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Comparison of fluorite geochemistry from REE deposits in the Panxi region and Bayan Obo, China

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ABSTRACT

Panxi region in west Sichuan province is one of the most economically significant REE mineralization belts in China, and includes the large Maoniuping and Daluxiang deposits and the minor Lizhuang deposit. The REE mineralization in these deposits is spatially and temporally associated with carbonatite–syenite complexes. Large proportional fluorites and REE minerals occurring as veins intrude Cretaceous granite and Oligocene syenite in Maoniuping, and Oligocene syenite and carbonatite in Lizhuang, and Miocene syenite in Daluxiang. Fluorite is also one of main gangue minerals in the world-class Bayan Obo REE deposit. We present a comparison of the trace element and isotopic compositions of fluorites from four REE deposits in the Panxi region and Bayan Obo. The fluorites from Maoniuping and Daluxiang are characterized by variable REE patterns, with either LREE enrichment or LREE depletion relative to MREE. Typically they have a larger range in La/Ho compared to Y/Ho ratios, and pronounced positive Y anomaly relative to chondrite-normalized REE patterns. Their REE distribution patterns are controlled by fluoride-complexes and the loss of separate LREE-rich minerals. Different Y/Ho (ca. 73 vs. 108) and initial Sr isotopic (ca. 0.7061 vs. 0.7077) ratios are observed between the fluorites from Maoniuping and Daluxiang, reflecting their different source compositions. This contrasts with the fluorites from Maoniuping and Lizhuang, which have similar initial Sr isotopes, and appear to be cogenetic. However, the Lizhuang fluorite shows a consistent depletion of LREE relative to MREE, as well as lower Y/Ho ratios and higher HREE content than that in Maoniuping. In this respect the Lizhuang fluorite may have precipitated from a late-stage fluid following abundant fluorite and REE mineral deposition in Maoniuping. Carbonate, more than fluoride complexing, appears to have a stronger control on REE fractionation in the Lizhuang fluorites.

The fluorites from three deposits in Panxi region show uniform initial Sr and Nd isotopic compositions similar to their associated carbonatites, but differ from ore-veins found intruding wall rocks, e.g. granite in Maoniuping and syenite in Daluxiang. This is not consistent with a model for fluorite formation involving interaction of F-rich, carbonatite-exsoloved fluid with wall rocks. Instead, the fluorite in Panxi region may precipitate from a residual carbonthermal fluid, which was dominated by Ca, CO_2 but also contained F, H_2O and REE, and derived from the fractioned carbonatitic magma. Fluorite deposition produced a sharp drop in the activity of F^-, which destabilized the REE fluoride complexes and caused deposition of REE minerals. In Bayan Obo, the fluorite typically has higher La/Ho than that in Panxi region and is characterized by a consistent LREE enrichment relative to MREE and negligible to positive Y anomalies. This is consistent with the compositional change of the hydrothermal fluids, which were infiltrated by external F-, LREE-rich fluids. The $^{87}Sr/^{86}Sr$ of Bayan Obo fluorite is relatively low radiogenic, and has a large range (0.7038–0.7065): similar characteristics to the carbonatite dykes found near the ore bodies. This supports a model for fluorite and REE mineral genesis involving the interaction of a carbonatite-derived fluid and the ore-hosted dolomitic marble.

1. Introduction

Rare earth elements (REE) are relatively abundant in the Earth's crust, but deposits with economic concentration levels are less common than for most other ores. China, the United States, Russia, India, Malaysia and Brazil constitute the largest percentage of the world's rare earth economic resources. China presently has more than 50% of the REE reserves in the world (Humphries, 2011), as represented by the largest world-class Bayan Obo deposit and REE mineralization belt in the Panxi region of West China. Bayan Obo has attracted geologists because of its giant REE reserves,

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however, the genesis of this deposit and its potential resources remain debated. The Panxi region is an important REE mineralization belt, extending 270 km between the cities of Mianning and Panzhihua. This belt includes different types of REE mineralization, e.g. carbonatite–syenite related light REE (LREE), granite-related heavy REE (HREE), volcanic-related Nb–LREE, and weathered granitoid-related Nb–REE.

Fluorite can accommodate relatively high REE contents, and is frequently used to trace the REE fluid compositions (Möller et al., 1976; Trinkler et al., 2005; Schönenberger et al., 2008; Sánchez et al., 2010). The mineral has very low Rb/Sr ratios, which allows us to determine the fluid sources by comparing its initial $^{87}Sr/^{86}Sr$ with those of igneous rocks in the area (Ruiz et al., 1985; Ruiz and Richardson, 1988; Simonetti and Bell, 1995; Sallet et al., 2005). Neodymium isotope studies (e.g. Halliday et al., 1990) and Sm–Nd dating of hydrothermal fluorite mineralization (e.g. Chesley et al., 1991, 1994) have shown that initial Nd isotope ratios reflect the composition of the ore fluids, and provide reliable ages for ore formation. In addition, fluorite is common gangue mineral in many different types of deposits. In magmatic and hydrothermal processes, fluorine-rich fluids are capable of transporting and enriching the REE to economic concentrations (Pan and Fleet, 1996; Salvi et al., 2000; Williams-Jones et al., 2000; Tagirov et al., 2002; Agangi et al., 2010), and consequently, fluorite is widely used as a geochemical exploration tool (Williams-Jones et al., 2000; Gültekin et al., 2003; Xu et al., 2003a). In this paper we compare the geochemistry of fluorites from Maoniuping, Daluxiang (also called Dalucao), and Lizhuang in Panxi region, and the large Bayan Obo system. These deposits contain about 1/2 of the world REE reserves. The purpose of the study has been twofold: first, to define the chemical composition of fluorite during ore-genesis in the different deposits; and secondly, to discuss a possible mechanism for controlling REE fractionation in fluorite, and further implication for the REE genesis in Panxi region and world-class Bayan Obo.

2. Geological setting

The Panxi region (Panzhihua-Xichang), located on the western margin of the Yangtze craton, underwent a complicated tectonic evolution from Proterozoic lithospheric accretion, development along a Paleozoic–Mesozoic continental margin, followed by a Cenozoic collision orogeny (Zhang et al., 1988). The basement of this region is composed of Archean high-grade metamorphic rocks and Proterozoic meta-sedimentary rocks. A large Late Permian igneous province, composed of flood basalts with minor picrite and picritic basalts, covers the western part of the Yangtze craton with an area of $\sim$500,000 km^2 (Ali et al., 2005). Voluminous volcanic sequences such as this are erupted in a relatively short period of time, are believed to be linked genetically with the impact of mantle plumes with the lithosphere (Chung and Jahn, 1995; Xiao et al., 2004). Until the Late Triassic, the plume-related rifting waned. The Indo-Asian collision at 65–55 Ma resulted in the Himalayan orogen (Yin and Harrison, 2000; Mo et al., 2003), which resulted in a strong east–west compression of the Panxi region.

The Maoniuping, Lizhuang and Daluxiang REE deposits are located in the north and middle Panxi region, and are tectonically controlled by Haha and Daluxiang faults, respectively. These deposits are associated with carbonatite–syenite complexes, in which the carbonatitic magmatism is represented by sills, dykes and stocks within the syenite intrusions. The syenite, in turn, intrudes Proterozoic crystalline basement rocks and Paleozoic–Mesozoic sedimentary sequences.

2.1. Maoniuping

The Maoniuping orefield is hosted by Devonian–Permian argillaceous clastic sediments, limestones and Tertiary talus. Igneous rocks are distributed extensively across the area, and include the Yanshanian granite (which has whole-rock and biotite K–Ar ages of 110–132 Ma, 78–134 Ma, respectively; Xu et al., 2007), an alkaline syenite–carbonatite complex and a Mesozoic rhyolite. REE mineralization occurs in a vein system, dominated by pegmatitic barite and calcite veins (widths >30 cm) and thread veins (<30 cm wide) (Yuan et al., 1995). Barite and calcite veins generally extend for more than 100 m, composed of pegmatitic bastnäsite (3–5%)–aegirine-augite–fluorite (3–32%)–barite and pegmatitic bastnäsite (3–5%)–fluorite (5–11%)–barite–calcite veins, respectively. The pegmatitic barite vein is widely distributed in the deposit, and shows euhedral–subhedral and pegmatitic textures contained within ribbon or taxitic structures. Pegmatitic calcite vein mainly occurs in Guantoushan (Fig. 1) and is characterized by euhedral–subhedral and pegmatitic textures within massive or taxitic structures. Associated thread veins consist of thread bastnäsite–aegirine-augite–barite–calcite–fluorite (<1%) veins, and are generally about 1 m long and are emplaced in the vicinity of the pegmatitic veins. Some of thread veins locally intrude into granite and rhyolite. The REE mineralization is associated with intense late-stage alteration, dominated by aegirine-augite alteration, calcitization, baritization and fluoritization. Fluorite, which appears in purple, green and white, is most common gangue mineral in the deposit. In pegmatitic barite veins, fluorite occurs as taxitic and lumpy aggregates (with 1–10 mm grains) and inhomogeneously distributes between aegirine-augite and barite. In pegmatite calcite veins, fluorite is interstitial to calcite and barite, and irregular in shape. Occasionally, the fluorite occurs as large aggregates (with 1–20 mm grains) associated with aegirine-augite, arfvedsonite, feldspar, quartz and bastnäsite.

K–Ar dating of biotite and magnesio-arfvedsonite from the pegmatite barite vein defines an age range of 31.8 ± 0.7 to 40.3 ± 0.7 Ma, and on magnesio-arfvedonite from the pegmatite calcite vein of 31.7 ± 0.7 Ma, and on biotite from the thread vein of 27.8 ± 0.5 Ma (Yuan et al., 1995; Tian et al., 2008a). These data indicate that the REE mineralization at Maoniuping is Oligocene in age. REE reserves are estimated to be more than 1.45 Mt with grades averaging from 1.04% to 9.05% REE_2O_3 (Yuan et al., 1995). Associated reserves include 0.33 million tons of Pb, 174 tons of Ag, 3.78 million tons of barite and 2.40 million tons of fluorite.

2.2. Lizhuang

The main strata in this area are Devonian and Early Permian carbonate sediments and Triassic carbonate or arenaceous-pelitic sediments, most of which underwent medium–low grade metamorphism. The Yanshanian Mianning granite and Himalayan alkaline syenite–carbonatite complex are emplaced within these sedimentary sequences. The orebodies are composed of small lenses and veins, 30–100 m length and 2–12 m thick (Hou et al., 2009), and intrude both syenite and carbonatite. On the basis of their texture and structure, four types of ores can be recognized: brown disseminated, yellow banded, stockwork and black powder-like (Hou et al., 2009). The brown disseminated and yellow banded ores are dominant in the Lizhuang deposit, and consist of calcite–fluorite–barite–bastnäsite, and calcite–fluorite–barite–biotite–quartz–bastnäsite, respectively. The stockwork consists of fluorite–barite–bastnäsite, and mainly intrudes syenite. Black powder-like ore is composed of aegirine-augite and bastnäsite, and occurs in carbonatite. The brown disseminated ore contains a higher proportion of fluorite (20–25%) and lower bastnäsite (3–6%) than is found in the yellow banded ore (10% and 12% for