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Mesoproterozoic and Paleozoic hydrothermal metasomatism in the giant Bayan Obo REE-Nb-Fe deposit: Constrains from trace elements and Sr-Nd isotope of fluorite and preliminary thermodynamic calculation

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ABSTRACT

Fluorite of various occurrences could portray the hydrothermal metasomatism occurred in the giant Bayan Obo REE-Nb-Fe ore deposit. Two Mesoproterozoic and Paleozoic hydrothermal events with distinguished fluid origin and geochemical properties have been studied. In Mesoproterozoic, discrete fluorite from the dolomite-dominating REE-Nb ores and banded fluorite aggregates from the banded REE-Nb-Fe ores are extremely enriched in LREE and depleted in HFSE compared with the primitive mantle. In Paleozoic, fluorite from veined-breccia REE-Nb ores varies significantly in trace element components, ranging from LREE-enriched HFSE-depleted fluorite to fluorite with "flat" REE pattern and extremely depletion of Zr. The veined fluorites have variable and higher radiogenic Sr isotopic components (initial $^{87}Sr/^{86}Sr$ ratios: 0.703464–0.708208) than the discrete and banded fluorite (0.703183–0.705047), indicating crustal contamination in the Paleozoic hydrothermal fluids from Precambrian basement rocks and Bayan Obo Group. Fluorites of different occurrences and associated bastnäsite and monazite have similar Nd isotopic components and Nd evolution history, which is mostly consistent with whole rock of the ore-hosting dolomite. The Sm-Nd system of some fluorite and bastnäsite were reset during the Paleozoic alteration triggered by the closure of Paleo-Asian Ocean. In such geological setting, according to the $\delta^{34}S$ of the dominating sulfur-bearing mineral, Paleozoic veined sulfides ($\sim 0 \pm 3‰$), the prime sulfur source was oceanic crust/MORB. Relatively high $\delta^{34}S$ of barite (~13–14‰) was caused by fractionation of sulfur isotopes at an equilibrium temperature of 400–430 °C, rather than contribution from ancient seawater. The trace element, Sr-Nd isotope of fluorite and sulfur isotope characters of sulfides indicate carbonatitic origin of the Mesoproterozoic hydrothermal fluids, while the Paleozoic fluids, derived from subducted Paleo-Asian oceanic crust, carried sulfur components from MORB, scavenged high radiogenic Sr components from Precambrian basement rocks or Bayan Obo group, may leached a deep-seated carbonatite stock and finally altered the Mesoproterozoic mineralized ore-hosting dolomite.

Both the Mesoproterozoic and Paleozoic hydrothermal fluids had initial temperature of ~400–500 °C, and gangue minerals (fluorite, sulfide and sulfate) precipitated at the temperature of ~320–440 °C. Preliminary thermodynamic calculations of the REE-F-C-Ca system constrained that the pressure of both fluids would not exceed 2 kbar. The drop of temperature and increase of pH are two critical factors to REE mineralization. Paragenesis of Fe-bearing minerals indicates an increase of fO_2 in the Mesoproterozoic hydrothermal fluids and a drop of fS_2 in the Paleozoic fluids in the Fe-O-S system. Furthermore, in the Ca-F-C-O system, the Mesoproterozoic hydrothermal fluids evolved with increasing aCa^{2+} and decreasing aF^-, while the Paleozoic fluids present characteristic of mixing origin again with significantly variable aCa^{2+} and aF^-.

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1. Introduction

Fluorite is one of the most common hydrothermal minerals in global REE-(Nb) deposits, especially in the carbonatite-related REE deposits (Temple et al., 1965; Wall et al., 1995; Andradeab et al., 1999; Groves et al., 2001; Wang et al., 2001). Considering its close association with REE-bearing minerals, fluorite has been conventionally regarded as resultant or by-product of REE mineralization processes (Williams-Jones et al., 2000; Gültekin et al., 2003). The role of fluorine that has played in the transport and deposition of REE in the hydrothermal fluids has been discussed and affirmed (Richardson and Holland, 1979; Migdisov et al., 2007, 2009, 2014; Williams-Jones et al., 2012). Therefore, fluorite has its inherent advantage in understanding the REE mineralization process and the properties of the ore-forming fluids.

The Bayan Obo REE-Nb-Fe deposit is the largest REE deposit in the world currently, with REE reserves over 57.4 million metric tons (Mt) (average grade 6% of REE oxides), Nb reserves of 2.16 Mt (average grade 0.13% of Nb_2O_3) and Fe reserves of at least 1500 Mt (average grade 35% of iron oxides) (Drew et al., 1990; Hao et al., 2002; Fan et al., 2016). The Bayan Obo REE-Nb-Fe deposit is hosted in a dolomite unit, whose origin has been controversial. Abundant research on geochemistry, geochronology and paleontology has been carried out, in order to distinguish the origin of the ore-hosting dolomite among hypotheses including 1) carbonatite intrusion (Liu et al., 1985; Yuan et al., 1992; Le Bas et al., 1997; Hao et al., 2002; Wang et al., 2002; Yang et al., 2004; Xu et al., 2008; Yang et al., 2011; Sun et al., 2012, 2013), 2) volcanic exhalative-sedimentary carbonatite (Bai et al., 1996; Xiao et al., 2003a,b, 2012) or 3) a sedimentary carbonate formation (Meng et al., 1982, Meng and Drew, 1992; Liang et al., 1993; Wei et al., 1994; Qiao et al., 1997; Yang et al., 2009; Zhang et al., 2012; Lai et al., 2012, 2016). In despite of these divergence, it has long been accepted that the hydrothermal processes have made significant and indispensable contribution to the REE mineralization at Bayan Obo (Chao et al., 1991; Campbell and Henderson, 1997; Smith et al., 1999; Xu et al., 2012). Extensive alteration to the ore-hosting dolomite was presumed to be multi-stages (Chao et al., 1991; Fan et al., 2016). There are mainly two alteration events occurred in Bayan Obo that were related to the REE enrichment process, a Mesoproterozoic alteration event and a Paleozoic one (Campbell et al., 2014; Fan et al., 2016), supported by geochronological of hydrothermal minerals and their associated REE-bearing minerals (Ren et al., 1994; Liu et al., 2004; Hu et al., 2009; Zhu et al., 2015).

The Mesoproterozoic hydrothermal event is characterized by the formation of discrete hydrothermal minerals in dolomite-dominating ores and banded ores. Discrete hydrothermal fluorite, monazite and apatite in the dolomite-dominating ores presented a Sm-Nd isochron age of 1250 ± 210 Ma (Zhang et al., 2001). Other Mesoproterozoic dating results of the dolomite-dominating ores include a deduced La-Ba isochrone age of monazite (1350 ± 149 Ma) (Nakai et al., 1989), Sm-Nd isochron age of discrete monazite and bastnäsite (1313 ± 41 Ma) (Ren et al., 1994), Th-Pb isochron age of discrete monazite (1231 ± 200 Ma) (Liu et al., 2005). Meanwhile, hydrothermal monazite and parisite grains from the banded REE-Fe ores present Sr-Nd isochron age of 1700 ± 480 Ma (Cao et al., 1994). Indirect dating of the Mesoproterozoic hydrothermal event concluded from fenitization around Wu carbonatite dyke, which occurred instantly after the intrusion of carbonatite at 1354 ± 59 Ma (Sm-Nd dating of whole rock) (Yang et al., 2011). Our former study has proved that the aegirine-rich and Na-amphibole-rich massive REE-Fe ores were product of fenitization similar to that around carbonatite dykes (Liu et al., 2018). A Mesoproterozoic hydrothermal event was also recorded by a Na-amphibole vein in wallrock of the ore-hosting dolomite which presented ^{40}Ar-^{39}Ar age of 1.26 Ga (Conrad and Mckee, 1992). In addition, a heat event was recorded by zircon in the ore-hosting dolomite with Th-Pb age of 1301 ± 12 Ma (Zhang et al., 2017). There were two heat events recorded by another discrete zircon from one banded REE ore sample, which has a Th-Pb age of 1325 ± 60 Ma at the core and 455.6 ± 28.3 Ma at the rim (Campbell et al., 2014).

The Paleozoic hydrothermal event is characterized by ores consisting of veins, blocks or mega-crystals of hydrothermal fluorite, aegirine, pyrite, barite, Na-amphiboles and REE/Nb-bearing minerals (e.g. bastnäsite, huanghoite, pyrochlore). The Th-Pb dating of huanghoite and pyrochlore monominerals from aegirine-rich veins gave an isochron age of 438 Ma (Chao et al., 1991). Meanwhile, the Sm-Nd isochron age of fluorite, aegirine, calcite and bastnäsite monominerals from veined-breccia type REE-Nb ores is approximate 440 Ma (Hu et al., 2009). The Re-Os dating of pyrite and molybdenite in the veined-breccia type REE-Nb ores is ~436 Ma (Liu et al., 1996, 2004). All above ages constrain a Paleozoic hydrothermal event distinct from the one caused by Mesoproterozoic ore-forming fluids.

A subsequent Permian skarnization event presents in the contact zone between the Mesoproterozoic ore-hosting dolomite and Permian granitic plutons (Zhang et al., 2003; Fan et al., 2009). These magmatic activities destroyed the REE-Nb-Fe ore bodies where it had intruded. Therefore, the skarnization has been regarded as irrelevant to the REE mineralization and beyond concerns of this study.

In most former studies, the Mesoproterozoic hydrothermal event was regarded as the major REE mineralization stage (Yang et al., 2011; Zhu et al., 2015; Wang et al., 2018). Besides, some other research paid attention to the contribution of Paleozoic hydrothermal fluids (Chao et al., 1992; Ling et al., 2013; Yang et al., 2017). Fluid inclusion studies support a carbonatitic origin of the ore-forming fluids (Smith and Henderson, 2000), and REE-fluorocarbonate-bearing fluid inclusions in fluorites from banded and veined type ores indicates the fluoritization occurred simultaneously with the REE mineralization (Fan et al., 2004). On the contrary, subduction released fluids were proposed as major ore-forming fluids according to oxygen isotope disequilibrium (Ling et al., 2013). In current studies, direct comparison between these two hydrothermal events is still insufficient, especially on their origin and geochemical characteristics.

Fluorite is one of the ubiquitous hydrothermal minerals both in the Mesoproterozoic and the Silurian hydrothermal events (IGCAS, 1988). Nearly all hydrothermal silicates with hydroxyl in the ores, e.g. Na-amphiboles and fluorophlogopite, suffered varying degree of fluorine exchange (Xu et al., 2005). Other fluorine-rich minerals in the ores include apatite and fluorocarbonates, the primary REE-bearing minerals (Smith et al., 2007). All these hydrothermal minerals reveal that the ore-forming fluids are intrinsically REE-rich and F-enriched as well.

In this study, fluorites of different occurrences formed in two alteration events were analyzed for their trace elements and Sr-Nd isotopic components. Bastnäsite and monazite associated with these fluorites were analyzed for Nd isotopic components. Besides, new sulfur isotope data of sulfide and barite associated with the Paleozoic fluorite were provided for further discussion on the systematic similarities and differences in origin and geochemical properties of the two hydrothermal fluids separated temporally by ~0.9 Ga. Preliminary thermodynamic calculations were conducted to explore the physico-chemical conditions and precipitation process of fluorocarbonates and fluorite in these two alteration events.

2. Geological setting

The Bayan Obo REE-Nb-Fe deposit is located on the north margin of North China Craton (NCC), adjacent to the south margin of Central Asian Orogenic Belt (Fig. 1a, b). Like Xiong'er and Yanliao rift basin on the north margin of NCC, the Bayan Obo-Langshan rift basin is regarded as part of the rift system formed during the breakup of the Columbia Supercontinent (Zhao et al., 2004; Yang et al., 2012; Liu et al., 2015; Zhong et al., 2015). During the formation of the Bayan Obo rift, basement rocks of NNC, including Archaean gneiss and Paleoproterozoic TTG are uncomfortably covered by a set of Mesoproterozoic-Neoproterozoic terrigenous-volcanic sedimentary rocks, termed as Bayan Obo