

REE Daughter Minerals Trapped in Fluid Inclusions in the Giant Bayan Obo REE-Nb-Fe Deposit, Inner Mongolia, China

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Abstract

The Bayan Obo REE-Nb-Fe deposit hosts the world's largest known REE resource. The deposit consists of replacement bodies hosted in dolomite marble and of magnetite, REE fluorocarbonates, fluorite aegirine, amphibole, calcite, and barite. Three types of fluid inclusions have been recognized: two-phase aqueous liquid-vapor (L-V), two- to three-phase CO₂ (C), and three-phase liquid-vapor-solid (L-V-S) inclusions. Microthermometry measurements indicate that the carbonic phase in C inclusions is nearly pure CO₂. During heating experiments, hexagonal or irregular-shaped daughter minerals in L-V-S inclusions complete dissolution at temperatures of 420–480°C and recrystallize again at about 400–320°C. These show that daughter minerals in multiphase inclusions in mineralizing veins were crystallized from trapped fluids, and are real daughter minerals. REE-carbonates, halite, sylvite, barite, calcite, and pyroxene (?) have been identified on the basis of crystal habit (microscopic and SEM) and EDX analysis. By comparison with Raman spectra of reference REE-carbonate mineral crystals, hexagonal or irregular-shaped daughter minerals in L-V-S inclusions might be cebaite and bastnaesite. The presence of REE-carbonates as an abundant solid in the ore-forming veins shows that the original ore-forming fluids were very rich in REE, and therefore had the potential to produce economic REE ores at Bayan Obo.

Introduction

THE BAYAN OBO REE-Nb-Fe deposit is located approximately 80 km south of the China–Mongolia border, at 109°57'13"E and 41°46'22"N. The deposit hosts the world's largest known rare-earth element (REE) resource (70%), as well as being a major Nb and Fe producer in China. REE reserves in the deposit are 57.4 million metric tons (Mt) with an average grade of 5.17 to 6.19 wt% REE₂O₃; Nb reserves are estimated at 2.2 million Mt with an average grade of 0.126 to 0.141 wt% Nb₂O₅ (Drew et al., 1990; Bai et al., 1996; Hao et al., 2002).

The present study focuses on the investigation and identification of the REE minerals, which occur as solid phases in fluid inclusions from REE-mineralizing veins in the Bayan Obo deposit. Earlier, Smith and Henderson (2000) made a preliminary fluid inclusion study of eight samples from different alteration and mineralizing stages at Bayan Obo, and concluded that REE were at some stages trans-

ported in CO₂-rich fluids, and remained mobile down to a relatively low temperature (<200°C). They did not mention the existence of REE daughter minerals in the fluid inclusions.

The significance of investigating solid phases in fluid inclusions is that they contain elements that were previously present in solution at higher temperatures, and therefore provide us with the means to estimate fluid compositions at the temperature of entrapment. In the case of REE daughter minerals, their presence and high volumetric proportion in fluid inclusions demonstrates REE mineralizing conditions and the ability of ore-forming fluids to carry large amounts of REE, accounting for the mineralization at Bayan Obo.

Geological Setting and Mineralization

The Bayan Obo deposit is contained within sediments of the Middle Proterozoic Bayan Obo Group, which consist predominantly of sandstones and slates, with the exception of the H8 dolomite unit, which hosts the vast majority of the ores (Fig. 1).

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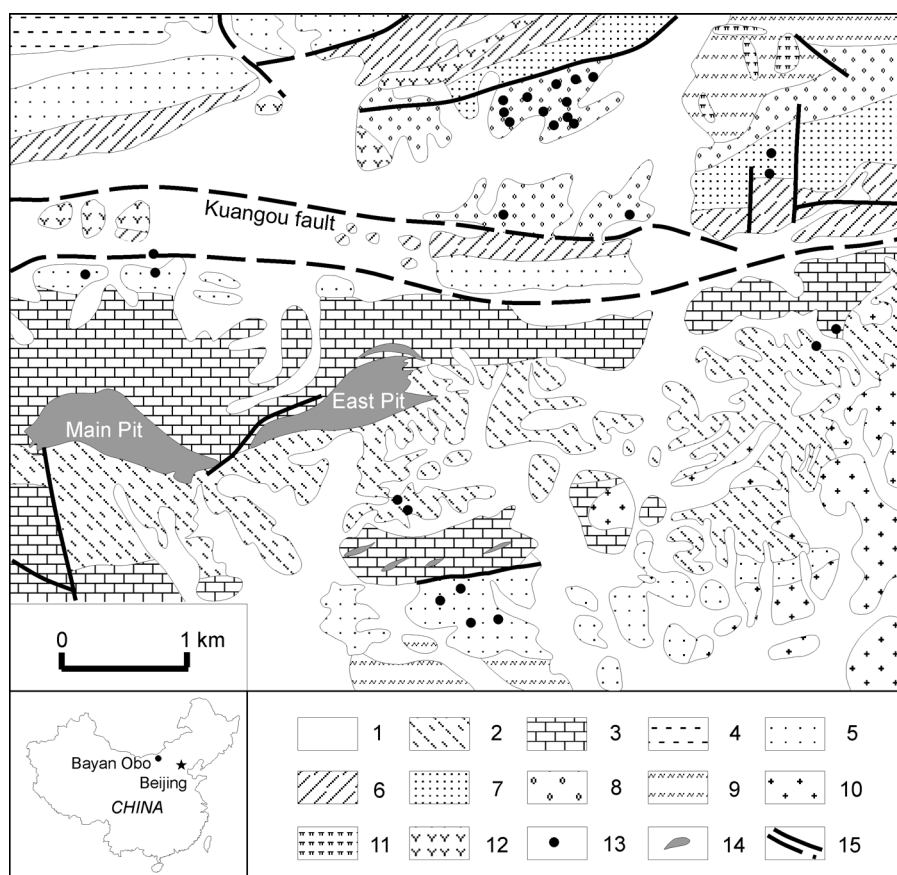


FIG. 1. Geological sketch map of the Bayan Obo REE-Nb-Fe deposit, showing the distribution of carbonatite dikes (outcrops of carbonatite dikes are after Tao et al., 1998). Legend: 1 = Tertiary sediments; 2 = H9 slate of the Bayan Obo Group; 3 = H8 dolomite of the Bayan Obo Group; 4 = H5 dark slate the Bayan Obo Group; 5 = H4 quartzite of the Bayan Obo Group; 6 = H3 slate of the Bayan Obo Group; 7 = H2 white quartzite of the Bayan Obo Group; 8 = H1 quartz conglomerate of the Bayan Obo Group; 9 = basement complex rocks; 10 = Hercynian granite; 11 = alkaline dikes; 12 = basic dikes; 13 = REE-Fe-Nb ore body; 14 = major fault; 15 = outcrop of carbonatite dike.

The origin of the ore-hosting dolomite is still disputed, and it has been proposed to be either sedimentary (Meng, 1982; Chao et al., 1992), or carbonatite related (Le Bas et al., 1992, 1997; Yuan et al., 1992; Yang et al., 2000; Hao et al., 2002; Wang et al., 2002). The paragenesis of the deposit is extremely complex with at least 11 stages ranging from deposition, through metamorphism and mineralisation, to the intrusion of Hercynian granitoids south of the deposit (Chao et al., 1992, 1993, 1997). Th-Pb dates from monazite for REE mineralization range from 555 to ~400 Ma (Wang et al., 1994). At the simplest level, the main-stage banded mineralization (~430 to 420 Ma) shows a generalized

paragenetic sequence of strongly banded REE and Fe ores showing alteration to aegirine, fluorite, and minor alkali amphibole. These rocks are cut by aegirine-rich veins containing apatite, bastnaesite, fluorite and quartz, and later aegirine-rich veins and pods associated with barite, bastnaesite, and Ba-REE-fluorocarbonates. The final stage in REE mineralization is associated with the formation of Nb-bearing minerals such as columbite, ilmenorutile, aeschynite, and fergusonite.

Several possible modes of formation have been proposed for the deposit (reviewed by Wu et al., 1996), including syngenetic sedimentary deposition (Meng, 1982), metasomatism associated with

granitic magmatism (Wang and Li, 1973), and deposition from exhalative, possibly carbonatite-related, hydrothermal fluids (Yuan et al., 1992). Most recently the works of Chao et al. (1992, 1993, 1997) have demonstrated an epigenetic origin for the deposit via multistage hydrothermal metasomatism. On this basis models involving metasomatism by fluids derived from either subduction (Chao et al. 1992, 1997; Wang et al., 1994), or carbonatite, or alkaline, magmatism (Drew et al., 1990; Hao et al., 2002; Yang et al., 2003) have been proposed. The interpretation of the carbonatite source for the metasomatic fluids is supported by the presence of carbonatite dykes (Fig. 1) cutting the sediments to the north and southeast of the deposit and the apparent carbonatitic affinities of the host dolomite (Le Bas et al., 1992, 1997; Yang et al., 2000).

Sample Description and Analytical Techniques

Samples examined in this study were taken from orebodies of the East Pit and the Main Pit at Bayan Obo (Fig. 1). Sample Q-54, from the East Pit, is altered dolomite marble with bands of apatite, monazite, and bastnaesite. The sample shows alteration to fluorite and aegirine, but large amounts of relict dolomite and calcite are still present. Sample Q-58, also from the East Pit, was collected from an undeformed bastnaesite-fluorite-quartz vein, 1 to 2 cm thick, which cuts banded ores similar to those described for sample Q-54. Sample Q-51 is from a bastnaesite-fluorite-quartz vein in the Main Pit.

A variety of optical, crystallographic, X-ray, and spectroscopic methods have been used to identify solids in fluid inclusions (Roedder, 1990) including those associated with carbonatites and related REE deposits (Rankin and Le Bas, 1974; Metzger et al., 1977; Ting et al., 1994; Bühn et al., 1999; Bühn and Rankin, 1999; Williams-Jones et al., 2000; Bühn et al., 2002). After combination of microthermometry and SEM-EDX techniques for a comprehensive geochemical characterization, we apply here confocal Laser Raman spectroscopy for the identification of possible REE daughter minerals compared with reference REE minerals.

Microthermometry

Doubly polished sections (about 200 to 300 μm thick) were prepared for fluid inclusion optical examination and microthermometric analysis. Heating and cooling experiments were carried out using

a Linkam THMS 600 heating/freezing stage at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). The stage was calibrated with pure CO_2 (-56.6°C) and pure H_2O (0°C and 374.1°C) synthetic fluid inclusion standards were supplied by FLUID INC (Bodnar and Sterner, 1987).

SEM-EDX

The sample wafers, which might trap solid daughter minerals in fluid inclusions based on optical examination, were broken, mounted on a gold stub, and placed in a KA-1000B Scanning Electron Microscope (SEM) for examination at IGGCAS. Energy-dispersive X-ray spectrometer analysis (EDX) of solid phases in the inclusions was carried out using a TN5400 detector operated at 25 KV accelerating voltage. The wafers were tilted for each individual mineral analysis to reach an optimal takeoff angle of the emergent X-rays, and to exclude interference with other solid phases in the inclusions and the host minerals. The qualitative detection of elements in the solid phases is from ^{11}Na to ^{92}U .

Laser Raman spectroscopy

Laser Raman spectroscopy was used to check reference REE minerals and to identify daughter minerals in fluid inclusions. Data were obtained using a Renishaw Raman MKI-1000 system equipped with a CCD detector and an Ar ion laser at IGGCAS. The laser beam with a wavelength of 514.5 nm was focused on reference REE minerals and daughter mineral crystals in fluid inclusions through 50 $\times$ and 100 $\times$ objectives of a light microscope.

Results and Discussion

Nature of fluid inclusions

Three types of fluid inclusions have been recognized on the base of their appearance at room temperature: two-phase aqueous liquid-vapor (L-V), two- to three-phase CO_2 (C) (Fig. 2A), and three-phase liquid-vapor-solid (L-V-S) (Fig. 2B) inclusions. L-V inclusions occur in fluorite, quartz, barite, and REE fluorocarbonates, and range up to 20 μm in diameter. Primary L-V inclusions are most abundant in the latest coarse-grained fluorite veins, which cut obviously banded REE and Fe ores. These primary L-V inclusions are related latest fluids. Most

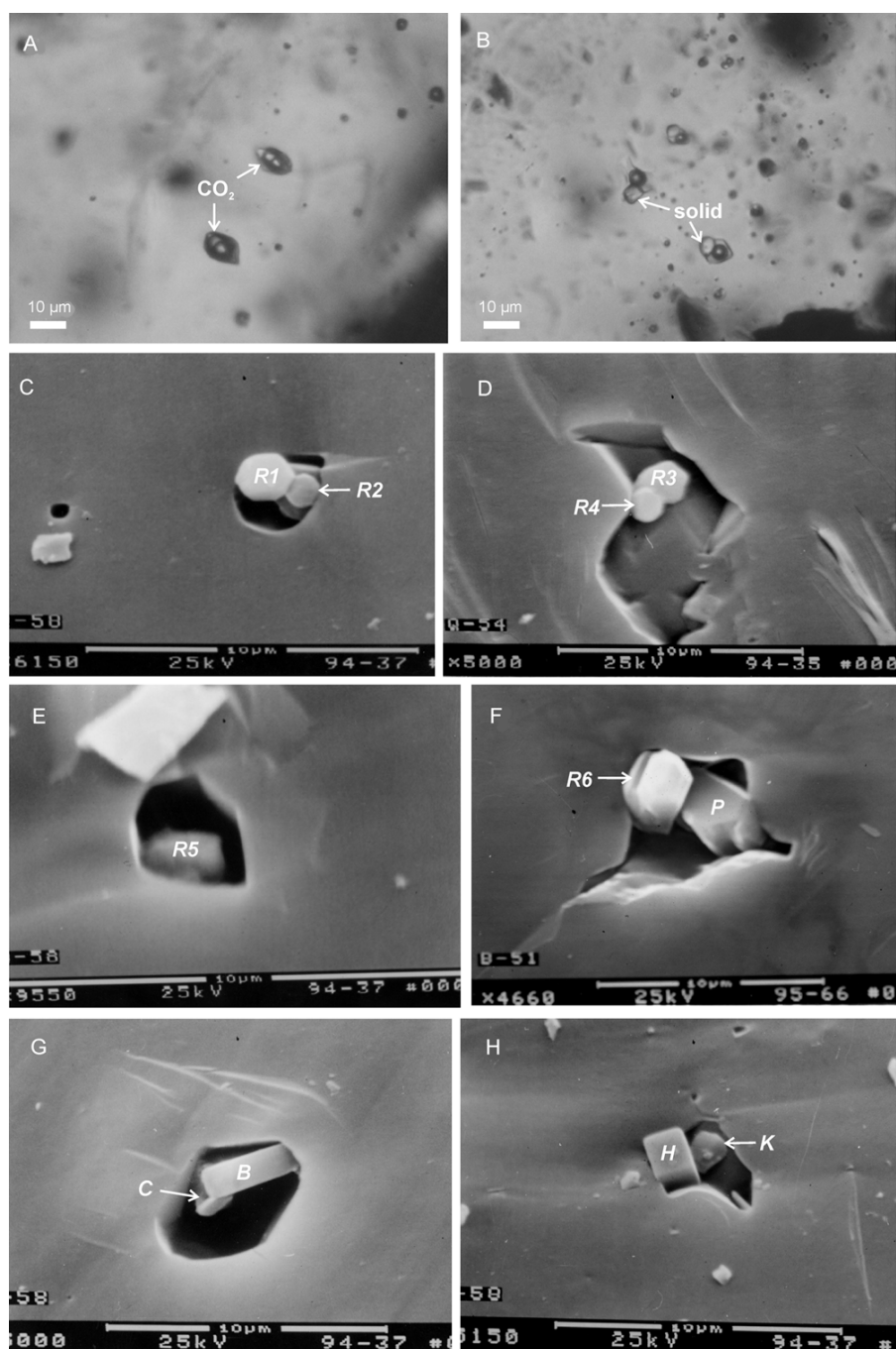


FIG. 2. Photomicrographs showing fluid inclusions and daughter minerals under microscope and SEM. A. CO₂-rich inclusion showing the typical "double bubble" of CO₂ vapor surrounded by CO₂ liquid. B. Daughter mineral-bearing inclusion. C. Typical hexagonal REE daughter minerals. D. Hexagonal shaped REE daughter minerals. E. REE daughter minerals. F. Hexagonal shaped REE and column-shaped pyroxene (?) minerals. G. Barite and calcite. H. Cubic halite and sylvite.

other L-V inclusions in quartz and REE fluorocarbonates occur along secondary planes.

CO₂ inclusions occur as isolated cavities or planar arrays in healed microfractures in fluorite and quartz. The inclusions are generally less than 20 µm in diameter and occur as three phases consisting of an aqueous liquid, a carbonic liquid, and vapor with relatively constant phase ratios. Melting of the carbonic phase (TmCO₂) occurs either at the CO₂ triple point of -56.6°C, or over a small interval with depressed melting temperatures between -57.0 and -56.7°C. These measurements indicate that the carbonic phase in these inclusions is nearly pure CO₂. Melting of the CO₂ clathrate (Tmclath) in the presence of CO₂ liquid occurs between 4.1 and 8.5°C. Partial homogenization (ThCO₂) of CO₂ liquid + CO₂ vapor to liquid CO₂ occurs between 20.2 and 29.5°C. On heating runs, more than one-half of the studied inclusions decrepitated prior to final homogenization, at temperatures from 200 to 280°C. Total homogenization temperatures to liquid, obtained mainly from inclusions with lower CO₂ contents and smaller diameters, range from 250 to 320°C.

L-V-S inclusions are common in samples from the Bayan Obo, and are concentrated mainly in fluorite, but are also found in quartz cores and in REE fluorocarbonates. They occur as isolated inclusions and are primary. During heating experiments, some L-V-S inclusions decrepitated or stretched prior to total homogenization. Only a few of them survived, and the hexagonal or irregular-shaped daughter minerals (REE fluorocarbonates?) were nearly always the last phase to be left in the inclusions. With continuous heating and then cooling, the hexagonal daughter minerals displayed the following three behaviors: (1) complete dissolution at temperatures of 420–480°C (these are also the total homogenization temperatures of the inclusions); (2) recrystallized to one or more new hexagonal daughter minerals at ~400–320°C. Cubic halite, if present, melted from 220 to 250°C during heating and formed again at ~260–280°C on cooling. The homogenization temperatures may represent the temperature of the mineralizing fluid prior to ore deposition.

SEM and energy-dispersive X-ray analysis

Solid phases trapped in the inclusions contain a complex and varied assemblage. The solid phases occur either singularly or, more commonly, in association with others (Figs. 2B–2H). The following have been identified on the basis of crystal habit

(microscopic and SEM) and EDX analysis: REE-carbonates, halite, sylvite, barite, calcite, and pyroxene (?) (Figs. 2C–2H and Fig. 3).

By far the most abundant solids in the inclusions are halite and sylvite (Fig. 2H), as documented by EDX spectra showing the existence of Na, K, and Cl (Figs. 3K–3H). Tabular crystal (B in Fig. 2G) with Ba, Ca, and S peaks (Fig. 3B) is barite, and coexisting lozenge-shape crystal C in Fig. 2G) with only a Ca peak is calcite. In one inclusion (Fig. 2F), a daughter crystal of an Mg-, Si-, Ca-, and Fe-bearing phase (Fig. 3P), possibly pyroxene (?), was observed.

SEM images exhibit typical hexagonal daughter minerals (Figs. 2C–2F). Figure 3(R1–R6) shows an energy-dispersive spectrum of these crystals with distinct peaks for La, Ce, Nd, and Ca, Mg, Fe. It is clear that these minerals are REE-carbonates.

Identification by Laser Raman spectroscopy

No standard Raman spectroscopy data exist for REE-fluorocarbonates. Thus, identification of REE-carbonates by Laser Raman spectroscopy is difficult. Three typical rare-earth fluorocarbonate minerals (cebaite, parisite, and bastnaesite), collected from Bayan Obo and confirmed by X-ray power, were used as reference materials for the REE-carbonate mineral crystals.

Figure 4 depicts Raman spectra of these reference materials, fluorite, and two daughter mineral crystals in fluid inclusions in fluorite and quartz. The reference REE fluorocarbonate minerals all show vibration frequency of CO₃²⁻ (~1090cm⁻¹) and F⁻ (at 260 to 470cm⁻¹, typically at 323cm⁻¹). The host mineral of the hexagonal daughter mineral Q58-y is fluorite. Compared with Raman peaks (Fig. 4), the spectra of Q58-y are very similar to those of fluorite. But a sharp peak at 1090cm⁻¹ may reflect the vibration frequency of CO₃²⁻. Obscured by fluorite Raman peaks, the other Raman peaks of Q58-y have not been distinguished. From crystal shape and compared with Raman spectra of reference REE-carbonate mineral (Fig. 4), the daughter mineral Q58-y might be cebaite (Ba₃Ce₂(CO₃)₅F₂). Under a light microscope, daughter mineral Q58-s is irregular in shape, and the host is quartz. The Raman spectra of Q58-s are similar to those of reference bastnaesite. Interference by the typical vibration frequency of quartz at 463cm⁻¹ is shown in the Raman spectra of Q58-s; the inclusion might be identified Q58-s as bastnaesite ((Ce, La)CO₃F).

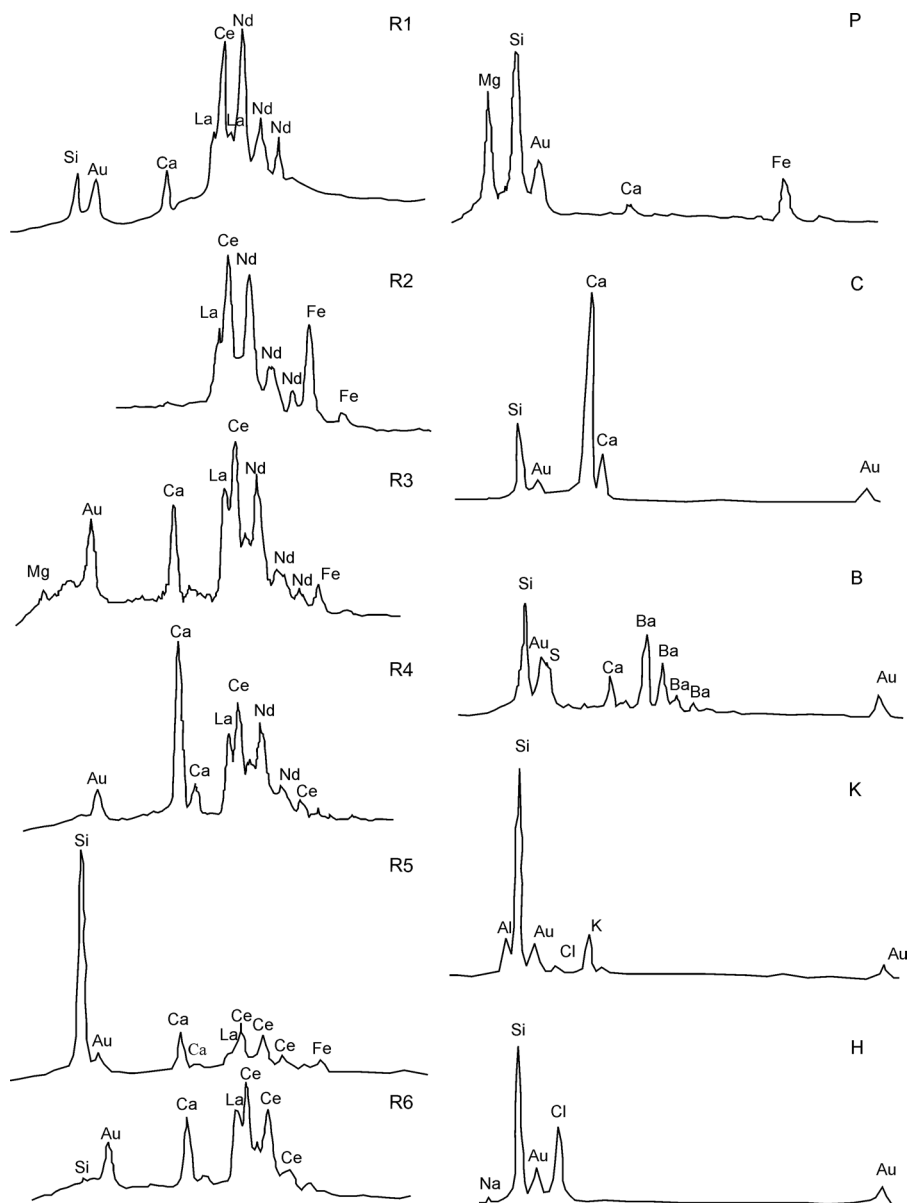


FIG. 3. Energy-dispersive spectra (EDX) of daughter minerals in opened fluid inclusions. Note the Si from the host quartz and Au from plating.

Conclusions

1. SEM-EDX and Raman spectroscopy of rare-earth daughter minerals in fluid inclusions shows that these minerals might be bastnaesite and cebaite. Microthermometry measures show that REE daughter minerals in multiphase inclusions in

mineralizing veins were crystallized from trapped fluids, and are real daughter minerals.

2. The presence of REE-carbonates as an abundant solids in the ore-forming veins shows that the ore-forming fluids were very rich in REE, and therefore had the potential to produce economic REE deposits at Bayan Obo without requiring large-scale convective fluid

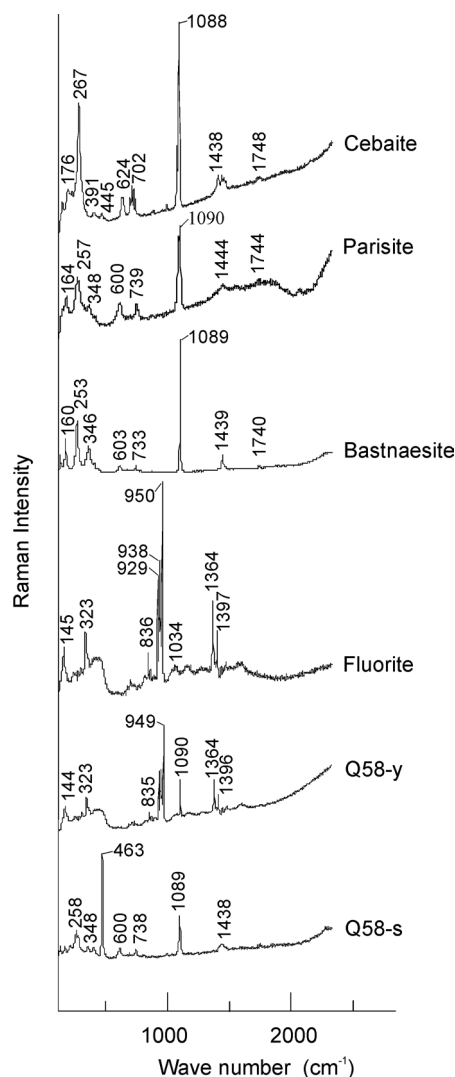


FIG. 4. Laser Raman spectra of the typical REE fluorocarbonate mineral, fluorite, and rare-earth daughter minerals in unopened fluid inclusions at Bayan Obo.

systems and high water-rock ratios typically envisaged for other magmatic-hydrothermal ore-forming environments (e.g., Hedenquist and Lowenstein, 1994).

3. Laser Raman spectrometry can be used as a reliable tool to identify unknown daughter minerals hosted in fluid inclusions when combined with mineral shapes and SEM-EDS analyses.

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