ORIGINAL ARTICLE

Carbonatites in China: A review for genesis and mineralization

Cheng Xu [a,*], Linjun Wang [b,c], Wenlei Song [a], Min Wu [b,c]

[a] *Laboratory of Orogenic Belts and Crustal Evolution, Peking University, Beijing 100871, China*
[b] *Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China*
[c] *Graduate School, Chinese Academy of Sciences, Beijing 100039, China*

Abstract   Carbonatites are commonly related to the accumulation of economically valuable substances such as REE, Cu, and P. The debate over the origin of carbonatites and their relationship to associated silicate rocks has been ongoing for about 45 years. Worldwide, the rocks characteristically display more geochemical enrichments in Ba, Sr and REE than sedimentary carbonate rocks. However, carbonatite's geochemical features are disputed because of secondary mineral effects. Rock-forming carbonates from carbonatites at Qinling, Panxi region, and Bayan Obo in China show REE distribution patterns ranging from LREE enrichment to flat patterns. They are characterized by a Sr content more than 10 times higher than that of secondary carbonates. The coarse- and fine-grained dolomites from Bayan Obo H8 dolomite marbles also show similar high Sr abundance, indicating that they are of igneous origin. Some carbonates in Chinese carbonatites show REE (especially HREE) contents and distribution patterns similar to those of the whole rocks. These intrusive carbonatites display lower platinum group elements and stronger fractionation between Pt and Ir relative to high-Si extrusive carbonatite. This indicates that most intrusive carbonatites may be carbonate cumulates. Maoniuping and Daluxiang in Panxi region are large REE deposits. Hydrothermal fluorite ore veins occur outside of the carbonatite bodies and are emplaced in wallrock syenite. The fluorite in Maoniuping has Sr and Nd isotopes similar to carbonatite. The Daluxiang fluorite shows Sr and REE compositions different from those in Maoniuping. The difference is reflected by both the carbonatites and rock-forming carbonates, indicating that REE mineralization is

related to carbonatites. The cumulate processes of carbonate minerals make fractionated fluids rich in volatiles and LREE as a result of low partition coefficients for REE between carbonate and carbonatite melt and an increase from LREE to HREE. The carbonatite-derived fluid has interacted with wallrock to form REE ore veins. The amount of carbonatite dykes occurring near the Bayan Obo orebodies may support the same mineralization model, i.e. that fluids evolved from the carbonatite dykes reacted with H8 dolomite marble, and thus the different REE and isotope compositions of coarse- and fine-grained dolomite may be related to reaction processes.

1. Introduction

Carbonatites are defined in the IUGS system of classification as igneous rocks composed of more than 50 modal per cent primary (magmatic) carbonate and containing less than 20 wt.% SiO_2 (Le Maitre, 2002). Varieties of carbonatite are named on the basis of the dominant carbonate mineral, e.g. calciocarbonatite, magnesiocarbonatite, and ferrocarbonatite (Woolley and Kempe, 1989). Rocks now known as carbonatites were originally described by Bose (1884) in the Lower Narbada Valley of India. Brøgger (1921) found the same type of rocks associated with alkaline complexes at Fen, Norway, and suggested a magmatic origin for them. However, many geologists did not accept this origin and viewed carbonatites as merely megaxenoliths of sedimentary material. Carbonatite did not attract the attention of geologists until extrusive natrocarbonatite lava was found at Oldoinyo Lengai volcano, Tanzania, in 1960. There are now more than 500 known occurrences of carbonatites. They have been found on all continents except for Antarctica and at two oceanic localities (e.g. Bell, 1998). Most carbonatites occur in rift environments, such as the East African Rift, although some carbonatites have been found in orogenic belts as well (Xu et al., 2007a). Over the last 50 years, the study of carbonatites has progressed significantly both in terms of experimental and isotopic studies. Experimental studies of synthetic carbonated upper mantle source-rocks have led to insights into the genesis of primary carbonatitic magmas, and those of carbonated nephelinite compositions heralded the promotion of liquid immiscibility as a potential explanation for carbonatite genesis (Koster van Groos and Wyllie, 1963; Kjarsgaard and Hamilton, 1989). Isotopic studies have confirmed that asthenospheric or lithospheric mantle sources (or both) have played a role in the genesis of many carbonatites (Marty et al., 1998; Bell and Tilton, 2001). Carbonatites can provide valuable information on the composition of mantle because: (1) their isotopic ratios are inherited from the mantle source, aided by very high Sr and Nd concentrations (Bell and Blenkinsop, 1987; Nelson et al., 1988); and (2) they have low viscosities (Treiman, 1989), ensuring a rapid ascent to the surface (Williams et al., 1986).

Most carbonatites occur with alkalic silicate rocks as flows, plugs, dykes, cone sheets, and sills. According to the summary by Bell (1998), the associations include: (a) carbonatite−nephelinite−phonolite, e.g. Napak, Uganda; Oldoinyo Lengai, Tanzania; (b) carbonatite−melilitolite, e.g. Oka, Canada; Kovdor, Russia; the Turiy Complex, Russia; (c) carbonatite−pyroxenite, e.g. Phalaborwa, South Africa; (d) carbonatite−syenite, e.g. Chilwa Island, Malawi; Khibina, Russia; Siilinjarvi, Finland; Panxi region, China; and (e) carbonatite−lamprophyre, e.g. Kandalaksha, Russia; northwest Namibia. Nevertheless, the petrogenesis of carbonatites remains controversial. There are several principal hypotheses identifying various processes which

may be responsible for the creation of this rock type: (1) direct melting of a carbonate-bearing mantle source (e.g. Sweeney, 1994; Harmer and Gitiins, 1998; Srivastava et al., 2005); (2) generation as immiscible liquids from CO_2-rich silicate magmas (e.g. Koster van Groos and Wyllie, 1963; Kjarsgaard and Hamilton, 1989); (3) products of extensive crystal fractionation from a CO_2-rich silicate magma (e.g. Lee and Wyllie, 1994; Veksler et al., 1998a). In addition, some of the best known, or potential, ore deposits for Cu, Nb, REE, Mo, fluorite, phosphate, and vermiculite are associated with carbonatites. They include the virtually 'inexhaustible' Nb reserves of Araxa; the bastnäsite deposit of Mountain Pass, Bayan Obo; and the Cu and multicommodity deposit of Phalaborwa, South Africa. Mariano (1989) has described some typical examples of ore deposits in carbonatites. A rare Mo deposit associated with carbonatites was found in Qinling (Xu et al., 2010b). Carbonatites contain the highest concentration of REE of any igneous rock, and are therefore good targets for REE exploration. However, the genesis of the world's largest REE deposit related with carbonatites, Bayan Obo, is still disputed (e.g. Chao et al., 1992; Yuan et al., 1992).

It should be noted that the above petrogenesis hypotheses were founded upon the study of carbonatites from rifting settings. It is not clear whether they can be used to explain the origins of carbonatites formed in orogenic settings. Therefore, in this paper, we review the carbonatite studies of Huayangchuan (HYC) and Huanglongpu (HLP) in the Qinling orogenic belt. The geochemical studies of carbonatites from REE deposits at Maoniuping (MNP), Daluxiang (DLX), and Bayan Obo (BY) are also reviewed.

2. Geological settings

2.1. Huayangchuan and Huanglongpu

The HYC and HLP carbonatites occur as dykes in the north border margin of the Qinling Orogenic belt, which is also called the Lesser Qinling (Fig. 1). The detailed geological framework and tectonic evolution of the Qinling region have been described by Xue et al. (1996), Meng and Zhang (2000), Ratschbacher et al. (2003), and Chen et al. (2009). Yu (1992) and Xu et al. (2007a) described the mineralogy of carbonatites from both HYC and HLP locations. Their carbonatite dykes are mostly composed of coarse, generally euhedral grains of calcite (>90%), with individual crystals typically 0.8−2.6 mm in size. Minor and accessory phases include microcline, aegirine-augite, arfvedsonite, phlogopite, quartz, celestite, barite, magnetite, sulphides, bastnäsite and apatite; there is a little difference in mineral compositions. At HLP, the rock contains minor amounts of molybdenite, and the calcite is pink. Rarely, radioactive minerals such as liandratite and
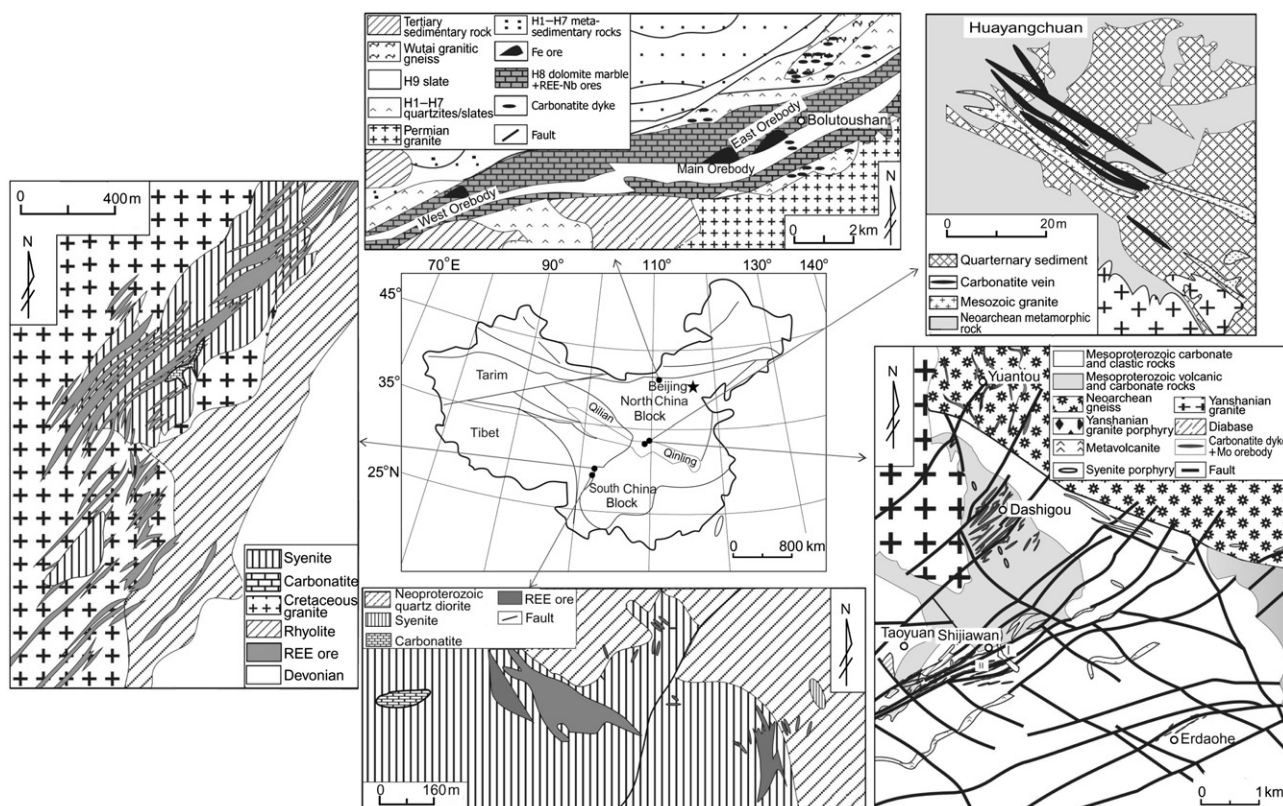
Figure 1   Geological sketch of the Huayangchuan, Huanglongpu, Daluxiang, Maoniuping and Bayan Obo carbonatites. Modified after Xu et al. (2007a, 2008b, 2010b).

thorite are found in the HYC carbonatite dykes. In both locations very-coarse quartz is irregularly distributed at the margin of the carbonatite dykes. Field observation indicates that the quartz mass was penetrated and broken during late emplacement of the carbonatite dyke. Minor syenite and syenite porphyry were found, but they are not closely associated with the carbonatites in space.

2.2. Maoniuping and Daluxiang

The DLX and MNP deposits are located on the northwest and central margin of the Panxi (Panzhihua-Xichang) region, respectively (Fig. 1). Their detailed geological framework and the tectonic evolution of this region have been described by Zhang et al. (1988). The two deposits have been studied by Yuan et al. (1995), Xu et al. (2003b, 2008b), and Hou et al. (2008). Xu et al. (2003a) and Hou et al. (2006) studied the petrogenesis of the carbonatites. The MNP carbonatite was emplaced as a sill and intrudes syenite. It is mainly composed of coarse-grained calcite (>1 mm) with minor and accessory microcline, aegirine, arfvedsonite, biotite, apatite, and bastnäsite-(Ce). K−Ar dating of the arfvedsonite gave an age of 31.7 ± 0.7 Ma for the MNP carbonatites (Pu, 2001). The DLX carbonatite intrudes syenite as dykes. The rock is medium- to coarse-grained, and consists of calcite and subordinate microcline, quartz, arfvedsonite, barium-rich celestine, strontiobarite, fluorite, aegirine, apatite, fluorocarbonates, monazite, and sulfides. Its zircon U−Pb age is 12.99 ± 0.94 Ma (Tian et al., 2008). Note that neither of the carbonatite bodies (DLX, MNP) contains abundant REE minerals (Xu et al., 2008b). Their orebodies mainly form as hydrothermal fluorite and barite veins emplaced into syenites. At Maoniuping, the orebodies are

divided into three groups according to their characteristic mineral associations (Yuan et al., 1995); (1) pegmatitic bastnäsite-(Ce) − aegirine-augite − fluorite − barite veins (barite veins) (>30 cm wide); (2) pegmatitic bastnäsite-(Ce) − fluorite − barite − calcite veins (calcite veins); and (3) thread bastnäsite-(Ce) − aegirine-augite − fluorite − barite − calcite veins (thread veins) (<30 cm wide). Barite and calcite veins generally have lengths more than 100 m and contain 0.5−5 wt% REE_2O_3. The thread veins are generally about 1 m long and are emplaced around the pegmatitic veins. Reserves of REE_2O_3 are estimated to be more than 1.45 million ton. Associated reserves include 0.33 million ton of Pb, 174 ton of Ag, 3.78 million ton of barite, and 2.40 million ton of fluorite. At DLX, the orebodies are also divided into three groups (e.g. Li, 2005): (1) pegmatitic bastnäsite-(Ce) − aegirine-augite − fluorite − strontiobarite veins (strontiobarite veins); (2) pegmatitic bastnäsite-(Ce) − aegirine-augite − fluorite − barium-rich celestine veins (barium-rich celestine veins); and (3) thread bastnäsite-(Ce) − aegirine-augite − strontiobarite − calcite veins (thread veins). The reserve of REE_2O_3 in the DLX deposit has not yet been estimated.

2.3. Bayan Obo

The BY deposit in Inner Mongolia is the largest REE deposit in the world. It is situated in the transitional zone between the platform and the Mongolian-Hercynian fold belt (109°59′E; 41°48′N). Basement strata in the region consist of the Proterozoic Wutai and Bayan Obo Groups. The deposit is hosted by the Bayan Obo group, which has been subdivided into nine lithological units, H1−H9 in ascending order (e.g. Bai and Yuan, 1985). With the exception of

H8, all consist predominantly of meta-sandstones and slates. The H8 is mainly composed of fine- and coarse-grained dolomitic marble and it is the dominant ore-bearing unit with an east−west length of 18 km. The stratiform ore body is spindle-shaped, widening in the middle (>1 km) and thinning its ends (Fig. 1). On the basis of textures and structures, three types of BY ore can be recognized: disseminated, banded, and massive. Disseminated carbonate-hosted ores range from 3 wt% to 6 wt% REE_2O_3. Banded ores commonly range from 6 wt% to 12 wt% REE_2O_3. In contrast, massive ores generally have <3 wt% REE_2O_3 (Chao et al., 1992). Fluorite, apatite and aegirine are the main gangue minerals. The BY deposit has estimated reserves of 600 million ton of iron oxides (Yuan et al., 1992) and in excess of 100 million ton of REE oxides (Ren, 1985). Despite much research on the mineralogy and geochemistry of the deposit (e.g. Campbell and Henderson, 1997; Smith et al., 2000; Yang et al., 2009), the origin of the ore deposit continues to be highly disputed.

3. Discussion

3.1. Magmatic vs. hydrothermal origin

At Lesser Qinling, carbonatites are intruded into the late Archaean to Mesoproterozoic basement in the form of veins. They contain substantial quantities of coarse quartz, and are not spatially associated with Qinling alkalic silicate rocks. Therefore, they are looked upon as hydrothermal veins (metamorphic, sea water, or meteorological water origin). A similar viewpoint has been used to explain the H8 dolomite marble in BY. Where the evidence for a sedimentary origin of the H8 marble listed by Chao et al. (1992) includes: (a) that the massive mid-Proterozoic dolomite rock occurs, between shales on top and quartzites, shales and lime-stones below; (b) that it is apparently stratiform, being 18 km along strike and more than 1 km thick; (c) detrital apatite and quartz occur in the marble, and clusters of apatite and magnetite crystals show elongation and parallelism to apparent stratification; (d) that the cathodoluminescent properties of the apatite have been interpreted to indicate a sedimentary origin; (e) some coarse-grained unmineralized carbonates contain low (400−800 ppm) REE contents (high REE concentrations in H8 marble are due to the presence of monazite); and (f), most C and O isotopes of H8 marbles show large variability similar to those of sedimentary origin.

It has been noted that not all carbonatites are associated with alkalic silicate rocks, and in some cases typical igneous minerals are also absent. Therefore, it is difficult to judge carbonatite genesis solely through field observation. A geochemical parameter is necessary to supplement field observations. It is accepted that carbonatites contain the highest LREE contents of all rocks. The total REE content in sedimentary carbonates rarely exceeds 200 ppm (Veizer et al., 1992; Calvo et al., 1995; Nothdurft et al., 2004), but this may not be a typical feature for all carbonatites. Carbonatites reported worldwide have widely variable REE contents ranging from ∼500 to >10,000 ppm. Coarse-grained dolomite marble in BY is a case in point, and contains relatively low total REE compositions (Fig. 3). Importantly, high REE compositions in whole rocks may be due to the suspected presence of secondary REE minerals. Secondary hydrothermal activities would lead to high C−O isotopic compositions. Carbonate minerals obviously dominate the composition of carbonatites. Thus, in situ analyses of carbonate minerals may provide

important information regarding their petrogenesis. Fig. 2 shows average trace element compositions of carbonatites worldwide, as well as HYC, HLP, MNP, DLX, and BY carbonatites and their rock-forming carbonate minerals. The latter have been determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). In addition, carbonate minerals from Miaoya (MY) and Shaxiongdong (SXD) in South Qinling, China are compared. Ferrocarbonatite has higher Th and LREE contents than calcio-carbonatite and magnesiocarbonatite. The calcites from Lesser Qinling carbonatites have lower Zr, Nb, Ta, Th, and U contents than the LA-ICPMS detection limits. In the Panxi region, Rb, Zr, Nb and Th compositions range from low detection limits to <1 ppm. The BY dolomites have slightly high levels of Nb. Similarly, the MY and SXD calcites have Rb, Zr, Nb, Ta and Th contents ranging from low detection limits to close to primary mantle values. Barium content in these carbonate minerals is variable, and content lower than the mantle value is characteristic of HYC. Note that all of carbonate minerals have high Pb and Sr abundances of ∼100 to >100 times mantle values, or close to that of whole rock carbonatites. Focusing on REE (Fig. 3), carbonate minerals from Panxi region and BY show high REE contents ranging from 70 to 600 times the chondritic value for La, to 50−100 times the chondritic value for Yb, and steep distribution patterns. In contrast, the calcite from Lesser Qinling has lower LREE (La 100−900 times the chondritic value) and higher HREE (Lu 150−400 times the chondritic value) contents. They are characterized by relatively flat REE patterns. The low REE compositions are determined for MY and SXD calcites, whose La abundance ranges from 6 to 30 ppm and 17−150 ppm respectively.

Sedimentary carbonates are characterized by low Sr and low total REE (<200 ppm and <25 ppm, respectively; Veizer et al., 1992; Nothdurft et al., 2004). Typical sedimentary carbonates in BY also have similarly low Sr and total REE contents (129−165 ppm, 20 ppm, respectively; Le Bas et al., 1997; Yang and Le Bas, 2004). It is clear that all carbonate minerals from the carbonatites described in China have quite high Sr content (>2000 ppm), as do most carbonate minerals from other carbo-natites in the world (>2000 ppm; Hornig-Kjarsgaard, 1998). Therefore, the Sr content in carbonate mineral is an alternative geochemical parameter that can be used to judge carbonatite origin.

3.2. Chemical compositions of whole rock

The genesis of carbonatite remains a contentious topic. Silica-te−carbonate liquid immiscibility has often been proposed as a possible mechanism. The separation of carbonatite immiscible liquids from carbonated silicate melts has been demonstrated experimentally in many synthetic silicate−carbonate systems (Hamilton et al., 1989; Jones et al., 1995; Veksler et al., 1998b). In such experiments, most of the REE, Pb, Nb, Th, and U are par-titioned preferentially into silicate liquids, whereas La, Sr, and Ba are strongly partitioned into carbonate liquid. Some researchers, thus view the petrogenesis of carbonatites and associated silicate rocks by a comparison of their chemical compositions (e.g. Srivastava and Sinha, 2004; Hou et al., 2006). It is unreasonable to depend upon the whole rock chemical compositions of carbo-natites to determine their petrogenesis. For example, the parental carbonatite liquids contain alkalis, which is evidenced by the fact that almost all carbonatites are surrounded by aureoles of alkali
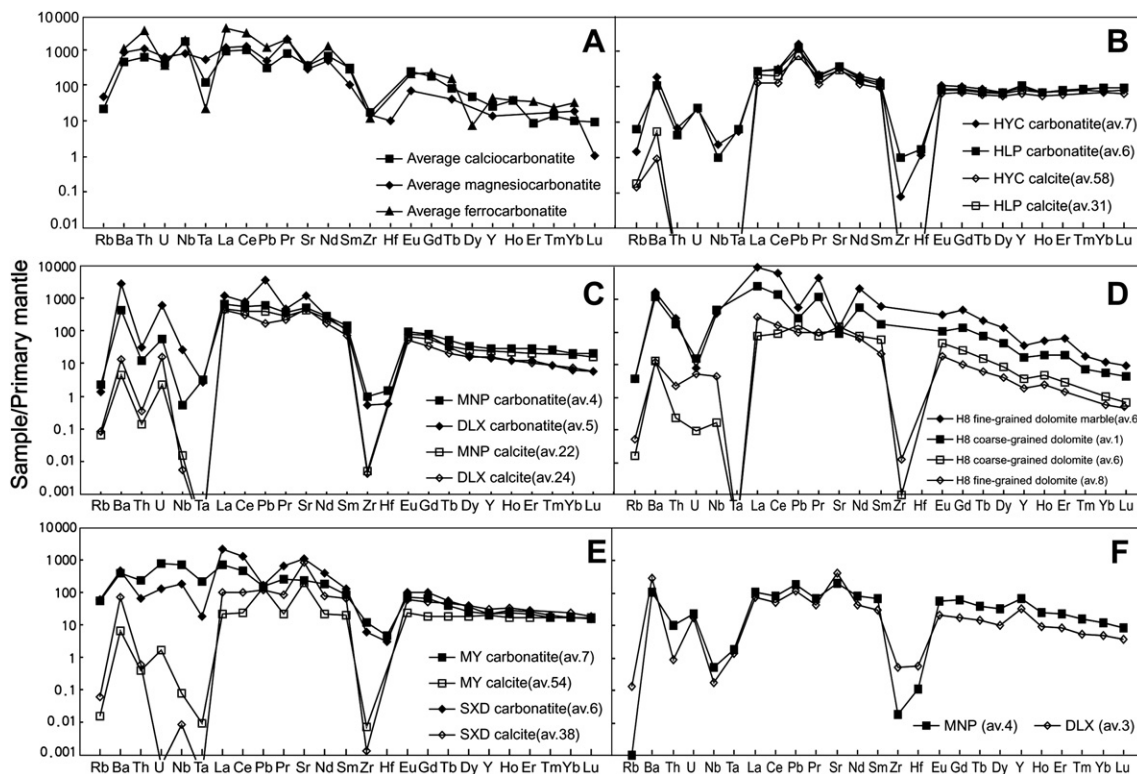
Figure 2 Primitive mantle-normalized trace element abundances of carbonatites and average carbonate minerals (A−E) and Daluxiang, Maoniuping fluorites (F). The data for average carbonatite worldwide (A) are from Woolley and Kempe (1989); for Huayangchuan (HYC) and Huanglongpu (HLP) from Xu et al. (2007a); for Daluxiang (DLX), Maoniuping (MNP) and Bayan Obo (BY) from Xu et al. (2008b); for Shaxiongdong (SXD) and Miaoya (MY) from Xu et al. (2008a, 2010b). The average fine- and coarse-grained dolomite marbles in Bayan Obo are from Xiao et al. (2003). Normalization values are from McDonough and Sun (1995).

metasomatized country rocks (fenites). A wide range of elements have thus been added to (or subtracted from) the country rocks. Therefore, the analysis of a crystallized intrusive carbonatite is not likely to approximate the compositions of its parental liquid.

When carbonate minerals are compared with whole rocks they show similar REE patterns (except for that of coarse-grained dolomite; Fig. 3). Calcites in the Lesser Qinling and Panxi region carbonatites have high REE contents, close to those of the whole
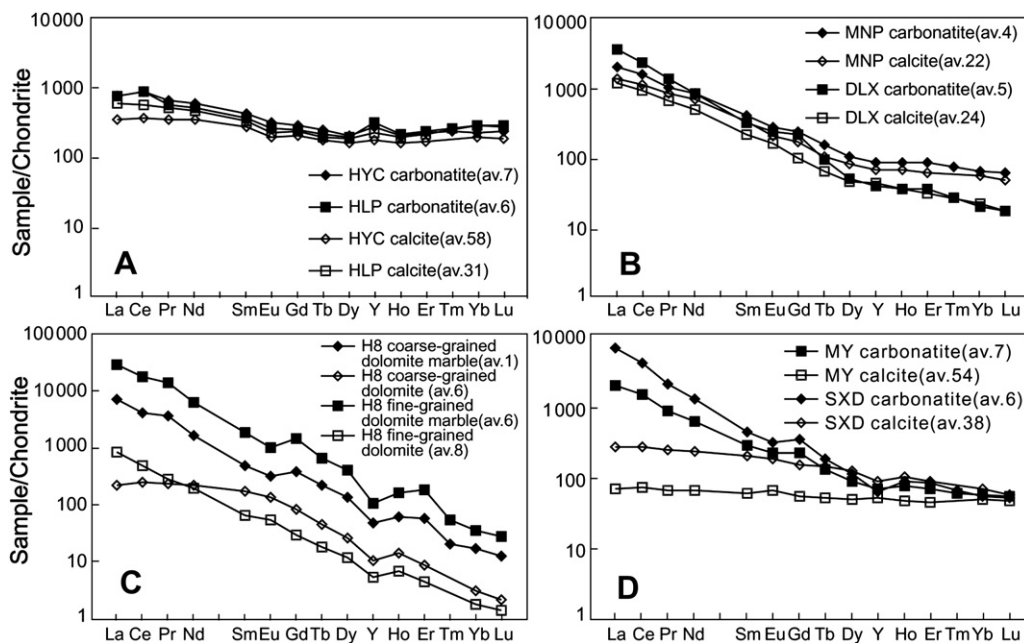

Figure 3 Chondrite-normalized REE abundances of carbonatites and average carbonate cores (C−F). Date sources and normalization values as in Fig. 2.

rocks. It is therefore clear that the REE compositions of these carbonatites do not represent melts because the calcites have the same REE concentrations as their associated whole rocks. These carbonatite compositions can only represent magmas if the carbonate mineral/melt partition coefficients (D) of all REE are ~1, which is unlikely. Furthermore, the $CaCO_3$ content (~90%) in the Lesser Qinling and Panxi region carbonatites is too high to represent a calciocarbonatite magma generated after metasomatism of wallrock lherzolite. The latter process would produce carbonate liquids containing no more than 75−87% $CaCO_3$ (Dalton and Wood, 1993). Thus, the carbonatites may be interpreted to be calcite-rich cumulates (e.g. Woolley and Church, 2005; Xu et al., 2007a). Similar conclusions can be drawn from a platinum group element (PGE) study of carbonatites by Xu et al. (2008c).

Concentrations of PGE in the intrusive carbonatites in Lesser Qinling, Panxi region, and South Qinling, as well as extrusive carbonatites in Lixian, China, are shown as primary mantle-normalized abundances in Fig. 4. The carbonatites have low total PGE concentrations ranging from 0.07 to 2.5 ppb. Their primary mantle-normalized patterns show a positive trend with enrichment in Pd relative to Ir (Fig. 4). The intrusive carbonatites are characterized by low Ni, Cu and Ir contents. Some carbonatites in the Panxi region have positive Pt anomalies, and in South Qinling show relatively low $(Pt/Ir)_N$ ratios among intrusive samples. Note that they do not on the whole show obvious differences in PGE compositions, although these intrusive carbonatites were emplaced in different tectonic settings and ages, and have different isotopic compositions. In contrast, the extrusive carbonatites show relatively higher Cu, Ni, and Ir abundances. However, the Si-rich sample has relatively higher PGE compositions, and no fractionation between Pt and Ir on the primary mantle-normalized plots ($(Pt/Ir)_N = 1.1$), relative to the Si-poor sample. The latter, in general, has a similar PGE concentration and distribution pattern to the intrusive carbonatites. Xu et al. (2008c) roughly modeled the PGE compositions of carbonatite parental melt. The modeled melt shows similar Ir, Ru, Rh, and slightly different Pt compositions to Si-rich intrusive carbonatite, except for Pd. This indicates that the silicate-rich extrusive carbonatites may approximate the compositions of the magmas from which they are derived because of their strongly energetic environment of emplacement and abundant silicate phase mantle materials. Both intrusive and silicate-poor extrusive carbonatites may experience different degrees of fractionation or segregation of PGE-rich phases during the ascent or emplacement of magmas,
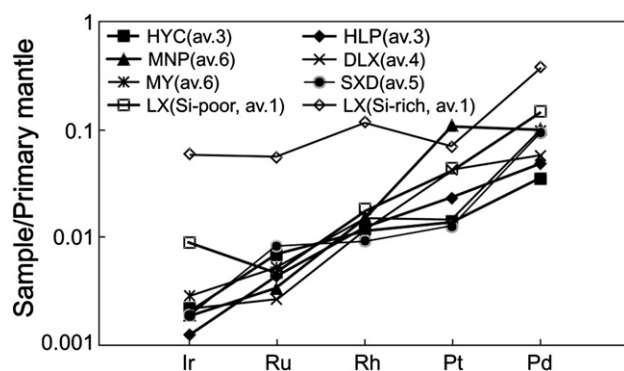
which leads to a depletion in PGE and Pt fractionation from Ir. Therefore, most chemical analyses of intrusive and silicate-poor extrusive carbonatites do not represent the compositions of the primary liquids from which they are derived.

3.3. REE mineralization

Economic deposits of REE are particularly topical at the moment because the world has awakened up to the fact that China dominates the market for the elements used in many high technology and sensitive applications. There is, therefore, likely to be interest from readers in a paper dealing with the behavior of REE in a rare earth-rich carbonatite. Mariano (1989) suggested that the REE mineralization in carbonatites can be classified into three categories, i.e. magmatic, hydrothermal, and supergene mineralization. This conclusion is vague and general, and does not clearly explain why and how carbonatites have formed REE deposits. Carbonatite contains the highest concentration of REE of any igneous rock, and is, therefore, a good target for REE exploration. However, these concentrations are usually small in volume and only a few economic deposits have been found, including Mountain Pass, USA (e.g. Mariano, 1989), Tundulu and Kangankunde in Malawi (e.g. Wall and Mariano, 1996), and Bayan Obo (e.g. Ren, 1985), Maoniuping (e.g. Yuan et al., 1995), and Daluxiang (e.g. Li, 2005) in China. The largest production and economic values in carbonatites result from apatite mining in Europe, Brazil, and South Africa, followed by Cu mining from Phalaborwa (Mariano, 1989). Various origins of the disputed BY deposit have been proposed with models involving fluids derived from carbonatite or alkaline magmatism (Yuan et al., 1992; Campbell and Henderson, 1997; Smith et al., 2000; Fan et al., 2006; Smith, 2007), subduction (Wang et al., 1994), A-type granite magmatism (Chao et al., 1997), or anorogenic magmatic-hydrothermal replacement relative to Proterozoic volcanic rocks (Wang et al., 2003). The MNP and DLX are large REE deposits and associated with carbonatites. Thus, comparison of the two carbonatitic REE deposits with BY can provide important information on the REE mineralization.

3.3.1. Fluorite guide

At MNP and DLX, fluorite (CaF_2) is one of main gangue minerals, and occurs in all orebodies. Because of the geochemical coherence of Ca and Sr, and because Ca is the main component in fluorite, the mineral contains quite high Sr content and low Rb/Sr ratios. Therefore, the fluid $^{87}Sr/^{86}Sr$ ratios from which fluorite precipitates can be defined (Ruiz et al., 1985; Ruiz and Richardson, 1988; Xu et al., 2001a; Sallet et al., 2005). The behavior of REE at elevated temperatures has been investigated theoretically and experimentally by Wood (1990), Haas et al. (1995) and Migdisov and Williams-Jones (2007). According to their data, F forms the strongest complexes with REE. The analytical data have shown that fluorite strongly concentrates REE and records the REE patterns of the liquids from which it crystallized (Xu et al., 2001b). Nd sources can be traced by comparing initial $^{143}Nd/^{144}Nd$ ratios between fluorite and potential Nd sources at the time of mineralization (Galindo et al., 1994, 1997; Simonetti and Bell, 1995). Therefore, Williams-Jones et al. (2000) suggested that the occurrence of fluorite was an excellent exploration guide for REE-fluorocarbonate mineralization in environments where alkaline igneous rocks or carbonatites have been emplaced. Although the fluorites at MNP have different colors and REE distribution patterns, they show consistent ε_{Sr} (22.2−25.2) and ε_{Nd} (−4.3 to −3.7) values (Xu et al., 2003b), which differ from nearly granites

Figure 4 Primary mantle-normalized PGE concentrations of carbonatites. Date sources are from Xu et al. (2008c) and normalization values as in Fig. 2.

(initial $^{87}Sr/^{86}Sr$ = 0.725747−0.787815, ε_{Nd} = −2.7 to 1.6; Xu et al., 2007b) in the ore area, but resemble the carbonatites (ε_{Sr} = 22.8−24.0, ε_{Nd} = −4.25 to −3.72; Xu et al., 2003a). Presently, the Sr and Nd isotopic compositions of fluorites at Daluxiang have been not reported. Note that the carbonatites and calcites in DLX show higher Sr and lower HREE contents than those from MNP, which is consistent with the differences found in the fluorites from the two locations (Fig. 2F). This implies that the REE ore-forming fluids are related to the carbonatite magmas.

However, REE minerals in MNP and DLX carbonatites are absent, and most REE reside in calcites. The hydrothermal fluorite−barite ore veins are outside of the carbonatite areas. Most occur in syenites, and some are found in granites. This indicates the ore veins are products of fluid/rock interactions. Similarly, Bühn and Rankin (1999) analyzed the carbonatite-derived fluid preserved as fluid inclusions in quartzitic country rocks of the Kalkfeld carbonatite complex, Namibia; the carbonatitic fluids contain up to 3 wt.% REE and 3 wt.% Sr. They proposed that the elemental sequence Fe = Mn > Sr = REE > Mg = F > Ba = Y > Ti > Th > U > (Zr, Cu, Pb, Rb, Cs) > K > Na = Cl represents an increasing tendency (from left to right) partitioning into the carbonatite-derived fluid relative to the crystallizing carbonatite melt. As this fluid migrates through and interacts with invaded host rocks, elements will tend to precipitate in the same qualitative sequence from left to right.

3.3.2. Carbonate cumulates for REE enrichment
The above study suggests that some carbonatites may be calcite-rich cumulates. It is important to qualitatively assess which one REE will preferentially partition into crystallizing carbonate mineral or differentiating fluid. However, the partitioning of trace elements between carbonate melts and rock-forming carbonates has not been studied experimentally. Experimental REE partitioning between calcite and aqueous solution shows that the distribution coefficients are more than 1 and increase from LREE to HREE (Zhong and Mucci, 1995; Tanaka et al., 2004). Bühn et al. (2001) proposed different partitioning assessments of REE between calcite and carbonatite melt with values <1, but similar increasing from LREE to HREE. Combining the calcite− and

dolomite−fluorapatite coefficients estimated by Dawson and Hinton (2003) with the apatite−carbonatite melt partition coefficients ($^{Ap/L}D_{REE}$) determined experimentally by Klemme and Dalpé (2003), gives $^{Carbonate/L}D_{REE}$ values in Table 1. Klemme and Dalpé (2003) performed their experiment at 1 GPa and 1250 °C. Additionally, apatite-hosted carbonatite melt inclusion data (formation at 2.2−3.8 GPa and ∼1120 °C) measured by Guzmics et al. (2008) for $^{Ap/L}D_{REE}$ were applied. This overall trend is an agreement that LREE are less compatible with respect to calcite and dolomite than HREE. Dolomite has lower partition coefficients for REE than calcite, which explains why dolomite generally contains lower REE levels than calcite.

A similar conclusion has been proposed by Xu et al. (2010b). They found that calcite in the Miaoya carbonatites shows low REE contents (100−260 ppm) and flat chondrite-normalized REE distribution patterns [average (La/Yb)$_N$ = 1.6] relative to whole rocks. The carbonatite contains abundant REE-rich minerals, including monazite and fluorapatite, both precipitated earlier than the calcite, and REE-fluorocarbonates that postdated the calcite. The fractional crystallization of LREE-rich phosphate minerals reduces the proportion of REE and especially LREE in the residual liquid prior to calcite precipitation. This leads to the crystallization of calcite characterized by low LREE contents. Subsequently, fractionation of voluminous calcite produces late-stage carbonatitic liquids extremely enriched in light lanthanides to form REE-fluorocarbonates. This result provides a good case to support the idea that carbonate mineral/melt partition coefficients are well below unity and increase from La toward Lu. If such is the case, then the crystallization and accumulation of carbonate mineral would therefore result in REE enrichment in carbonatite-expelled fluids, which interact with wallrock and form hydrothermal ore veins.

3.3.3. Carbonatitic fluids interaction with wallrocks
It is known that coarse- and fine-grained dolomite marbles have different REE distribution patterns, and the former has relatively low REE compositions. This REE difference is also reflected in coarse- and fine-grained dolomite in whole rocks, and both types of dolomites have different $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios (Xu et al., 2008b). Why do they have different chemical compositions? The above study suggests

Table 1 Modeling partition coefficients (D) between calcite (Cal), dolomite (Dol) and carbonatite melt (L).

	$^{Cal/Ap}D$	$^{Dol/Ap}D$	$^{Ap/L}D$ KD	$^{Ap/L}D$ G	$^{Cal/L}D$ in KD	$^{Cal/L}D$ in G	$^{Dol/L}D$ in KD	$^{Dol/L}D$ in G
La	0.24	0.05	0.331	1.369	*0.079*	*0.329*	*0.017*	*0.068*
Ce	0.22	0.05	0.401	1.71	*0.088*	*0.376*	*0.020*	*0.086*
Pr	0.22	0.05	0.451	1.946	*0.099*	*0.428*	*0.023*	*0.097*
Nd	0.21	0.05		2.002		*0.420*		*0.100*
Sm	0.25	0.04	0.547	2.12	*0.137*	*0.530*	*0.022*	*0.085*
Eu	0.34	0.06		2.031		*0.691*		*0.122*
Gd	0.29	0.06	0.582	2.149	*0.169*	*0.623*	*0.035*	*0.129*
Tb	0.39	0.08		2.125		*0.829*		*0.170*
Dy	0.35	0.06						
Y	0.41	0.05	0.501	1.871	*0.205*	*0.767*	*0.025*	*0.094*
Ho	0.34	0.05		1.963		*0.667*		*0.098*
Er	0.32	0.05						
Tm	0.38	0.08						
Yb	0.53	0.12		1.403		*0.744*		*0.168*
Lu	0.83	0.08	0.329	1.176	*0.273*	*0.976*	*0.026*	*0.094*

The calcite, dolomite and apatite (AP) partition coefficients are from Dawson and Hinton (2003). The $^{Ap/L}D$ in KD is from Klemme and Daplé (2003), run BS 19, and $^{Ap/L}D$ in G from Guzmics et al. (2008). The italics are modeling data.

that the coarse- and fine-grained H8 dolomite marbles are igneous in origin. The fine-grained dolomite may be a re-crystallization product (Le Bas et al., 1997). Fig. 3 shows that coarse-grained dolomite has lower REE content than whole rock indicating that most of the REE reside in REE minerals. The experimental data of Wyllie et al. (1996) suggest that initially low REE concentrations in the magma are dispersed among major rock-forming constituents (predominantly carbonates), and REE mineralization does not develop. This "camouflage effect" explains why calcite in most carbonatites is characterized by relatively high REE contents, and implies that the primary carbonatite magmas forming the coarse-grained dolomite marble have quite high REE compositions, which preferentially crystallized REE minerals. This implication is consistent with the carbonatite-type REE deposit at MY (Xu et al., 2010a). Note that many carbonatite dykes were found near the BY orebodies. It is accepted that they are of igneous origin (Le Bas et al., 1992; Tao et al., 1998; Yang et al., 2003). According to the REE mineralization model at MNP and DLX, fluids, rich in alkaline and volatile and containing abundant REE, were expelled from these carbonatite dykes, and interacted with coarse-grained dolomite marble. The metasomatic replacement made coarse-grained dolomite re-crystallize and form REE minerals.

4. Conclusions

The following conclusions can be drawn from this review:

1. The Sr content is an alternative geochemical parameter to distinguish between magmatic and sedimentary for carbonatite origin;
2. The most intrusive carbonatites may be carbonate cumulates, and their chemical analyses cannot represent the compositions of parental magmas from which they are derived; extrusive carbonatite is essential for understanding the wider aspects of carbonatite magmas, and for identifying the most relevant applications of experimental results;
3. It is clear that carbonatites are important sources of REE. The fluids expelled from carbonatites are enriched in REE and volatiles, which interact with wallrock to form REE-carbonates − fluorite/barite ore veins. However, the question as to why the largest production and economic values in carbonatites are apatite and Cu, but not REE, has yet to be answered satisfactorily.

Acknowledgments

References

Bai, G., Yuan, Z.X., 1985. Carbonatites and related mineral resources. Bulletin of Institute of Mineral Deposits, Chinese Academy of Geological Sciences 13, 107−140.

Bell, K., 1998. Radiogenic isotope constraints on relationships between carbonatites and associated silicate rocks: a brief review. Journal of Petrology 39, 1987−1996.

Bell, K., Blenkinsop, J., 1987. Nd and Sr isotopic composition of East African carbonatites: implications for mantle heterogeneity. Geology 15, 99−102.

Bell, K., Tilton, G.R., 2001. Nd, Pb, and Sr isotopic compositions of East African cabonatites: evidence for mantle mixing and plume inhomogeneity. Journal of Petrology 42, 1927−1945.

Bose, P.N., 1884. Geology of the Lower Narbada Valley between Nimáwar and Káwant. Geological Survey of India 21, 1−72.

Brøgger, W.C., 1921. Die Eruptivegesteine des Kristianiagebietes. IV. Das Fengebiet in Telemarken, Norwegen. Norske Vidensk. Skrift. Mat-Naturv. Kl. 1920, 408 pp.

Bühn, B., Rankin, A.H., 1999. Composition of natural, volatile-rich Na-Ca-REE-Sr carbonatitic fluids trapped in fluid inclusions. Geochimica et Cosmochimica Acta 63, 3781−3797.

Bühn, B., Wall, F., Le Bas, M.J., 2001. Rare-earth element systematics of carbonatitc fluorapatites, and their significance for carbonatite magma evolution. Contributions to Mineralogy and Petrology 141, 572−591.

Calvo, J.P., Jones, B.F., Bustillo, M., Fort, R., Zarza, A.M.A., Kendall, C., 1995. Sedimentology and geochemistry of carbonates from lacustrine sequences in the Madrid Basin, central Spain. Chemical Geology 123, 173−191.

Campbell, L.S., Henderson, P., 1997. Apatite paragenesis in the Bayan Obo REE−Nb−Fe ore deposit, Inner Mongolia, China. Lithos 42, 89−103.

Chao, E.C.T., Back, J.M., Minkin, J.A., Ren, Y.C., 1992. Host-rock controlled epigenetic, hydrothermal metasomatic origin of the Bayan Obo REE-Fe-Nb ore deposit, Inner Mongolia, P.R.C. Applied Geochemistry 7, 443−458.

Chao, E.C.T., Back, J.M., Minkin, J.A., Ren, Y.C., 1997. The sedimentary carbonate giant Bayan Obo REE-Fe-Nb ore deposit of Inner Mongolia, China: a cornerstone example for giant polymetallic ore deposit of hydrothermal origin. US Geological Survey Bulletin 2143, 1−65.

Chen, Y.J., Zhai, M.G., Jiang, S.Y., 2009. Significant achievements and open issues in study of orogenesis and metallogenesis surrounding the North China continent. Acta Petrological Sinica 25, 2695−2726.

Dalton, J.A., Wood, B.J., 1993. The compositions of primary carbonate melts and their evolution through wallrock reaction in the mantle. Earth and Planetary Science Letters 119, 511−525.

Dawson, J.B., Hinton, R.W., 2003. Trace-element content and partitioning in calcite, dolomite and apatite in carbonatite, Phalaborwa, South Africa. Mineralogical Magazine 67, 921−930.

Fan, H.R., Hu, F.F., Yang, K.F., Wang, K.Y., 2006. Fluid unmixing/immiscibility as an ore-forming process in the giant REE−Nb−Fe deposit, Inner Mongolian, China: evidence from fluid inclusions. Journal of Geochemical Exploration 89, 104−107.

Galindo, G., Pankhurst, R.J., Casquet, C., Coniglio, J., Baldo, E., Rapela, C.W., Saavedra, J., 1997. Age, Sr- and Nd-isotope systematics, and origin of two fluorite lodes, Sierras Pampeanas, Argentina. International Geology Review 39, 948−954.

Galindo, C., Tornos, F., Darbyshire, D.P.F., Casquet, C., 1994. The age and origin of barite-fluorite (Pb-Zn) veins of the Sierra Del Guadarrama (Spanish Central, Spain): a radiogenic (Nd-Sr) and stable isotope study. Chemical Geology 112, 351−364.

Guzmics, T., Zajacz, Z., Kodolányi, J., Halter, W., Szabó, C., 2008. LA-ICP-MS study of apatite- and K feldspar-hosted primary carbonatite melt inclusions in clinopyroxenite xenoliths from lamprophyres, Hungary: implications for significance of carbonatite melts in the earth's mantle. Geochimica et Cosmochimica Acta 72, 1864−1886.

Haas, J.R., Shock, E.L., Sassani, D.C., 1995. Rare earth elements in hydrothermal systems: estimates of standard partial modal thermodynamic properties of aqueous complexes of the rare earth elements at high pressures and temperatures. Geochimica et Cosmochimica Acta 59, 4329−4350.

Hamilton, D.L., Bedson, P., Esson, J., 1989. The behavior of trace elements in the evolution of carbonatites. In: Bell, K. (Ed.), Carbonatites: Genesis and Evolution. Unwin Hyman, London, pp. 405−427.

Harmer, R.E., Gitiins, J., 1998. The case for primary, mantle-derived carbonatite mamga. Journal of Petrology 39, 1895−1903.

Hornig-Kjarsgaard, I., 1998. Rare earth elements in sovitic carbonatites and their mineral phases. Journal of Petrology 39, 2105−2121.

Hou, Z.Q., Tian, S.H., Xie, Y.L., Yuan, Z.X., Yang, Z.S., Yin, S.P., Fei, H.C., Zou, T.R., Li, X.Y., Yang, Z.M., 2008. Mianning-Dechang

Himalayan REE belt associated with carbonatite-alkalic complex in the eastern Indo-Asian collision zone, southwest China: geological characteristics of REE deposits and a possible metallogenic model. Mineral Deposits 27 (2), 145−176.

Hou, Z.Q., Tian, S.H., Yuan, Z.X., Xie, Y.L., Yin, S.P., Yi, L.S., Fei, H.C., Yang, Z.M., 2006. The Himalayan collision zone carbonatites in western Sichuan, SW China: petrogenesis, mantle source and tectonic implication. Earth and Planetary Science Letters 244, 234−250.

Jones, J.H., Walker, D., Picket, D.A., Murrel, M.T., Beate, P., 1995. Experimental investigations of the partitioning of Nb, Mo, Ba, Ce, Pb, Ra, Th, Pa and U between immiscible carbonate and silicate liquids. Geochimica et Cosmochimica Acta 59, 1307−1320.

Kjarsgaard, B.A., Hamilton, D.L., 1989. The genesis of carbonatites by immiscibility. In: Bell, K. (Ed.), Carbonatites: Genesis and Evolution. Unwin Hyman, London, pp. 388−404.

Klemme, S., Dalpé, C., 2003. Trace-element partitioning between apatite and carbonatite melt. American Mineralogist 88, 639−646.

Koster van Groos, A.F., Wyllie, P.J., 1963. Experimental data bearing on the role of liquid immiscibility in the genesis of carbonatites. Nature 199, 801−802.

Le Bas, M.J., Keller, J., Tao, K.J., Wall, F., Williams, C.T., Zhang, P.S., 1992. Carbonatite dykes at Bayan Obo, Inner Mongolia, China. Mineralogy and Petrology 46, 195−228.

Le Bas, M.J., Spiro, B., Yang, X.M., 1997. Oxygen, carbon and strontium isotope study of the carbonatitic dolomite host of the Bayan Obo Fe-Nb-REE deposit, Inner Mongolia, China. Mineralogical Magazine 61, 531−541.

Lee, W.J., Wyllie, P.J., 1994. Experimental data bearing on liquid immiscibility, crystal fractionation, and the origin of calciocarbonatites and natrocarbonatites. International Geology Review 36, 797−819.

Le Maitre, R.W., 2002. Igneous Rocks: A Classification and Glossary of Terms. Cambridge University Press, Cambridge, U.K.

Li, X.Y., 2005. Geological characteristics of Dalucao REE deposit in Dechang County, Sichuan Province. Mineral Deposits 24, 151−160.

Mariano, A.N., 1989. Nature of economic mineralization in carbonatites and related rocks. In: Bell, K. (Ed.), Carbonatites: Genesis and Evolution. Unwin Hyman, London, pp. 149−175.

Marty, B., Tolstikhin, I., Kamensky, I.L., 1998. Plume-derived rare gases in 380 Ma carbonatites from the Kola region (Russia) and the argon isotopic composition in the deep mantle. Earth and Planetary Science Letters 164, 179−192.

McDonough, W.F., Sun, S.S., 1995. The composition of the earth. Chemical Geology 120, 223−253.

Meng, Q.R., Zhang, G.W., 2000. Geologic framework and tectonic evolution of the Qinling orogen, central China. Tectonophysics 323, 183−196.

Migdisov, A.A., Williams-Jones, A.E., 2007. An experimental study of the solubility and speciation of neodymium (III) fluoride in F-bearing aqueous solutions. Geochimica et Cosmochimica Acta 71, 3056−3069.

Nelson, D.R., Chivas, A.R., Chappell, B.W., McCulloch, M.T., 1988. Geochemical and isotopic systematics in carbonatites and implications for the evolution of ocean-island sources. Geochimica et Cosmochimica Acta 52, 1−17.

Nothdurft, L.D., Webb, G.E., Kamber, B.S., 2004. Rare earth element geochemistry of Late Devonian reef carbonates, Canning Basin, Western Australia: confirmation of a seawater REE proxy in ancient limestones. Geochimica et Cosmochimica Acta 68, 263−283.

Pu, G.P., 2001. The evolution history of REE mineralization and major features of Himalayan REE deposit in Panzhihua-Xichang area, Sichuan. In: Chen, Y.C., Wang, D.H. (Eds.), Study on Himalayan Endogenic Mineralization. Geological Publishing House, Beijing, pp. 104−116.

Ratschbacher, L., Hacker, B.R., Calvert, A., Webb, L.E., Grimmer, J.C., McWilliams, M.O., Ireland, T., Dong, S.W., Hu, J.M., 2003. Tectonic of the Qinling (Central China): tectonostratigraphy, geochronology, and deformation history. Tectonophysics 366, 1−53.

Ren, J., 1985. A brief account on the geology of rare earth mineralization in China. In: Xu, G., Xiao, J. (Eds.), New Frontiers in Rare Earth Science and Applications, vol. 1. Science Press, Beijing, pp. 39−41.

Ruiz, J., Kesler, S.E., Jones, L.M., 1985. Strontium isotope geochemistry of fluorite mineralization associated with fluorine-rich igneous rocks from the Sierra Madre Occidental, Mexico: possible exploration significance. Economic Geology 80, 33−42.

Ruiz, J., Richardson, C.K., 1988. Strontium isotope geochemistry of fluorite, calcite and barite of the Cave-In-Rock fluorite district, Illinois. Economic Geology 88, 203−210.

Sallet, R., Moritz, R., Fontignie, D., 2005. The use of vein fluorite as probe for paleofluid REE and Sr−Nd isotope geochemistry: the Santa Catarina Fluorite District, Southern Brazil. Chemical Geology 223, 227−248.

Simonetti, A., Bell, K., 1995. Nd, Pb, and Sr isotope systematics of fluorite at Amba Dongar carbonatite complex, India: evidence for hydrothermal and crustal fluids mixing. Economic Geology 90, 2018−2027.

Smith, M.P., 2007. Metasomatic silicate chemistry at the Bayan Obo Fe−REE−Nb deposit, Inner Mongolia, China: contrasting chemistry and evolution of fenitising and mineralizing fluids. Lithos 93, 126−148.

Smith, M.P., Henderson, P., Campbell, L.S., 2000. Fractionation of the REE during hydrothermal processes: constraints from the Bayan Obo Fe-REE-Nb deposit, Inner Mongolia, China. Geochimica et Cosmochimica Acta 64, 3141−3160.

Srivastava, R.K., Heaman, L.M., Sinha, A.K., Sun, S.H., 2005. Emplacement age and isotope geochemistry of Sung Valley alkaline-carbonatite complex, Shillong Plateau, northeastern India: implications for primary carbonate melt and genesis of the associated silicate rocks. Lithos 81, 33−54.

Srivastava, R.K., Sinha, A.K., 2004. Early Cretaceous Sung Valley ultramafic-alkaline-carbonatite complex, Shillong Plateau, northeastern India: petrological and genetic significance. Mineralogy and Petrology 80, 241−263.

Sweeney, R., 1994. Carbonatite melt compositions in the earth mantle. Earth and Planetary Science Letters 128, 259−270.

Tanaka, K., Ohta, A., Kawabe, I., 2004. Experimental REE partitioning between calcite and aqueous solution at 25 °C and 1 atm: constraints on the incorporation of seawater REE into seamount-type limestones. Geochemical Journal 38, 19−32.

Tao, K.J., Yang, Z.M., Zhang, P.S., Wang, W.Z., 1998. Systematic geological investigation on carbonatite dykes in Bayan Obo, Inner Mongolia, China. Scientia Geologica Sinica 33, 73−83.

Tian, S.H., Hou, Z.Q., Yang, Z.S., Yang, Z.M., Yuan, Z.X., Wang, Y.B., Xie, Y.L., Liu, Y.C., Li, Z., 2008. Zircon U-Pb ages, Hf isotopic compositions and geological significance: a case study of carbonatite and nordmarkite from the Dalucao REE deposit, Sichuan Province. Acta Petrologica Sinica 24, 544−554.

Treiman, A.H., 1989. Carbonatites magma: properties and processes. In: Bell, K. (Ed.), Carbonatites: Genesis and Evolution. Unwin Hyman, London, pp. 89−104.

Veizer, J., Plumb, K.A., Clayton, R.N., Hinton, R.W., Grotzinger, J.P., 1992. Geochemistry of Precambrian carbonates: V. Late Paleoproterozoic seawater. Geochimica et Cosmochimica Acta 56, 2487−2501.

Veksler, I.V., Nielsen, T.F.D., Sokolov, S.V., 1998a. Mineralogy of crystallized melt inclusions from Gardiner and Kovdor ultramafic alkaline complexes: implications for carbonatite genesis. Journal of Petrology 39, 2015−2031.

Veksler, I.V., Petibon, C., Jenner, G.A., Dorfman, A.M., Dingwell, D.B., 1998b. Trace element partitioning in immiscibility and silicate liquid: an initial experimental study using a centrifuge autoclave. Journal of Petrology 39, 2095−2104.

Wall, F., Mariano, A.N., 1996. Rare earth minerals in carbonatites: a discussion centred in the Kangankunde carbonatite, Malawi. In: Jones, A.P., Wall, F., Williams, C.T. (Eds.), Rare Earth Minerals: Chemistry, Origin and Ore Deposits. Mineralogical Society Series, vol. 7. Chapman and Hall, London, pp. 193−225.

Wang, J., Tasumoto, M., Li, X., Premo, W.R., Chao, E.C.T., 1994. A precise [232]Th-[208]Pb chronology of fine-grained monazite: age of the Bayan Obo REE-Fe-Nb ore deposit, China. Geochimica et Cosmochimica Acta 58, 3155−3169.

Wang, Y.X., Qiu, Y.Z., Gao, J.Y., Zhang, Q., 2003. Proterozoic anorogenic magmatic rocks and their constraints on mineralization in the Bayan

Obo deposit region, Inner Mongolia. Science in China, Series D 46 (Suppl), 26−40.

Williams, R.W., Gill, J.B., Bruland, K.W., 1986. Ra-Th disequilibria systematics: timescale of carbonatites magma formation at Oldoinyo Lengai volcano, Tanzania. Geochimica et Cosmochimica Acta 50, 1249−1259.

Williams-Jones, A.E., Samson, I.M., Olivo, G.R., 2000. The genesis of hydrothermal fluorite-REE deposits in the Gallinas Mountains, New Mexico. Economic Geology 95, 327−342.

Wood, S.A., 1990. The aqueous geochemistry of the rare-earth elements and yttrium, 1. Review of available low-temperature data for inorganic complexes and the inorganic REE speciation of nature waters. Chemical Geology 82, 159−186.

Woolley, A.R., Church, A.A., 2005. Extrusive carbonatites: a brief review. Lithos 85, 1−14.

Woolley, A.R., Kempe, D.R.C., 1989. Carbonatites: nomenclature, average chemical composition. In: Bell, K. (Ed.), Carbonatites: Genesis and Evolution. Unwin Hyman, London, pp. 1−14.

Wyllie, P.J., Jones, A.P., Deng, J., 1996. Rare earth elements in carbonate-rich melts from mantle to crust. In: Jones, A.P., Wall, F., Williams, C.T. (Eds.), Rare Earth Minerals: Chemistry, Origin and Ore Deposits. The Mineralogical Society Series, vol. 7. Chapman and Hall, London, pp. 77−103.

Xiao, R.G., Fei, H.C., An, G.Y., Zhang, H.C., Hou, W.R., 2003. Lithology and genesis of dolomite marble in Bayan Obo mine, Inner Mongolia. Geoscience 17, 287−293.

Xu, C., Campbell, I.H., Allen, C.M., Chen, Y.J., Huang, Z.L., Qi, L., Zhang, G.S., 2008a. U-Pb zircon age, geochemical and isotopic characteristics of carbonatite and syenite complexes from the Shaxiongdong, China. Lithos 105, 118−128.

Xu, C., Campbell, I.H., Allen, C.M., Huang, Z.L., Qi, L., Zhang, H., Zhang, G.S., 2007a. Flat rare earth element patterns as an indicator of cumulate processes in the Lesser Qinling carbonatites, China. Lithos 95, 267−278.

Xu, C., Campbell, I.H., Kynicky, J., Allen, C.M., Chen, Y.J., Huang, Z.L., Qi, L., 2008b. Comparison of the Daluxiang and Maoniuping carbonatitic REE deposits with Bayan Obo REE deposit, China. Lithos 106, 12−24.

Xu, C., Huang, Z.L., Liu, C.Q., Qi, L., Li, W.B., 2003a. Geochemistry of carbonatites in Maoniuping REE deposit, Sichuan Province, China. Science in China, Series D 46, 246−256.

Xu, C., Huang, Z.L., Liu, C.Q., Qi, L., Li, W.B., 2003b. Sources of ore-forming fluids in the Maoniuping REE deposit, Sichuan Province, China-evidence from REE, radiogenic Sr, Nd, and stable isotopes. International Geology Review 45, 635−645.

Xu, C., Huang, Z.L., Qi, L., Fu, P.Q., Liu, C.Q., Li, E.D., 2007b. Geochemistry of Cretaceous granites from Mianning in the Panxi region, Sichuan Province, southwestern (SW) China: implications for their generation. Journal of Asian Earth Sciences 29, 737−750.

Xu, C., Huang, Z.L., Qi, L., Li, W.B., 2001a. Sr-Nd isotope geochemistry of fluorites: a review. Geology−Geochemistry 29, 27−34.

Xu, C., Huang, Z.L., Qi, L., Xiao, H.Y., Li, W.B., Liu, C.Q., 2001b. Source and evolution of ore-forming fluids of Maoniuping rare earth deposit: evidence from REE geochemistry of fluorite. Geology and Prospecting 37, 24−28.

Xu, C., Kynicky, J., Chakhmouradian, A.R., Campbell, I.H., Allen, C.M., 2010a. Trace-element modeling of the magmatic evolution of rare-earth-rich carbonatite from the Miaoya deposit, central China. Lithos 118, 145−155.

Xu, C., Kynicky, J., Chakhmouradian, A.R., Qi, L., Song, W.L., 2010b. A unique Mo deposit associated with carbonatites in the Qinling orogenic belt, central China. Lithos 118, 50−60.

Xu, C., Qi, L., Huang, Z.L., Chen, Y.J., Yu, X.H., Wang, L.J., Li, E.D., 2008c. Abundances and significance of platinum group elements in carbonatites from China. Lithos 105, 201−207.

Xue, F., Lerch, M.F., Kroner, A., Reischmann, T., 1996. Tectonic evolution of the East Qinling Mountains, China, in the Palaeozoic: a review and new tectonic model. Tectonophysics 253, 271−284.

Yang, X.M., Le Bas, M.J., 2004. Chemical compositions of carbonate minerals from Bayan Obo, Inner Mongolia, China: implications for petrogenesis. Lithos 72, 97−116.

Yang, X.M., Yang, X.Y., Zheng, Y.F., Le Bas, M.J., 2003. A rare earth element-rich carbonatite dyke at Bayan Obo, Inner Mongolia, North China. Mineralogy and Petrology 78, 93−110.

Yang, X.Y., Sun, W.D., Zhang, Y.X., Zheng, Y.F., 2009. Geochemical constraints on the genesis of the Bayan Obo Fe−Nb−REE deposit in Inner Mongolia, China. Geochimica et Cosmochimica Acta 73, 1417−1435.

Yu, X.H., 1992. Geological, mineralogical characteristics and origin of the carbonatites from Huayangchuan, Shanxi Province. Earth Science 17, 151−158.

Yuan, Z.X., Bai, G., Wu, C.Y., Zhang, Z.Q., Ye, X.J., 1992. Geological features and genesis of the Bayan Obo REE ore deposit, Inner Mongolia, China. Applied Geochemistry 7, 429−442.

Yuan, Z.X., Shi, Z.M., Bai, G., 1995. Rare Earth Element Deposit in Maoniuping, Mianning, Sichuan Province. Geological Publishing House, Beijing.

Zhang, Y.X., Lu, Y.N., Yang, C.X., 1988. The Panxi Rift. Geological Publishing House, Beijing, pp. 224−270.

Zhong, S., Mucci, A., 1995. Partitioning of rare earth elements (REEs) between calcite and seawater solutions at 25 °C and 1 atm, and high dissolved REE concentrations. Geochimica et Cosmochimica Acta 59, 443−453.