas rims formed as a result of hydrothermal processes associated with the REE-Nb mineralization. Smith et al. (2015) concluded that grain and sub-grain geochemical heterogeneity for the ore-hosting dolomite at Bayan Obo indicates that a polyphase genetic process must be considered and that a detailed micro-analytical study might provide a final resolution to this issue. Thus, this study presents a comprehensive micro-analytical investigation of the H8 dolomite from Bayan Obo, including petrographic, geochemical (major and trace), and isotopic (Sr and Pb) data, in an effort to provide additional insights into the origin of the host dolomite marble at Bayan Obo. The investigated dolomite samples were taken from a 1700-m-deep drill core so as to avoid the effects of weathering and/or post-solidification alteration affecting near surface samples.

Geological background

The Bayan Obo REE-Nb-Fe deposit is located on the northern margin of the North China Craton (NCC), bordered by the Central Asian Orogenic Belt to the north (Fig. 1). The basement rocks within the area consist of Neoproterozoic mylonitic

granite gneiss, Paleoproterozoic syenite, granodiorite, and granite gneiss (Fan et al. 2016). The Bayan Obo deposit is hosted by the low-grade metamorphosed clastic rock sequence of the Mesoproterozoic Bayan Obo Group (Fig. 1), which were deposited within the Bayan Obo marginal rift during the Mesoproterozoic continental breakup of the North China Craton (Zhang et al. 2017b). The North China Craton underwent a period of rifting during the breakup of the supercontinent Columbia starting at ~ 1.8 Ga and culminating at ~ 1.2 Ga (Zhao et al. 2003). This resulted in the intrusion of mafic dyke swarms over wide areas of Columbia. The Mesoproterozoic rifting is characterized by occurrences of basaltic to basaltic-trachyandesite and carbonatite dykes within the Bayan Obo area (Yang et al. 2009). The dominant sedimentary rocks of the Bayan Obo Group include sandstone, slate, and limestone (Fig. 1). The Bayan Obo Group has been subdivided into two sequences, a lower regressive series (H1–H10) and an upper transgressive series (H11–H18) in ascending chronological order (Drew and Meng 1990; Yang et al. 2009). Late Paleozoic dioritic-granitic plutons composed of gabbro, gabbroic diorite, granitic diorite, adamellite, and biotite granite are widely distributed in the south and east of Bayan Obo deposit. These magmatic rocks were formed in a post-collisional tectonic regime during closure of the Paleo-Asian Ocean (Fig. 1; Fan et al. 2016).

The ore host rock is traditionally assigned to the dolomite marble unit H8, which is overlain by H9 K-rich slate. The Bayan Obo deposit is located at the center of the Kuangou syncline, which consists of several chevron folds, shear zones, and thrust faults (Yang et al. 2017). The deposit is exploited in

three open pits, the Main, Eastern, and Western, which host predominantly Fe reserve accompanied by REE and Nb reserves. The Western Open Pit consists of several smaller orebodies. The principal iron minerals are magnetite and hematite, whereas the main REE-bearing minerals are bastnäsite and monazite. Within the ore, the REE abundances generally decrease from east to west and vary from millimeter to kilometer scale (Smith et al. 2015). The lenticular-shaped Main and Eastern orebodies exhibit a series of shear zones that may have acted as channels for the ore-forming or alteration fluids (Smith et al. 2015; Yang et al. 2017).

Carbonatite dykes

Since the discovery of carbonatite dykes at Bayan Obo in the early 1990s, nearly 100 dykes have been identified in the vicinity of the deposit (Yang et al. 2011). They intrude into the basement rocks and/or the Bayan Obo Group and generally strike northeast or northwest (Yang et al. 2011). Fenitization is common at the contact between carbonatite dykes and their country rocks, which is characterized by the presence of sodic amphibole, albite, and phlogopite (Yang and Le Bas 2004). Most of the dykes are deformed, sheared, and locally recrystallized though some of their geochemical signatures are preserved (Yang and Le Bas 2004; Le Bas et al. 2007). The carbonatite dykes have been dated using a variety of techniques and the reported ages define two peaks at approximately 1.3 and 0.4 Ga (Zhu et al. 2015; Smith et al. 2015). Similar to the ore-hosting H8 marble, the carbonatite dykes show large variations in both mineralogy and

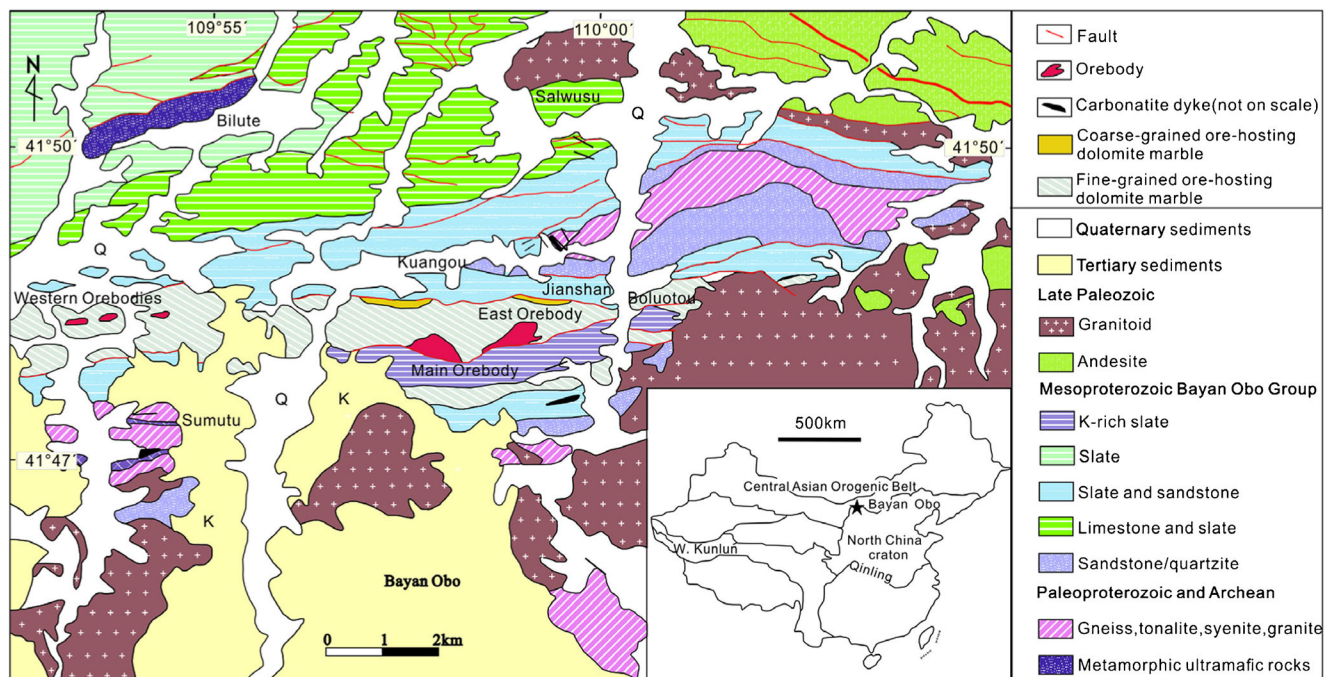


Fig. 1 Geological map of the Bayan Obo district, Inner Mongolia, northern China. Modified after Yang et al. (2011) and Fan et al. (2016)

geochemistry (Yang et al. 2011; Smith et al. 2015; Yang et al. 2017) and are divided into calcite, calcite-dolomite, and dolomite carbonatites (Yang et al. 2011). In general, the carbonatite dykes consist predominantly of dolomite and/or calcite, with accessory apatite, monazite, barite, bastnäsite, magnetite, fluorite, and quartz (Yang and Le Bas 2004; Le Bas et al. 2007; Yang et al. 2011). Previous studies proposed that there is a petrogenetic link between the Bayan Obo carbonatite dykes and the ore-hosting dolomite marble (Le Bas et al. 2007; Yang et al. 2011; Sun et al. 2013; Zhu et al. 2015).

Sedimentary carbonate rocks

The sedimentary limestone and dolostone north of the Kuangou fault exhibit weak deformation (Yang et al. 2009) and are characterized by medium to thick bedding and massive structure. The limestone and dolostone typically contain fine-grained detrital quartz with some late-stage, cross-cutting quartz veins and veinlets. The Bayan Obo sedimentary carbonate rocks are characterized by relatively high SiO₂ and Al₂O₃ abundances coupled with relatively low MnO and P₂O₅ contents (Sun et al. 2013). The Mesoproterozoic sedimentary carbonate rocks from the Bayan Obo area are characterized by higher $\delta^{56}\text{Fe}$ values compared to the homogeneous Fe isotope composition of the Bayan Obo Fe ore, which is incompatible with a sedimentary origin for the latter (Sun et al. 2013). The Sailinhuodong dolomitized micrite that is ~25 km southeast of the Bayan Obo deposit, characterized by a Pb-Pb age of approximately 1.2–1.4 Ga, was proposed to be stratigraphically correlated with the ore-hosting H8 dolomite marble (Yang et al. 2009). Differences in trace element patterns and C and O isotope data with those for H8 dolomite marble suggest that the micrite formed by dolomitization during diagenesis or later metamorphism (Yang et al. 2009). Limestone samples taken from the north of the Kuangou fault yield a Pb-Pb isochron age at 1619 ± 150 Ma (Yang et al. 2017).

H8 ore-hosting dolomite marble

The H8 dolomite marble extends across the Gobi Desert over an east-west length of 18 km and a width of 2–3 km, together with the quartzite, quartz sandstone, and slate of the Mesoproterozoic Bayan Obo Group (Yang and Le Bas 2004; Yang et al. 2017). Coarse-grained dolomite marble occurs in a small volume mainly within the Western pit and the northern part of the Main Orebody, whereas the fine-grained dolomite marble is widely distributed and constitutes the main host of the Bayan Obo deposit (Zhu et al. 2015). The coarse-grained dolomite marble contains high P₂O₅ abundances that is attributed to abundant, coarse-grained apatite (visible at the hand specimen scale), whereas fine-grained apatite (not visible) characterizes the fine-grained marble (Le Bas et al. 1997).

Le Bas et al. (1997) showed that the chemical compositions of both the coarse-grained and fine-grained dolomite marbles are different compared to carbonates from the Bayan Obo limestones. Yang et al. (2017) summarized the bulk trace element compositions for both coarse and fine-grained dolomite marbles and found that the fine-grained marble displayed similar REE contents, chondrite normalized REE patterns, and primitive mantle-normalized trace element patterns consistent with those of carbonatite. The geochronology of the marble has been well studied using a wide range of dating techniques including Sm-Nd and Rb-Sr isochrons, Th-Pb analyses of monazite, bastnäsite and zircon, Ar-Ar analyses of amphibole, and Re-Os analyses of pyrite and molybdenite (Smith et al. 2015; Zhu et al. 2015; Yang et al. 2017). In general, the reported ages are highly variable for the Bayan Obo host rocks and range from 1.4 to 0.3 Ga with two dominant peaks at 1.3 and 0.4 Ga, which coincide with the ages reported for the carbonatite dykes. A detailed Sm-Nd isotopic investigation of both the coarse- and fine-grained dolomite suggests that the 1.3 Ga age represents the timing of carbonatite formation and the earliest stage of REE mineralization, whereas a significant thermal event at 0.4 Ga was associated with late-stage REE mineralization (Zhu et al. 2015).

Analytical methods

Whole rock trace element analysis for all samples of dolomite marble was carried out in the State Key Laboratory for Mineral Deposits Research (MDR) at Nanjing University. The detailed analytical procedure for bulk rock trace element analysis can be found in Gao et al. (2003). About 50 mg of powdered sample was dissolved using concentrated HF+HNO₃ mixture in high-pressure Teflon capsules sealed in steel vessels. The trace element concentrations were measured using a Finnigan Element II ICP-MS. Rh was used as an internal standard to monitor the instrument drift. The analytical precision is estimated to be better than 10% (at 2 σ level) for all trace elements based on the BCR standards and duplicate analyses.

Major element composition of dolomite grains was determined with a JEOL JXA-8100 Electron Probe Micro Analyzer equipped with four wavelength-dispersive spectrometers in the State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences (Wuhan). An accelerating voltage of 15 kV, a beam current of 20 nA, and a 10- μm spot size were used to analyze dolomite. Data were corrected on-line using a ZAF (atomic number, absorption, fluorescence) procedure. The content of carbon was calculated based on the mole ratio of C/O = 1:3. The peak counting time was 10 s for Na, Mg, K, Ca, Fe, and Sr and 20 s for Mn. The background counting time was one-half of the peak counting time on the high- and low-

energy background positions. The standards used for calibration processes include sanidine (K), pyrope garnet (Fe), diopside (Ca, Mg), jadeite (Na), rhodonite (Mn), and celestite (Sr).

In situ trace element composition for dolomite was measured in 100- μm -thick thin sections using a RESOLUTION 193-nm laser ablation system coupled to a Thermo iCapQ ICP-MS at GPMR. Samples and standards were ablated with a repetition rate of 10 Hz, 33 μm laser spot size, and energy density of 3–5 J/cm^2 . Every ten sample analyses were bracketed by a set of NIST612, BCR-2G, BHVO-2G, and BIR-1G standards. The detailed analytical methods are similar to that described in Chen et al. (2011). All off-line integration of background and analytical signals and time-drift correction and quantitative calibration for trace element analyses are conducted using ICP-MS DataCal (Liu et al. 2008). The analytical uncertainty for most trace element concentration determinations is within 10% and better than 5% for the REEs (Chen et al. 2011).

In situ Sr isotope analysis for dolomite was conducted using the RESOLUTION laser ablation system coupled to Nu Plasma II multi-collector (MC) ICP-MS at GPMR. Analyses were carried out using a spot size of 50 μm with a repetition rate of 10 Hz and an energy density of $\sim 3\text{--}5 \text{ J}/\text{cm}^2$. The measurements involved correction of spectral interferences for Kr, Rb, and doubly charged REE as described in Chen and Simonetti (2014). An in-lab coral standard was analyzed as the external standard. The average $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition obtained for the coral standard is 0.70923 ± 0.00004 (2σ , $n = 23$), which is consistent with the recommended value 0.70923 ± 0.00002 as determined by ID-TIMS at MDR (Pu et al. 2005).

In situ Pb isotope analysis for dolomite was conducted using the Geolas 2005 excimer ArF laser ablation system coupled to a Neptune Plus MC-ICP-MS instrument at GPMR. Detailed analytical protocol can be found in Zhang et al. (2015). ^{208}Pb , ^{207}Pb , and ^{206}Pb were measured using Faraday cups, whereas ^{204}Pb , ^{202}Hg , and ^{200}Hg were measured using ion counters. The isobaric interference of ^{204}Hg on ^{204}Pb was subtracted by monitoring the ^{202}Hg ion signal using the natural $^{204}\text{Hg}/^{202}\text{Hg}$ ratio of 0.2301 (Souders and Sylvester 2008). A typical spot diameter of 55 to 90 μm was used in the analysis with a constant repetition rate of 8 Hz and laser fluence of $\sim 5 \text{ J}/\text{cm}^2$. Typical accuracies of $^{20x}\text{Pb}/^{206}\text{Pb}$ and $^{20x}\text{Pb}/^{204}\text{Pb}$ were found to be within 0.05% and 0.09% of the reported values, respectively (Zhang et al. 2015).

In situ Th-Pb dating and trace element characterization of monazite were obtained using the RESOLUTION laser ablation coupled to the iCapQ ICP-MS at GPMR. The detailed analytical procedure can be found in Ying et al. (2017). Monazite 44069 was used as the external standard to monitor both instrumental drift and laser-induced elemental fractionation (LIEF). Both standards and samples were ablated with a beam size of 33 μm , 10 Hz pulse rate, and a corresponding energy density of $\sim 5\text{--}8 \text{ J}/\text{cm}^2$. Each analysis incorporated a

background acquisition of approximately 20–30 s followed by a 60-s sample acquisition. The intensities of ^{202}Hg , ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th , and ^{238}U were acquired, whereas ^{235}U was calculated from ^{238}U on the basis of the ratio $^{238}\text{U}/^{235}\text{U} = 137.88$. The weighted mean Th-Pb ages were calculated using the ISOPLOT/EX 3.23 (Ludwig 2003). Stoichiometric Ce was adopted as an internal standard to normalize the elemental concentrations for monazite (Ying et al. 2017).

Results

Petrography of Bayan Obo H8 marble

Bayan Obo H8 marble displays a variety of textures, which include both fine- and coarse-grained dolomite as identified by previous studies (Le Bas et al. 1997, 2007; Yang et al. 2011; Lai et al. 2012). Based on the petrographic textures observed from the deep drill core samples, the ore-hosting marble is further divided into three facies in this study, and these are (1) coarse-grained marble (CM), (2) fine-grained marble (FM), and (3) heterogeneous grain-size marble (HM).

Coarse-grained marble consists predominantly of dolomite (85 vol.%) with grain size $> 200 \mu\text{m}$. Mosaic-textured twinned dolomite has triple junctions in CM (Fig. 2a). The most common accessory mineral is monazite, occurring as euhedral to subhedral granular crystals with a majority disseminated along dolomite grain boundaries or fracture-forming veins, whereas some are included within dolomite crystals (Fig. 2b). Apatite is the most abundant accessory mineral in one of the CM samples and contains monazite inclusions (Fig. 2c). Magnetite is also common in the coarse-grained marble. Late-stage hydrothermal minerals include pyrite, siderite, fluorite, bastnäsite, and quartz, but these are scarce in CM samples and usually occur as fillings along fractures.

Fine-grained marble consists predominantly of dolomite (grain size $< 200 \mu\text{m}$), bastnäsite, and fluorite (Fig. 2d). Bastnäsite is the main REE-bearing mineral within FM, either disseminated along dolomite grain boundaries or forming veinlets or aggregates with fluorite (Fig. 2e). Monazite is rarely identified in FM, and only a few anhedral crystals are found intergrowth with fluorite; other accessory minerals include barite, magnetite, and phlogopite (Fig. 2f).

Heterogeneous grain-size marble consists of both coarse- and fine-grained dolomite in the same rock sample (Fig. 2g). The coarse dolomite is typically embedded within a matrix of fine-grained dolomite (Fig. 2g). This texture is similar to those previously identified by Wang et al. (2010) and Lai et al. (2012). Fluorite and bastnäsite are commonly found between coarse- and fine-grained dolomite. Bastnäsite is the dominant

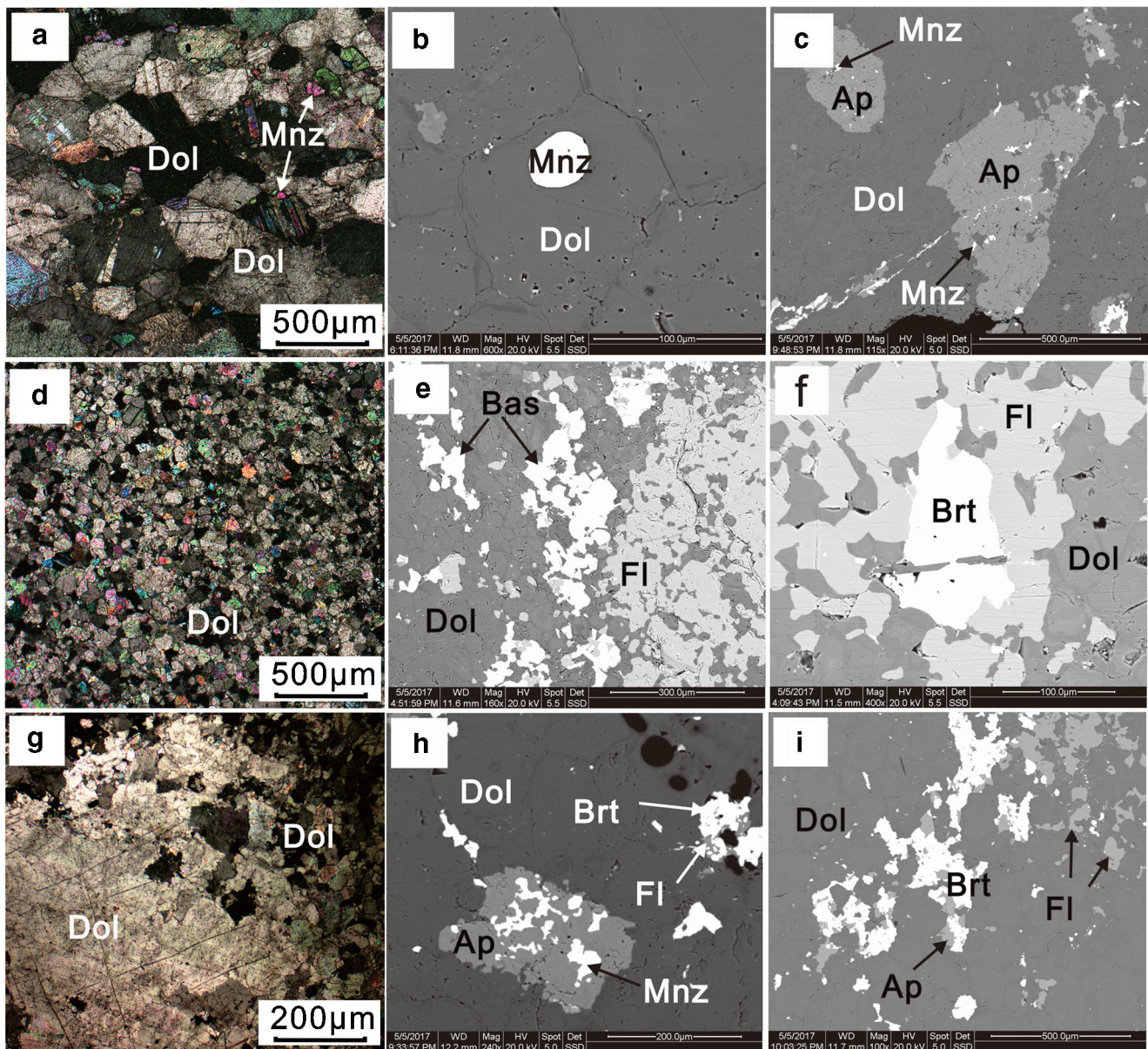


Fig. 2 Photomicrographs of coarse-grained marble (CM; **a, b, c**), fine-grained marble (FM; **d, e, f**), and heterogeneous grained marble (HM; **g, h, i**) from Bayan Obo. **a** Cross-polarized microscope image shows the dominant dolomite (dol) and monazite (mnz). **b, c** Back-scattered electron (BSE) image displays monazite included in **b** dolomite and **c** apatite (ap). **d** Cross-polarized microscope image shows the fine-grained marble. **e, f** BSE images illustrate the common-mineral association of **e** fluorite

and **f** bastnäsite (bas) with minor barite (brt). **g** Plain-polarized microscope image displays a coarse grain (> 500 μm) of dolomite surrounded by fine grain dolomite (< 200 μm) in HM. **h, i** Complex mineral associations are outlined in the BSE images of HM (e.g., apatite and monazite, barite and fluorite, apatite and barite). Abbreviations: Ap, apatite; Bas, bastnäsite; Brt, barite; Dol, dolomite; Fl, fluorite; Mnz, monazite

REE mineral within HM, and other accessory minerals include fluorite, apatite, monazite, quartz, and barite (Fig. 2h, i).

Chemical composition of H8 marble and constituent dolomite

The whole rock trace element compositions for the three types of marbles are presented in Fig. 3 and Electronic Supplementary Material (ESM) Table 1. Previous

geochemical data for carbonatite dyke and limestone from the Bayan Obo area are compared in the primitive mantle-normalized trace element spider diagram and the chondrite-normalized REE plot (Fig. 3). The trace element compositions for the Bayan Obo marbles display similar primitive mantle-normalized patterns and light REE (LREE)-enriched chondrite normalized trends (Fig. 3). Trace element plots show negative anomalies of Zr, Hf, Ta, and U and positive anomalies of Ba, Th, and Nb,

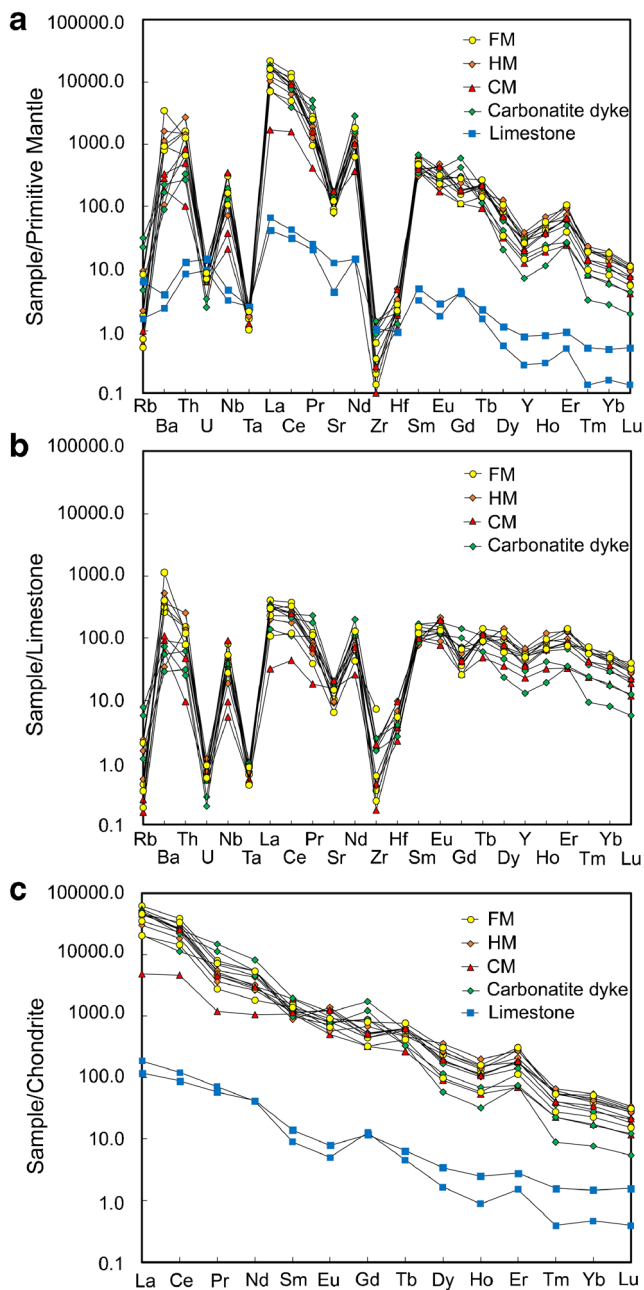


Fig. 3 **a** Primitive mantle and **b** limestone-normalized trace element spider diagrams and chondrite-normalized REE diagram (**c**) for Bayan Obo marble. The trace element data for carbonatite dyke and limestone in the Bayan Obo district are from Lai et al. (2012) and Zhang et al. (2009), respectively. Primitive mantle and chondrite values are from Sun and McDonough (1989)

which are identical to those for dolomite carbonatite dyke in the vicinity of the Bayan Obo deposit (Fig. 3a; Lai et al. 2012). Dolomite marble, along with dolomite carbonatite dyke, displays strong depletions of Rb, U, Ta, Zr, and Hf in the limestone-normalized pattern (Fig. 3b). The total REE concentrations in H8 marble are highly variable (4917 to 42,717 ppm) but enriched

compared to that for the limestone (Fig. 3c). The ratio of LREE to heavy REE (HREE) fractionation $[(La/Lu)_{CN}]$ of the H8 marble is much larger (> 1000) compared to the limestone (Fig. 3c and ESM Table 1).

The major element composition of the host dolomite is shown in ESM Table 2 and Fig. 4a. All dolomites are ferroan (FeO = 4.38–11.88 wt.%) with relatively constant CaO contents (26.90–28.93 wt.%). Abundances of MgO and FeO display a negative linear relationship that suggests co-substitution in the dolomite crystal structure. The dolomite from the H8 marble contains abundant SrO and MnO contents > 0.15 wt.% (Fig. 4a).

In contrast to the whole rock trace element composition, the in situ trace element compositions for dolomite are quite distinct in the different types of marbles. Dolomite in CM contains higher REE contents (573 ppm on average) and $(La/Lu)_{CN}$ ratios (29 on average) compared to FM dolomite (159 ppm and 11 on average; Fig. 4b and ESM Table 3). Interestingly, REE contents and $(La/Lu)_{CN}$ ratios display positive linear relationships as a function of the grain size for dolomite from CM and FM (Fig. 4c). Coarse-grained dolomite in HM displays two distinct REE patterns (Fig. 4d). One is similar or slightly depleted compared to that for the fine-grained dolomite within HM. In contrast, coarse-grained dolomite from HM Sample BO1551.6 displays LREE-depleted patterns with MREE enrichment compared to other HM dolomite. The MREE-HREE fractionation for sample BO1551.6 coarse dolomite is similar to that for the coarse-grained marble (Fig. 4b, d). Detailed geochemical transects were conducted on the coarse-grained dolomite within both CM and HM, but no systematic core-to-rim trends were found (Fig. 5).

In situ Sr isotopic composition of H8 dolomite

In situ $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic compositions for H8 dolomite are presented in Fig. 6, ESM Fig. 1, and ESM Table 3. The $^{87}\text{Sr}/^{86}\text{Sr}$ values for the dolomite marble range between 0.70292 and 0.71363 (Fig. 6 and ESM Fig. 1), which is similar to the reported range for the H8 marble (Le Bas et al. 1997; Zhang et al. 2003). CM dolomite displays homogeneous $^{87}\text{Sr}/^{86}\text{Sr}$ values with a relatively narrow range from 0.70295 to 0.70314 (ESM Fig. 1 and ESM Table 3). This limited variation is consistent with the reported bulk rock Sr isotope ratios (0.70295–0.70316) for coarse-grained dolomite marble (Le Bas et al. 1997) and the least altered bulk carbonatite (Le Bas et al. 2007). The Sr isotope compositions for dolomite from FM show slightly variable $^{87}\text{Sr}/^{86}\text{Sr}$ values that range from 0.70297 to 0.70465 (ESM Fig. 1 and ESM Table 3), which overlaps the reported range (0.70299 to 0.70358) for the bulk fine-grained dolomite marble (Le Bas et al. 1997). HM dolomite displays the largest Sr isotopic variation

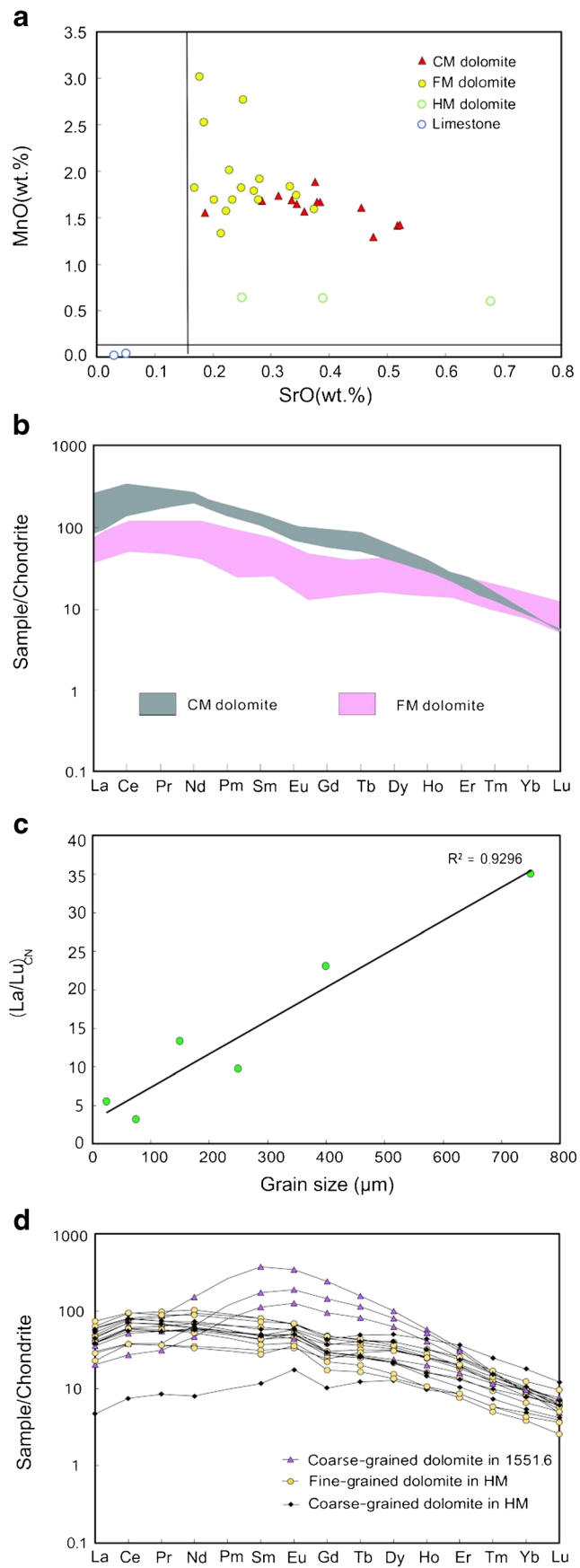


Fig. 4 Chemical composition of dolomite from Bayan Obo marbles. **a** SrO and MnO contents of dolomite. **b** Chondrite-normalized REE distributions for dolomite within CM and FM. **c** Diagram of REE fractionation $((La/Lu)_{CN})$ and grain size for dolomite within CM and FM. **d** Chondrite-normalized REE patterns for dolomite within HM. Chondrite values are taken from Sun and McDonough (1989)

(0.70302 to 0.71363), which is recorded within a single coarse dolomite grain (Fig. 5). Generally, the Sr isotopic composition for dolomite within HM is characterized by a mean $^{87}Sr/^{86}Sr$ value of 0.70402 with most analyses (67%) < 0.704.

In situ Pb isotopic composition of H8 dolomite

In situ Pb isotopic compositions of H8 dolomite are listed in ESM Table 4 and shown in Fig. 7. The $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios for all dolomite display a limited range with values between 15.82–16.38 and 15.10–15.42, respectively (Fig. 7a). Overall, the ^{207}Pb - ^{206}Pb isotopic compositions plot between the 1.2- and 1.3-Ga secondary isochrons, which is similar to the ages reported for the H8 marble and carbonatite dykes (Fig. 7a; Zhu et al. 2015; Zhang et al. 2017b). In general, the ^{207}Pb - ^{206}Pb isotopic compositions for dolomite in the H8 marble are similar to values for mantle-derived samples, distinct from those typically generated from the upper or lower crust sources (Li et al. 2001). However, the $^{208}Pb/^{204}Pb$ ratios display a large variation (35.45 to 39.75) with the CM dolomite characterized by a small variation (35.50 to 36.58), whereas dolomite from FM and HM is highly variable with values that range from 35.45–38.98 to 35.62–39.75, respectively (Figs. 7b and 8a).

In situ Th-Pb ages of monazite within CM

Monazite is among the most abundant REE-bearing minerals in the Bayan Obo deposit and is the predominant accessory mineral phase in CM. Similar to other minerals commonly used U-Th-Pb dating such as zircon and apatite (Campbell et al. 2014), monazite is enriched in Th (447–3338 ppm) and depleted in U (~0.05 ppm; ESM Table 5). Monazite in CM forms euhedral inclusions in dolomite, and is disseminated in the marble, or forms veins as described above. All monazites display variable Th-Pb ages that range from 1078 to 406 Ma, which are consistent with the previously reported monazite Th-Pb age range for Bayan Obo by Ling et al. (2013). A histogram (ESM Fig. 2) indicates that the predominant calculated age is Early Paleozoic, and the three types of monazite yield a similar age distribution.

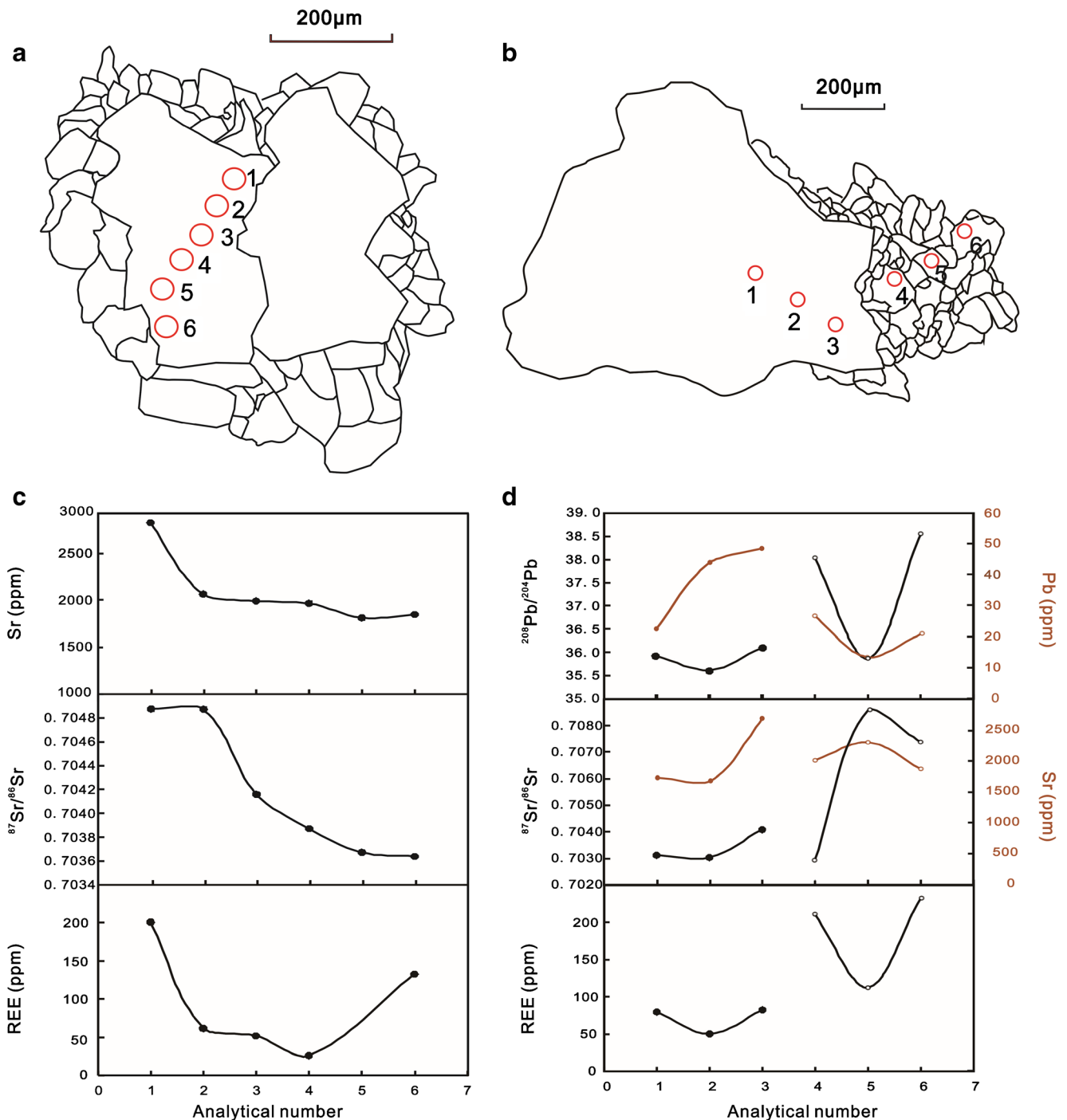


Fig. 5 Geochemical and isotopic transect data of coarse-grained dolomite (a) together with surrounding fine-grained dolomite (b). c Transect data of the coarse-grained dolomite within HM shown in a. d Transect data of

coarse-grained dolomite with surrounding fine-grained dolomite within HM shown in b

Discussion

A magmatic or sedimentary origin for Bayan Obo dolomite marble?

The interpretation of the geochemical data reported here is complicated, especially when multiple geological processes

were involved in the history of the Bayan Obo deposit (Smith et al. 2015; Fan et al. 2016; Yang et al. 2017). Since its discovery, it has been argued whether the host dolomite rock at Bayan Obo is of sedimentary or igneous origin. Previous studies, focused on whole rock geochemical data, generally suggest source signatures consistent with mantle carbonatite and/or sedimentary limestone (Smith et al. 2015;

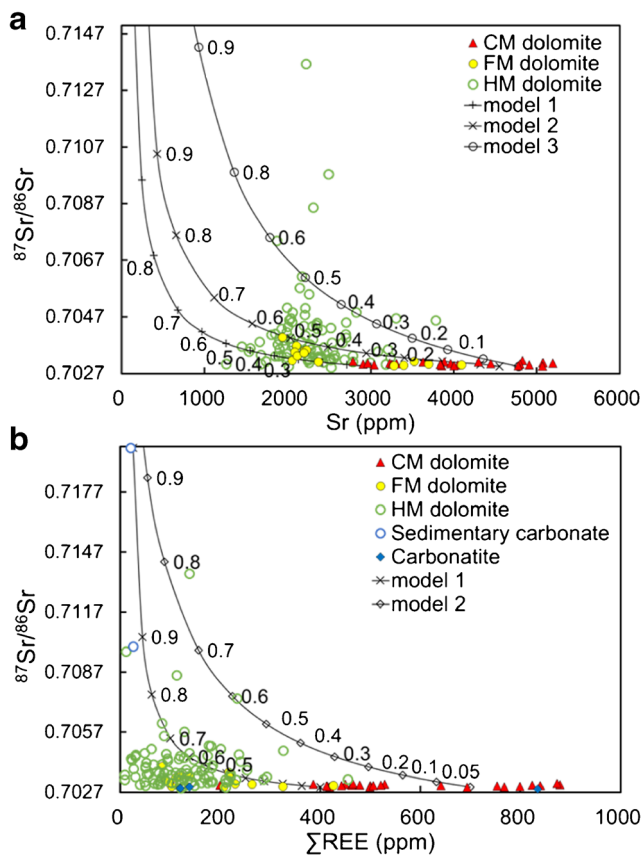


Fig. 6 Sr isotopic composition for dolomite from Bayan Obo marbles. **a** $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Sr concentration (ppm). Mixing model curves between the sedimentary (e.g., limestone) evolved fluid and the mantle-like dolomite (e.g., CM dolomite). The $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.71992, 0.71992, and 0.72620 for the sedimentary rocks at Bayan Obo (Le Bas et al. 1997) are adopted in models 1, 2, and 3 for hydrothermal fluid. The Sr contents in the hydrothermal fluid are 100, 200, and 500 ppm for models 1, 2, and 3, respectively. The most depleted $^{87}\text{Sr}/^{86}\text{Sr}$ isotope composition of 0.70295 for CM dolomite is adopted for the mantle-like dolomite, a Sr concentration of 3000 ppm is used for model 1, and 4779 ppm is used for models 2 and 3, respectively (ESM Table 2). **b** $^{87}\text{Sr}/^{86}\text{Sr}$ vs. REE (ppm). Mixing model curves are characterized by the same Sr isotope ratio in **a**, REE abundances of 400 and 700 ppm are adopted for the mantle-like dolomite, whereas 25 and 20 ppm are used for sedimentary evolved fluid in models 1 and 2, respectively. The parameters for the endmembers are summarized in ESM Table 6. Tick marks show the fraction of hydrothermal fluid mixed with the mantle-like dolomite

Fan et al. 2016; Yang et al. 2017; Song et al. 2018). Previous isotopic investigations are briefly summarized here: (1) $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for the dolomite marble vary from -4.6‰ to 1.4‰ and 5.9‰ to 16.5‰ , which overlap the range of values typical for primary, mantle-derived carbonatite to sedimentary limestone (Yang et al. 2017); (2) $\delta^{34}\text{S}$ values for bulk dolomite marble vary from -4.6‰ to 7.8‰ with a dominant and characteristic mantle value of approximately -1‰ . In contrast, sulfur isotopic compositions for sulfide and barite from the Bayan Obo marble display a large variation and heavier compositions from -3.9‰ to 11.1‰ and 10.0‰ to 14.6‰ (Yang

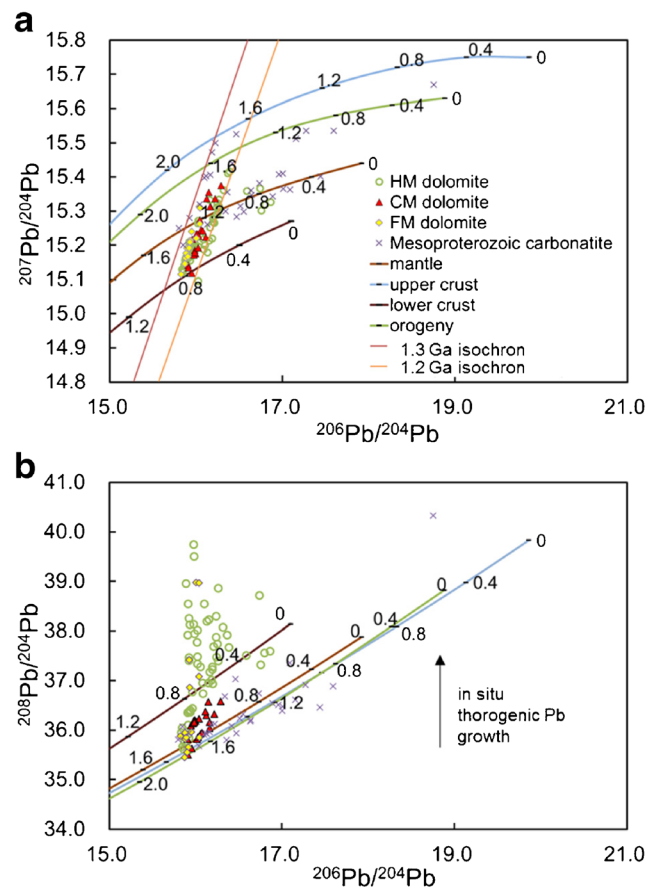


Fig. 7 Pb isotope compositions for dolomite from Bayan Obo marble. **a** $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$. **b** $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$. The Upper and Lower crust Pb evolution curves for China are based on Li et al. (2001), whereas the Orogeny and Mantle Pb growth curves are from Zartman and Doe (1981)

et al. 2017); (3) $\delta^{26}\text{Mg}$ values of the H8 dolomite marbles range between 0.10‰ and 1.13‰ (Sun et al. 2013; Ling et al. 2013), which fall between the representative values for carbonatite and sedimentary dolostone; (4) the average $\delta^{56}\text{Fe}$ value is $-0.07 \pm 0.24\text{‰}$ for bulk dolomite marble and $0.01 \pm 0.14\text{‰}$, $0.08 \pm 0.18\text{‰}$, and -0.21‰ for magnetite, hematite, and dolomite within the Bayan Obo deposit, respectively. The narrow range of the near-zero $\delta^{56}\text{Fe}$ values for both the marble and Fe oxide minerals are consistent with an igneous origin (Sun et al. 2013); (5) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the dolomite marble lie between 0.702 and 0.705, which is different compared to those for limestone (Le Bas et al. 1997); in contrast, individual mineral phases indicate a larger range from 0.7024 to 0.7097 (Song et al. 2018); (6) $\varepsilon_{\text{Nd}}(t)$ values (-2.63 to -0.06) for carbonatite dyke and REE ore are similar and yield Sm/Nd isochron ages of between ~ 1.3 and ~ 0.4 Ga (Zhu et al. 2015; Yang et al. 2017). Alternatively, Song et al. (2018) argued that the marble formed by a single-stage evolution from a Sm-Nd source that formed prior to 913 Ma years ago, which further suggests that REE ores at Bayan Obo form as products of Mesoproterozoic carbonatitic magmatism.

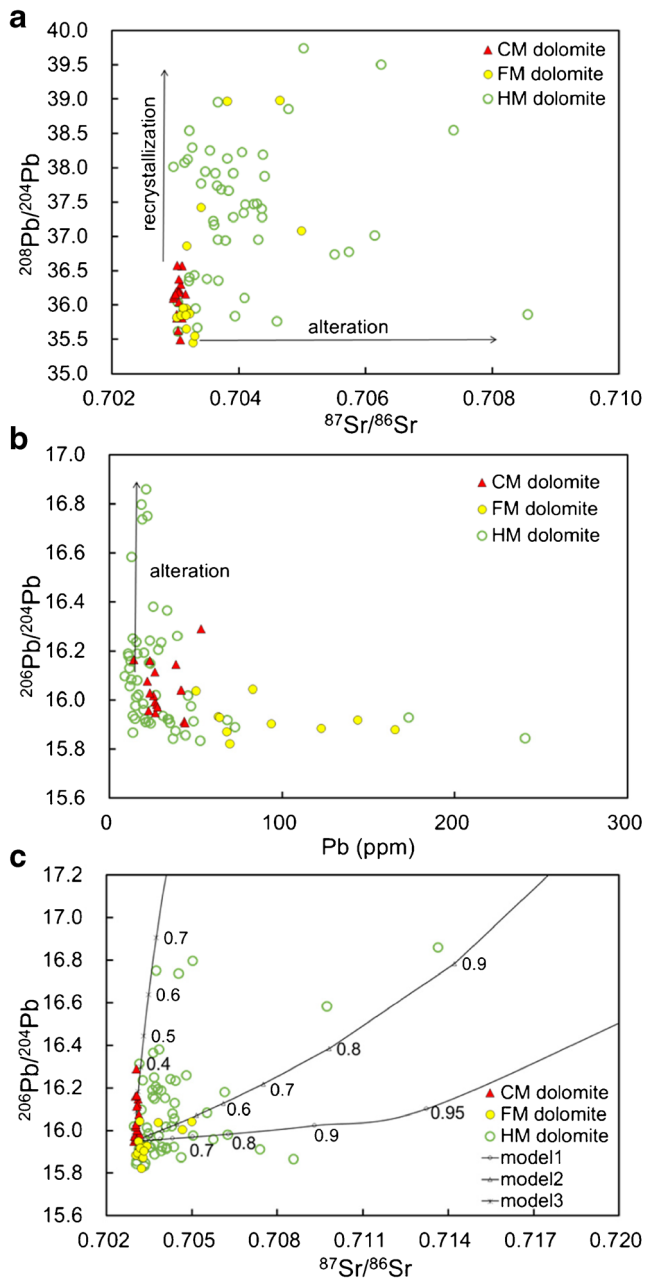


Fig. 8 Isotopic and chemical variations for dolomite from Bayan Obo marble. **a** $^{208}\text{Pb}/^{204}\text{Pb}$ vs. Pb concentration. **b** $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$. **c** $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope modeling in **c** is similar to Fig. 6a, and composition of 0.71992 and 0.72620 is adopted in models 1 and 2 and model 3 for the hydrothermal fluid, respectively. The Sr contents in the hydrothermal fluid are 500, 200, and 100 ppm for models 1, 2, and 3, respectively. The $^{206}\text{Pb}/^{204}\text{Pb}$ isotope composition for the hydrothermal fluid evolved from the surrounding rocks is estimated using the upper crust $^{206}\text{Pb}/^{204}\text{Pb}$ ratio of 19.13 at 400 Ma (Li et al. 2001). The Pb contents in the hydrothermal fluid are proposed at 0.1, 7, and 1.5 ppm for models 1, 2, and 3, respectively. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope composition of 0.70295 and $^{206}\text{Pb}/^{204}\text{Pb}$ of 16.00 is used for the mantle-like carbonatite, and Sr concentration of 4779 ppm and Pb concentration of 38 ppm for Bayan Obo dolomite are used (ESM Table 3). “Recrystallization” in **a** represents a process of the recrystallization of minerals within the complex with redistribution of elements in different mineral phases (e.g., monazite and dolomite), whereas “alteration” in **a** and **b** represents a process that involves open-system behavior with additional fluid source from surrounding rocks

with 1.2 and 1.3 Ga secondary isochrons, and these are consistent with the Mesoproterozoic ages determined by Sm-Nd and Th-Pb for both dolomite marble and carbonatite dykes at Bayan Obo (Campbell et al. 2014; Zhu et al. 2015; Zhang et al. 2017b). These combined results support primary carbonatite melt derivation from a mantle source region during the Mesoproterozoic. A carbonatite origin is also corroborated by the whole rock geochemical data and dolomite major element abundances for all marbles investigated here (Figs. 3 and 4). However, $^{208}\text{Pb}/^{204}\text{Pb}$ ratios are highly variable, especially for dolomite from FM and HM samples (Figs. 7b and 8a). Bastnäsite and monazite together with other U-Th-Pb-bearing minerals such as zircon and apatite from Bayan Obo are all enriched in Th compared to low U abundances (Wang et al. 1994; Ling et al. 2013; Campbell et al. 2014; Zhang et al. 2017b; ESM Table 5). Thus, all the dominant Th-Pb-bearing minerals accumulated abundant radiogenic ^{208}Pb since their formation in the Mesoproterozoic (Zhu et al. 2015; Zhang et al. 2017a). The Early Paleozoic age peak obtained by in situ monazite Th-Pb dating (ESM Fig. 2) is the most dominant and is consistent with those determined by other geochronological systems (Wang et al. 1994; Ling et al. 2013). Thus, the Early Paleozoic metasomatic event that has been proposed in previous studies is confirmed by our results. During this Early Paleozoic metasomatic event, radiogenic ^{208}Pb could have been mobilized and possibly released from the REE-bearing monazite and bastnäsite. The anomalous, highly radiogenic $^{208}\text{Pb}/^{204}\text{Pb}$ signatures in dolomite from FM and HM suggest incorporation of thorogenic ^{208}Pb during the Early Paleozoic.

The Mesoproterozoic fenitization process commonly identified for the Bayan Obo carbonatite possibly disturbed the radiogenic isotopic systems of the dolomite marble as well. The Mesoproterozoic country rocks with an estimated $^{208}\text{Pb}/^{204}\text{Pb}$ ratio of 37.16 are not high enough to serve as the radiogenic end member to explain the dolomite marble

Compared to the abundant C, O, Sr, and Nd isotope data obtained for Bayan Obo, Pb isotope compositions were rarely investigated. This feature is possibly due to the abundant fine-grained Th-bearing mineral phases (monazite, bastnäsite) in the bulk rock and consequently the difficulty in separating these minerals from the matrix dolomite. Dolomite grains with negligible Th and U abundances are preferred for determining the primary Pb isotope composition of the parental carbonatite magma and corresponding mantle source (ESM Table 3). Most dolomite grains display $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios consistent with derivation from a mantle source (Fig. 7a). The $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios yield slopes consistent

isotope composition (Fig. 7b; Li et al. 2001). In summary, the in situ Pb isotopic compositions for the host dolomite at Bayan Obo suggest a Mesoproterozoic magmatic origin combined with overprinting by Early Paleozoic metasomatism.

The Early Paleozoic metasomatism: nature of the fluids

In situ Sr isotope data for both coarse- and fine-grained dolomite help to identify the protolith and possibly the nature of the metasomatic fluid involved in the history of the Bayan Obo H8 dolomite. The Sr isotopic composition for CM dolomite displays a limited range of 0.70295–0.70316 (Fig. 6), which confirms a mantle origin. These dolomites are enriched in Sr (2783–5192 ppm with an average of 3997 ppm; Fig. 6a), which would buffer their Sr isotope compositions from possible contamination or alteration by sedimentary rock with much lower Sr abundances (129–165 ppm; Le Bas et al. 1997). This explanation may not apply for the FM and HM dolomites since they are characterized by lower Sr abundances (1446–4094 ppm with an average of 2337 ppm). The sedimentary carbonate rocks in the Bayan Obo area are characterized by much higher, radiogenic Sr isotope compositions ($^{87}\text{Sr}/^{86}\text{Sr} = 0.72620$; Le Bas et al. 1997; Zhang et al. 2003). Thus, the Sr isotopic compositions of coarse-grained dolomite marble confirm their mantle origin, with minimal fluid contamination during the Early Paleozoic metasomatism. This agrees well with the previous interpretation that the coarse-grained dolomite represents a Mesoproterozoic carbonatite (Le Bas et al. 2007).

FM and HM dolomite both show a range of Sr isotopic compositions, mainly between 0.703 and 0.705 (Fig. 6). The variable Sr isotopic compositions identified from HM and FM dolomite would represent derivation from a heterogeneous mantle source or contribution from metasomatic fluids compared to the lower Sr isotope ratios in CM dolomite (approximately 0.703; Fig. 6). A minor amount of HM dolomite displays radiogenic Sr isotope ratios (up to 0.71363), which indicates contribution of Sr from the surrounding sedimentary rocks. Alternatively, the extremely radiogenic Sr isotope signatures reflect the presence of phlogopite within dolomite marble that formed during the Paleozoic metasomatic event (Fig. 6). The radiogenic Sr isotopic composition of dolomite may originate from Rb-bearing minerals, such as phlogopite within the marble, that released radiogenic ^{87}Sr during the Paleozoic metasomatism in an analogous fashion to the radiogenic ^{208}Pb . Phlogopite is a minor phase in the marble and Rb/Sr ratios for the whole rock carbonatites are low (< 0.0028 ; ESM Table 1). Thus, radiogenic Sr generated by the “local” phlogopite should be negligible and not abundant enough to cause the large variation in the Sr isotopic compositions. Previous studies have also reported similar Sr isotopic variations (0.703–0.705) for carbonatite dykes at Bayan Obo (Le

Bas et al. 2007; Yang et al. 2011). Le Bas et al. (2007) attributed the radiogenic Sr isotopic composition to contamination by the wall rocks via fenitization, whereas Yang et al. (2011) proposed a heterogeneous magma source. Both studies based their interpretations on whole rock Sr isotopic analyses, which are hampered by the complex petrography involving the random distribution of Rb-bearing accessory minerals. Field evidence indicates that carbonatite dykes typically reacted with the surrounding country rocks to form fenite aureoles (Le Bas et al. 2007; Yang et al. 2011; Smith et al. 2015). The fact that one carbonatite sample in the contact zone is characterized by an elevated Sr isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr} = 0.703845$; Le Bas et al. 2007) indicates that wall rock contamination is a more plausible interpretation in contrast to a heterogeneous mantle source hypothesis. The Sr isotopic composition for the sedimentary limestones in the Bayan Obo area ranges from 0.71992 to 0.72620 (Le Bas et al. 1997). As shown in Fig. 6a, the Sr abundances for dolomite from FM and HM are generally lower compared to dolomite from CM. It is thus plausible that the more radiogenic Sr isotopic signatures in dolomite from FM and HM compared to CM are the result of contamination by fluids during Early Paleozoic metasomatism. For example, the majority of the Sr isotope ratios and Sr concentrations reported here for the Bayan Obo marbles (CM, FM, and HM; ESM Table 3) can be modeled using binary mixing calculations involving carbonatite and host rock-derived fluids (Fig. 6a and ESM Table 6). Moreover, dolomites with radiogenic Sr isotope ratios are characterized by depleted REE patterns that are similar to the sedimentary carbonate (Zhang et al. 2003) and can therefore also be modeled using similar binary mixing calculations between carbonatite and fluids (Fig. 6b).

The alteration of Mesoproterozoic carbonatite by a fluid in an Early Paleozoic deformation/metamorphism event can explain the range of Sr isotope composition. Similarly, radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ compositions for HM dolomite that are characterized by lower Pb concentrations, which can be contaminated by fluids released from surrounding sedimentary rocks, may reflect this alteration process (Fig. 8b). The Sr isotopic composition of the Bayan Obo limestone (north of the deposit) is estimated to be ~ 0.720 , with corresponding Sr abundance of approximately 150 ppm (Le Bas et al. 1997; Zhang et al. 2003, 2009). The abundance of Pb in limestone is typically low (< 0.1 ppm; di Battistini et al. 2001), but it is higher in slate (> 1 ppm; Li et al. 2017), and the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios for Early Paleozoic upper crust are 18.71 and 15.73, respectively (Zartman and Doe 1981). The average Sr and Pb abundances in the FM dolomite are 2653 and 38 ppm, respectively (ESM Table 3). Thus, depending on the nature of the metasomatic fluids released from surrounding rocks during the Early Paleozoic, different Sr-Pb isotope contamination trends can be generated (Fig. 8c). Crust-derived hydrothermal fluids that percolated through the

carbonatite could have introduced more radiogenic Sr and Pb, a process similar to that reported for the Barra do Itapirapua carbonatite from Southern Brazil (Andrade et al. 1999). The combined Sr and Pb isotopes and trace element compositions recorded in the dolomite from the three marble facies are best explained by the involvement of hydrothermal fluids leached from the surrounding sedimentary rocks, and these are characterized by radiogenic Sr and Pb isotopes and depleted Sr and REE abundances (Figs. 6 and 8c).

H8 dolomite: primary or secondary?

In previous studies, the host H8 dolomite at Bayan Obo was separated into coarse- and fine-grained types (Le Bas et al. 1997, 2007; Wang et al. 2010; Yang et al. 2011; Lai et al. 2012). The coarse-grained marble investigated in this study consists of mosaic-textured dolomite with triple junctions and disseminated monazite, which represents the primary carbonatite mineral assemblage (Le Bas et al. 1997, 2007; Zhu et al. 2015). These textures best correspond to those of CM dolomite investigated here, which is characterized by uniform mantle Sr and Pb isotopic compositions (Figs. 6 and 7). The combined Sr-Pb-Nd isotopic signatures for CM dolomite are interpreted to represent the original Bayan Obo carbonatite melt (Song et al. 2018).

Coarse dolomite grains were also identified within HM, which are attributed to a distinct petrogenetic history compared to the coarse-grained dolomite in CM. Inter-grain geochemical variation within coarse-grained dolomite from Bayan Obo was investigated previously by Lai et al. (2012) and Ling et al. (2013). They argued that the low Sr concentrations in grain cores were characteristic of sedimentary carbonate rocks that underwent hydrothermal metasomatism by carbonatitic fluids. The varied Sr abundance within a single dolomite grain could also be caused by diffusion within the crystal. In spite of the variable Sr abundances, their Sr isotopic compositions lack consistent core-to-rim patterns (Fig. 5a, b). Hence, these chemical and isotopic features for the carbonates are best explained by invoking recrystallization during Early Paleozoic metasomatism. The highly variable REE abundances of coarse dolomite grains (Figs. 4d and 5) could be attributed to inherent changes in the REE abundances of the alteration fluid or replacement during metasomatism with the preferential removal of the LREEs (Smith et al. 2000). In addition, Smith et al. (2015) showed that the coarse-grained dolomite displays variable microstructures as illustrated by cathodoluminescence images. For instance, several dolomite samples are characterized by ferroan dolomite cores with Sr-rich luminescent overgrowths, and the most ferroan dolomite fracture fill is intergrown with monazite (Smith et al. 2015). These microtextures may be linked to the re-equilibration of dolomite chemistry as a result of the Paleozoic metasomatism, which reflect a distinct stage of fluid flow.

The geochemical signature of fine-grained FM and HM dolomite is similar to the coarse-grained dolomite from HM. The FM and HM dolomite is characterized by enriched Mn contents, similar to those of CM dolomite, whereas the REE and Sr abundances are lower (Figs. 4 and 6). The decrease in Sr content is typically observed for secondary or late-stage carbonate in other carbonatite complexes (Zaitsev and Chakhmouradian 2002). Previously, the fine-grained dolomite was proposed to have formed from extensive REE mineralization and recrystallization of the coarse-grained marble (Le Bas et al. 2007; Yang et al. 2011) or vice versa (Lai et al. 2012). Both models assume that these dolomites (CM and FM) formed from a common source in a closed system. However, this may not be the case since the enriched Sr isotopic composition likely originates from fluids evolved from surrounding rocks (Fig. 6a). The heavier carbon and oxygen isotope compositions for fine-grained dolomite marble compared to coarse-grained dolomite marble also suggest involvement of fluids from the surrounding limestone (Le Bas et al. 1997).

Thus, the combined in situ geochemical and isotopic compositions for various dolomite grains at Bayan Obo suggest these underwent different formational histories. The geochemical signature of fine-grained dolomite within FM resembles both the fine-grained and coarse-grained dolomite within HM, whereas the coarse-grained dolomite within HM is different from the coarse-grained dolomite within CM. FM and HM dolomite are recrystallized, whereas CM dolomite represent primary crystallization from Mesoproterozoic carbonatite melt that underwent little open-system alteration. Previous investigations by Smith et al. (2000) and Campbell et al. (2014) reported REE fractionation using mineral compositions in relation to fluid evolution for Bayan Obo. The early monazite is characterized by high La/Nd ratios of ~3–7, consistent with CO₂ magma/fluids, whereas the ratios for late REE fluorocarbonates are ~0.6–2, which may be attributed to transport by aqueous fluids (Smith et al. 2000). This is also consistent with the HREE enrichment in zircon rims relative to their cores (Campbell et al. 2014). Our observations suggest that the recrystallized dolomite either coarse or fine shows lower REE and Sr abundances and is characterized by lower La/Nd ratios, which is consistent with the chemical compositions recorded within REE minerals and zircon from the Bayan Obo H8 marble (Smith et al. 2000; Campbell et al. 2014).

Formation history of the Bayan Obo deposit

The H8 marble hosting the Bayan Obo deposit displays various petrographic, mineralogical, and chemical signatures as evidenced in both coarse- and fine-grained dolomite. The geochemical data reported here, combined with the in situ Th-Pb data from different monazite within CM, suggest that

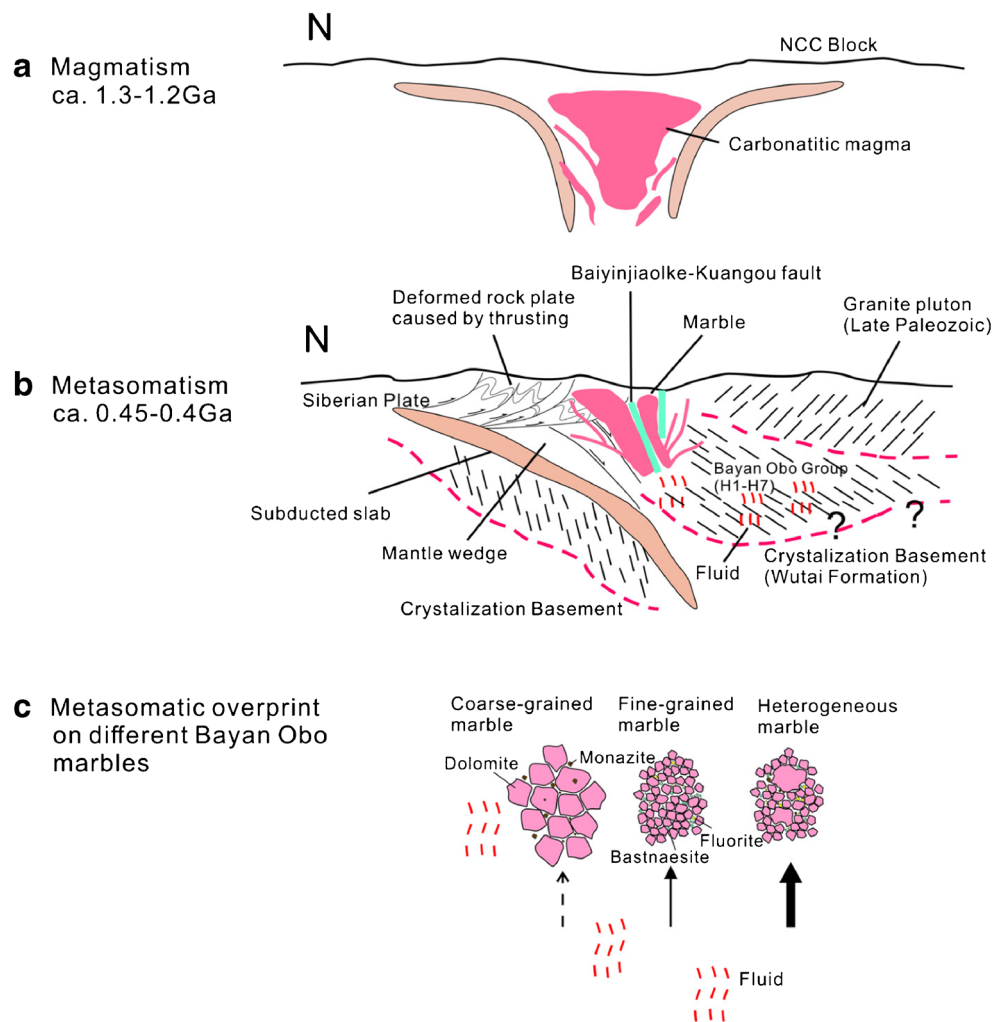
Mesoproterozoic magmatism and Early Paleozoic metasomatism played dominant roles in the formation of the Bayan Obo deposit (Smith et al. 2015). Geochemically, the whole rock trace element compositions and the major element composition of dolomite are similar to those of mantle-derived carbonatites and clearly distinct compared to that of sedimentary limestone and carbonate phases contained within. Sm-Nd isotope results for the entire complex are homogeneous and indicate derivation from the same mantle source, and these were not perturbed by subsequent metasomatic activity (Zhu et al. 2015; Song et al. 2018). In contrast, the various chemical signatures reported in this study are heterogeneous and reflect the various degrees of metasomatism that occurred during the Early Paleozoic.

The coarse-grained marble represents the crystallization product of Mesoproterozoic carbonatite melt with little open-system alteration. These may have been thermally affected by the widespread Early Paleozoic metasomatic events, as indicated by the variable Th-Pb ages recorded by monazite within CM. The monazite occurs as inclusions within dolomite, disseminated among

dolomite or forming veins, and all display a similar age range of ~400 to ~1100 Ma, which is younger than the Sm-Nd ages determined for both coarse-grained and fine-grained marble at Bayan Obo (Zhu et al. 2015). The range of ages obtained using Th-Pb dating of CM monazite is consistent with varied degrees of Pb loss or incomplete re-equilibration of the Mesoproterozoic isotope systems during dissolution-precipitation (Smith et al. 2015; Zhu et al. 2015). Similarly, Downes et al.'s (2016) study of the Cummins Range carbonatite reported discrepant ages for monazite and zirconolite; the former defines a younger and variable range of ages between ~900 and ~590 Ma within strongly foliated dolomite carbonatite, whereas zirconolite from clinopyroxenite yield an emplacement age of 1009 Ma. Thus, the coarse dolomites in CM are believed to represent primary dolomite grains that crystallized from a carbonatite magma, whereas monazite within the marble was affected by the thermal event resulting in the re-equilibration of Th-Pb system during Early Paleozoic metasomatism (Fig. 9).

In summary, we propose that the Bayan Obo deposit formed as the result of the intrusion of carbonatite magma during the

Fig. 9 Model for the genesis of the Bayan Obo deposit. **a** The Bayan Obo carbonatite intruded during the Mesoproterozoic rifting stage of the North China Craton breakup from the Columbia supercontinent (Zhao et al. 2003). **b** The Bayan Obo complex was metasomatized and deformed during the Early Paleozoic. The deformation and metamorphism possibly occurred during Early Paleozoic subduction between the Siberian Craton and the North China Craton (Yang et al. 2017); however, magmatic evidence associated with the slab subduction in the northern margin of North China Craton is absent. **c** Different marbles from the Bayan Obo deposit were metasomatized to various degrees, with the fine-grained and heterogeneous-marble representing the highest degrees of alteration, whereas the coarse-grained marble experienced the least amount of metasomatism



Mesoproterozoic, which is possibly related to the newly identified 1.33–1.30 Ga Yanliao large igneous province (Zhang et al. 2017b; Fig. 9a). During the Early Paleozoic (~440 Ma), subduction of the Siberian plate may have triggered the hydrothermal metasomatic activity that affected the Bayan Obo carbonatite complex (Fig. 9b). The latter event imparted the highest degree of alteration on the fine-grained marble and heterogeneous-grained marble (Fig. 9c). Dolomite grains within the FM and HM are recrystallized and characterized by radiogenic $^{208}\text{Pb}/^{204}\text{Pb}$ and enriched Sr isotope signatures. The coarse-grained carbonatite experienced the least amount of metasomatism during the Early Paleozoic, which is solely recorded by the highly variable U-Th-Pb ages from monazite.

Conclusions

Unweathered marbles from a 1700-m drill core of the giant Bayan Obo REE-Nb-Fe deposit have been examined for their petrographic and in situ geochemical and isotopic signatures. Marbles are divided in three types, CM, FM, and HM. The whole rock geochemical data, major and trace element, and the combined Sr and Pb isotope compositions of dolomite suggest that the Bayan Obo deposit formed as a result of emplacement of mantle-derived carbonatite magma during the Mesoproterozoic, which underwent different degrees of metasomatism during the Early Paleozoic. The coarse-grained dolomite within CM represents pristine crystallization products from the Mesoproterozoic carbonatite magma that have experienced negligible metasomatism. In contrast, both fine- and coarse-grained dolomites within FM and HM were recrystallized during the Early Paleozoic metasomatic activity. This extensive hydrothermal activity involving the surrounding crustal rocks plays a crucial role in the formation of giant REE deposits. However, widespread, open-system Early Paleozoic alteration complicates interpretation of geochemical and isotopic data from this giant REE-Nb-Fe deposit. Hence, based on the results reported in this study, it is strongly recommended that detailed petrographic investigations should be conducted prior to interpretation of associated whole rock geochemical data and, if permitted, micro-scale in situ analysis is highly recommended.

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