

Genesis of the carbonatite-syenite complex and REE deposit at Maoniuping, Sichuan Province, China: Evidence from Pb isotope geochemistry

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The Maoniuping REE deposit is the second largest light rare earth elements deposit (1.45 million tons of REE₂O₃) in China, located in the Panxi rift, Sichuan Province. It is a vein-type deposit hosted within, and genetically related to the Himalayan alkalic carbonatite-syenite complex.

The initial ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb ratios from the Maoniuping carbonatites are similar to syenites, which, however, show more radiogenic ²⁰⁷Pb/²⁰⁴Pb ratios. This could not only be attributed to contamination by crustal materials. The Pb-Pb isotope plots from carbonatites and syenites define a linear array between EM1 and EM2. It suggests their sources were located in a heterogeneous lithospheric mantle and produced by the mixture of EM1 with EM2.

The initial ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb ratios from fluorites, galenas, pyrites and feldspar are similar to carbonatites and syenites, and different from granites. Their ²⁰⁷Pb/²⁰⁴Pb ratios also plot to between syenites and carbonatites. This suggests the REE ore-forming fluids were derived from carbonatite and syenite magmas. The Pb isotopic results are consistent with a model for REE deposition involving mixing of the F-rich, syenite-derived fluid with Ca-, CO₂-bearing fluid evolved from carbonatite magma. The early fluorites have higher ²⁰⁷Pb/²⁰⁴Pb ratio than the later ones, which shows that the REE ore-forming fluids were not contaminated by country rocks fluids.

Keywords: genesis, carbonatite, syenite, Pb isotope, Maoniuping REE deposit

INTRODUCTION

Fluid inclusion and stable isotope investigations of various ore deposits have shown that magmatic fluids can be an important and even dominant constituent of various ore fluids. Examples include the early-stage mineralization events in the cores of porphyry-type deposits (Hall *et al.*, 1974; Sheppard and Taylor, 1974; Sheppard and Gustafson, 1976; Larson, 1987) and base and precious metal deposits (Kelly and Rye, 1979; Burrows and Spooner, 1987; Thorn, 1988; Richards and Spooner, 1989; Rye, 1993; Campbell *et al.*, 1995). For these deposits, however, it is in general difficult to determine the geochemical properties of the magmatic component of the ore fluid involved in the mineralization event because the magmatic signature has been partially contaminated through interaction with meteoric ground water, or by an overprint of a late stage fluid forming secondary fluid inclusions as the hydrothermal system wanes.

The Maoniuping REE deposit, hosted in a carbonatite-syenite complex, is the second largest light REE deposit in China, less voluminous than the Baiyan'ebao Fe-Nb-REE deposit in Inner Mongolia Autonomous Region. The deposit is characterized by large scale, shallow buried, and coarse grain of bastnaesite. The reserve of REE₂O₃ is estimated to be more than 1.45 million tons of REE₂O₃. An unpublished report by the Chinese No. 109 Geological Team gives the grades of various primary ores ranging from 2.7 to 3.9% REE₂O₃, while the grades of secondary ores (weathered and oxidized) ranging from 10.0 to 13.6% REE₂O₃. Associated reserves include 0.33 million tons of Pb, 174 tons of Ag, 3.78 million tons of barites and 2.40 million tons of fluorites. Previous C, O, Sr and Nd isotopic investigations of carbonatites from the Maoniuping deposit have suggested that the carbonatite-syenite complex was generated from liquid immiscibility of CO₂-rich alkalic silicate magma (Xu *et al.*, 2002a). The PGE geochemistry of carbonatites also show carbonatites underwent multi-source evolution (Xu *et al.*, 2003). The fluorites associated with REE mineralization show different chondrite-normalized REE patterns, i.e., LREE-rich, LREE-flat and LREE-depleted models (Xu *et al.*, 2002b). They have identical initial Sr (0.706031–0.706237) and Nd (0.512409–0.512437) isotope ratios,

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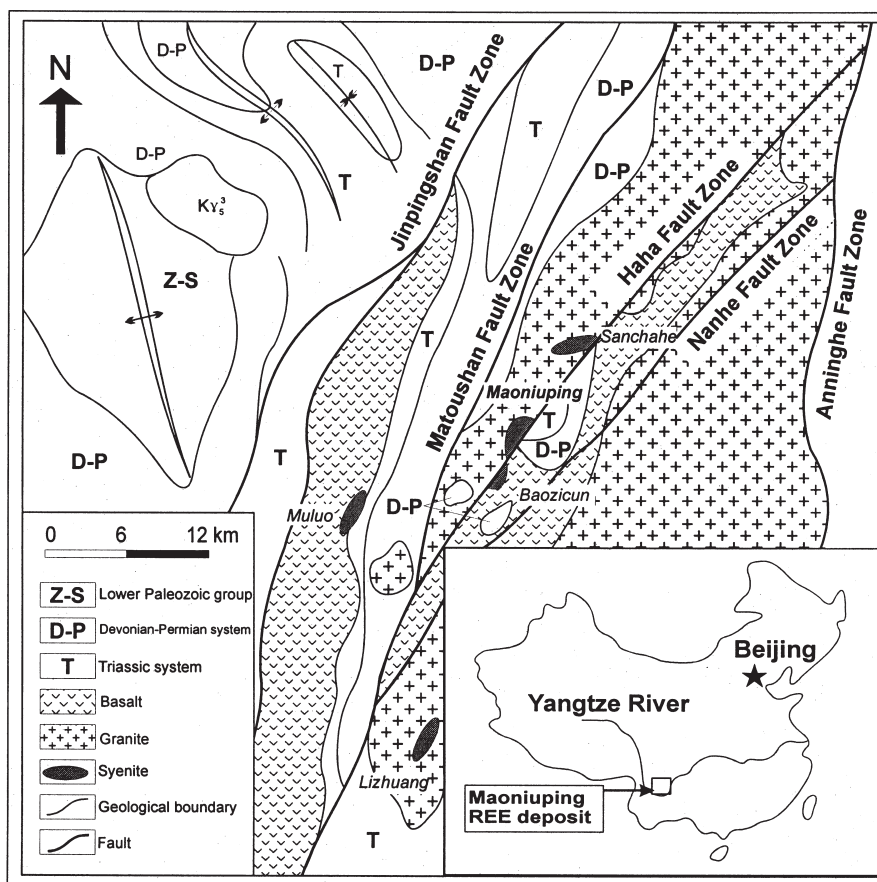


Fig. 1. Simplified geological map of the Maoniuping REE deposit (modified after Yuan *et al.*, 1995).

similar to carbonatites and syenites. Xu *et al.* (2002b) have suggested that the three REE type fluorites were the products of the same source, but at different stages of evolution, and the LREE-rich fluorites (Samples No.: MNP-6, MNP-135) were formed at a relatively early stage. The Pb isotope, however, in the Maoniuping deposit is few documented. Because of high Sr (average 3462 and 12383 ppm, respectively) and Nd (average 109 and 525 ppm, respectively) contents in the Maoniuping fluorites and carbonatites (Xu *et al.*, 2002a, b) Sr and Nd isotopes may be less sensitive indicator of crustal contamination in carbonatites and REE ore-forming fluids than Pb isotope.

In the present paper, Pb isotopic compositions of country rocks and gangue minerals from the Maoniuping deposit are presented according to the Sr and Nd isotopes for the same samples. The Pb isotope ratios from fluorites are the second documented after Simonetti and Bell (1995). The purpose of the study has been twofold: first, to identify the source of Pb in carbonatites and associated syenites, in order to improve our understanding of the origin of parental melt to carbonatites; and secondly, to further discuss the sources of the REE ore-forming fluids.

LOCAL GEOLOGY

The Maoniuping REE deposit is located on the north margin of the Panxi (Panzhuhua-Xichang) rift, and is tectonically located in the middle zone of the NE-trending Haha fault (Fig. 1). The Panxi rift was formed on the Yangtze platform during the early Paleozoic, and evolved in the late Paleozoic and Mesozoic, ending in the early Cenozoic, with the beginning of the Himalayan orogeny. The Maoniuping mineralization zone is about 10 km long and 200 to 600 m wide. Most of REE orebodies are composed of pegmatitic bastnaesite ores, pegmatitic calcite veins and networks of ores, with the gangue minerals of fluorite, barite, calcite, quartz, mica and aegirine-augite. Fluorite occurs in every orebodies. Their grain sizes range from 0.5 to 20 mm, with colors of purple, green and colorless. K-Ar dating of biotites from the orebodies yielded 27.8 ± 0.5 – 40.3 ± 0.7 Ma (Pu, 1988, 1993).

In the Maoniuping area, the exposed strata are the Middle Devonian siltclastolite, carbonate and Quaternary proluvium and talus. Igneous rocks are distributed extensively, including granites, alkalic carbonatite-syenite complex and Mesozoic rhyolites. The granites intruded into

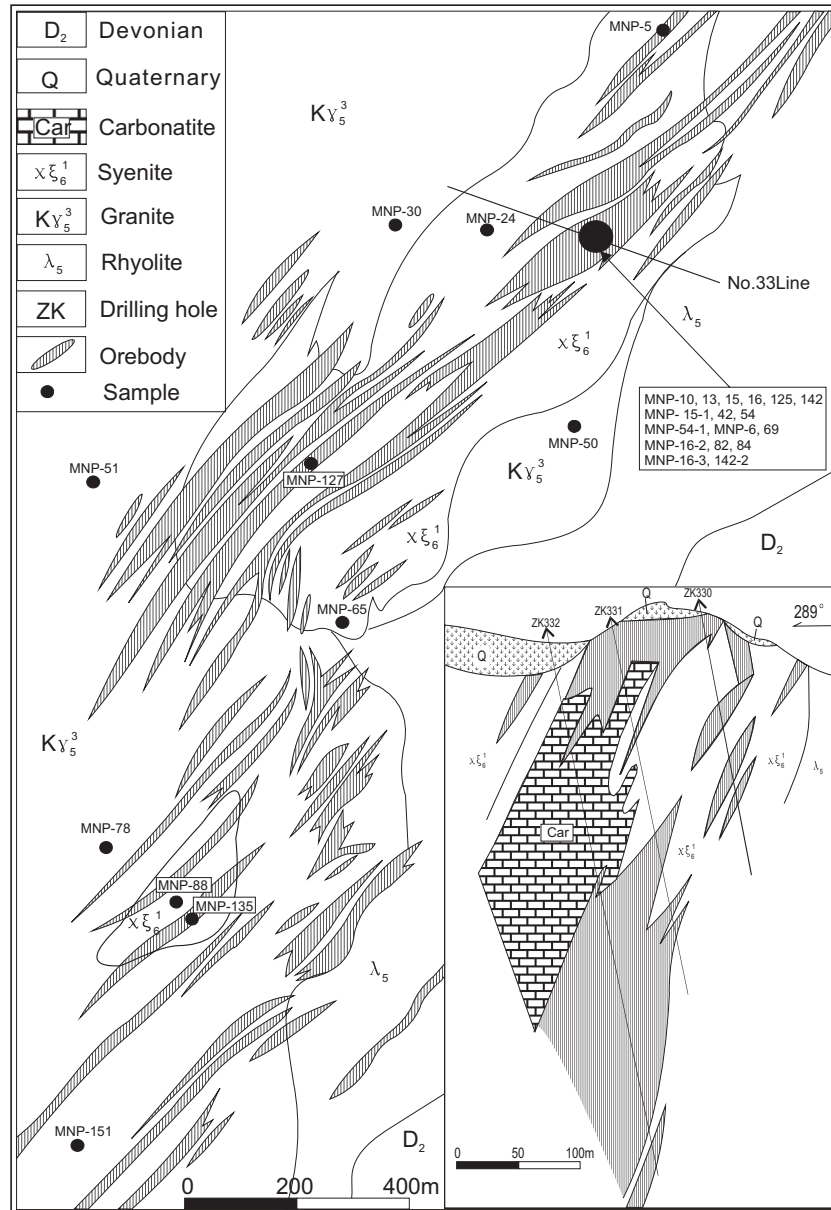


Fig. 2. Geological scheme of the igneous rocks in the ore district (modified after Yuan et al., 1995).

the central part of the Maoniuping anticline, with a NNE strike, a length of 90 km, a width of 6 to 14 km, and an area of 700 km². The whole-rock K-Ar ages range from 78 to 134 Ma (Chen and Pu, 1991).

The alkalic carbonatite-syenite complex is spatially and temporally associated with REE mineralization (Fig. 2). Syenites are composed of K-feldspar, albite and quartz, with minor amounts of fluorite, calcite, aegirine, mica, epidote, and the accessory minerals such as pyrite, galena, apatite, hematite, titanite and REE mineral. Elongate carbonatites intruding the center of the syenites, extend 400 m without pinching. Carbonatites are classified

into two distinct groups, yellowish pink sövite and white sövite. Both groups are composed mainly of coarse-grained calcite (>95%) with pegmatoid appearance, up to 3 cm across commonly. Biotite, aegirine, arfvedsonite and orthoclase are common to carbonatite, but galena and pyrite are rare. Country rock at the margins of carbonatites is fenitized and replaced by arfvedsonite. According to Pu (2001), the K-Ar age of carbonatite is 31.7 ± 0.7 Ma, which is similar to that of syenite (20–48 Ma). Carbonatites are an economically important source of REE minerals and fluorites (e.g., Mariano, 1989). Several examples of REE mineralization in carbonatites are

Table 1. Lead isotope analyses of igneous rocks and gangue minerals from the Maoniuping REE deposit, China

Sample No.	Type	REE patterns* Evolutional stages	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
MNP-10	Carbonatite		17.887	15.362	38.141
MNP-13	Carbonatite		18.223	15.538	38.323
MNP-15	Carbonatite		18.417	15.429	38.233
MNP-16	Carbonatite		18.264	15.556	38.683
MNP-125	Carbonatite		18.220	15.587	38.452
MNP-142	Carbonatite		18.001	15.435	38.083
MNP-15-1	Syenite		18.270	15.648	38.611
MNP-24	Syenite		18.263	15.694	38.788
MNP-42	Syenite		18.259	15.605	38.496
MNP-54	Syenite		18.356	15.613	38.592
MNP-65	Syenite		18.437	15.605	38.590
MNP-88	Syenite		18.465	15.657	38.685
MNP-50	Granite		19.103	15.627	39.194
MNP-30	Granite		18.996	15.617	39.168
MNP-51	Granite		19.022	15.595	39.005
MNP-78	Granite		18.982	15.592	38.953
MNP-6	Fluorite	LREE-rich Early stage	18.323	15.586	38.405
MNP-135	Fluorite	LREE-rich Early stage	18.458	15.632	38.285
MNP-5	Fluorite	LREE-flat Late stage	18.177	15.536	38.386
MNP-127	Fluorite	LREE-flat Late stage	18.557	15.549	38.290
MNP-69	Fluorite	LREE-loss Late stage	18.241	15.538	38.331
MNP-151	Fluorite	LREE-loss Late stage	18.246	15.559	38.391
MNP-82	Pyrite		18.279	15.527	38.268
MNP-84	Pyrite		18.244	15.495	38.219
MNP-16-2	Pyrite		18.169	15.490	38.495
MNP-142-2	Galena		18.346	15.589	38.788
MNP-16-3	Galena		18.336	15.538	38.553
MNP-54-1	Feldspar		18.283	15.628	38.552

*The REE patterns and evolutional stages are from Xu *et al.* (2002b).

known, including Karonge Angola (van Wambeke, 1977), Tundulu and Kangankunde, Malawi (Wall and Mariano, 1996), and Barra do Itapirapuã, Brazil (Andrade *et al.*, 1999). The largest known REE deposit, the sediment-hosted bastnaesite deposit of Bayan Obo in China, is thought to be derived from hydrothermal fluids released by a nearby carbonatite (Campbell and Henderson, 1997; Le Bas *et al.*, 1997).

ANALYTICAL METHODS

Fresh calcite, galena and pyrite were selected from carbonatites, feldspar from syenite. The whole minerals were crushed down to grains of 1 mm in size, sieved and washed, and then hand-picked for analyses. Syenite and granite samples were determined on whole rock. All sam-

ples were further crushed to 150–200 mesh size and dissolved in Teflon PFA, using HCl + HNO₃ mixture for fluorite, HCl for calcite, HNO₃ for galena and pyrite, and HF + HNO₃ mixture for silicate samples. Pb was separated in HBr, HCl and HNO₃ media using standard anion ion-exchange techniques. Total procedure blanks were less than 1 ng for Pb. Isotope ratios were determined on a VG-354 at the Institute of Geology and Geophysics, Chinese Academy of Sciences. The replicate analyses of NBS 981 gave $^{206}\text{Pb}/^{204}\text{Pb} = 16.9483 \pm 0.027\%$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4973 \pm 0.034\%$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.6830 \pm 0.035\%$ within error limits of White *et al.* (2000; $^{206}\text{Pb}/^{204}\text{Pb} = 16.9467 \pm 0.045\%$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4899 \pm 0.025\%$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.6825 \pm 0.021\%$). The 2σ uncertainties were $\sim 0.04\%$ per mass unit.

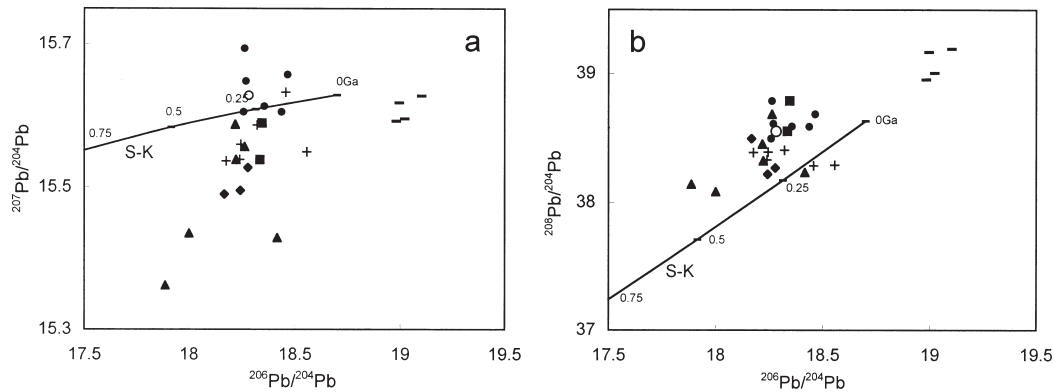


Fig. 3. Present-day Pb isotope ratios for Maoniuping igneous rocks and gangue minerals. ▲ = carbonatite, ● = syenite, - = granite, + = fluorite, ◆ = pyrite, ■ = galena, ○ = feldspar, S-K = Stacey-Kramers (1975) Pb evolution curve. a. $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$. b. $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$.

RESULTS

The analytical data are given in Table 1 and shown in Fig. 3. Present day Pb isotope ratios for the carbonatite, syenite, fluorite, galena, pyrite, and feldspar samples are considered to approximate initial ratios because of relatively young age of the complex (~30 Ma) and low U/Pb (0.03–0.09, 0.001–0.002, 0.007–0.04, 0.02) and Th/Pb (0.17–0.41, 0.002–0.19, 0.002–0.08, 0.02 for syenite, carbonatite, fluorite and feldspar, respectively) ratios.

The Pb data from the Maoniuping carbonatites are least radiogenic, by far, of any that have been analyzed from young carbonatites world-wide (<200 Ma; Tilton and Bell, 1994), with the one exception of the Jacupiranga carbonatites from Brazil (Huang *et al.*, 1995). In Fig. 3a, carbonatite samples show large spread in $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, and plot to the right of the Stacey-Kramers (1975) Pb evolution curve. While the syenite samples exhibit more radiogenic $^{207}\text{Pb}/^{204}\text{Pb}$ ratios. All but one of the syenite samples fall to the left of the S-K Pb evolution curve. The feature is not consistent with Pb isotopic data from the East African carbonatite (Simonetti and Bell, 1994), and MORB and OIB (Tatsumoto, 1978). A feldspar sample shows similar Pb isotope ratios to syenites, which excludes Th- or U-rich mineral contributions to the radiogenic Pb in syenites. In Fig. 3b carbonatites overlap with syenites, and plot close together to the left of the S-K Pb evolution curve.

Compared to the fluorites at Amba Dongar carbonatite complex (Simonetti and Bell, 1995), the Maoniuping fluorites contain less radiogenic Pb isotope ratios. The LREE-rich fluorite samples (early stage) show higher $^{207}\text{Pb}/^{204}\text{Pb}$ (average 15.609) ratios than LREE-flat and -depleted ones (late stage, average 15.546). The $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios from the galena, pyrite and fluorite samples plot to between the carbonatites and

syenites, the right of the S-K Pb evolution curve. In Fig. 3b all of them also lie between carbonatites and syenites. An interesting feature emerging from most of the Maoniuping samples relates to a linear array between $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. While the granite samples have more radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, deviate from the line. Because the U and Pb concentrations in granites are not determined, an age correction to obtain initial ratios is not possible. However, a 130 Ma event seems also to be exhibited by the other samples, as may be indicated from the sample MNP-78, which also differs from carbonatites, syenites and gangue minerals. The result is consistent with the study of Sr-Nd isotopes (Xu *et al.*, 2002b).

DISCUSSION

Sources of carbonatites and syenites

The Maoniuping carbonatites and syenites spatially and temporally associated with REE mineralization, thus their relationship is important in study of REE ore-forming fluids. Calculated ϵ_{Sr} and ϵ_{Nd} values for the carbonatite samples show narrow variation of 22.8–24.0 and –4.25––3.72, respectively, similar to those of the syenite samples (Fig. 4C; Xu *et al.*, 2002a). However the carbonatite fractions are found to have lower initial $^{207}\text{Pb}/^{204}\text{Pb}$ (average 15.485) ratios than the syenite fractions (average 15.637). Crustal contamination is responsible for the isotope variation in many continental magmatic rocks (Depaolo, 1981). With more data this hypothesis can now be evaluated and a number of problems identified.

(1) If the carbonatites were formed from a contaminated silicate magma by liquid immiscibility, this would possibly lead to elevation of the Pb isotope ratios. However the Maoniuping carbonatites do not have radiogenic Pb isotope compared with other young carbonatites. The

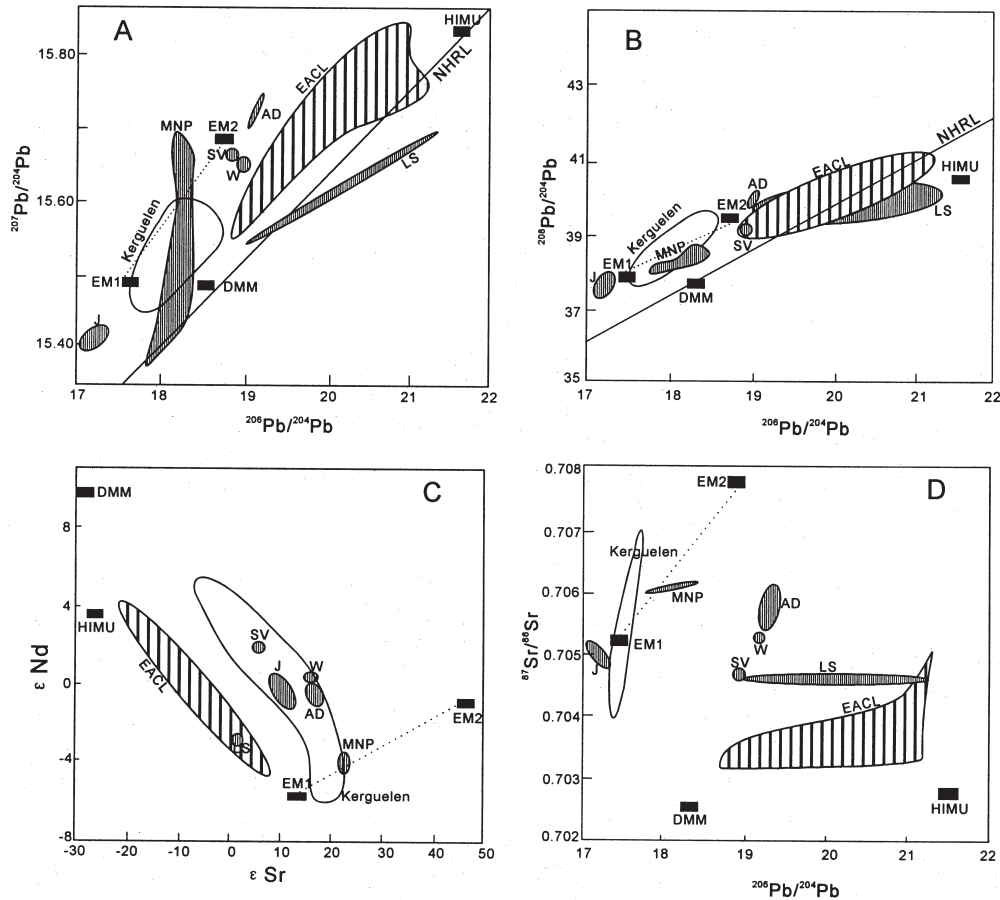


Fig. 4. Correlation plots (A) $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$, (B) $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$, (C) ϵ_{Nd} vs. ϵ_{Sr} , (D) $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ for some young (<200 Ma) carbonatites. Data sources for carbonatites: EACL-East African Carbonatite Line (Bell and Blenkinsop, 1987; Kalt et al., 1997); W-Walloway, Australia (Nelson et al., 1988); J-Jacupiranga, Brazil (Toyoda et al., 1994); SV-Sung Valley, India (Veena et al., 1998); AD-Amba Dongar, India (Simonetti et al., 1995); LS-Loe Shilman, Pakistan (Tilton et al., 1998); MNP-Maoniuping REE deposit, China (including data for syenites; Sr and Nd isotopes in Xu et al., 2002a). Data for Kerguelen OIB are cited from Weis et al. (1991). End-member components (EM1, EM2, HIMU and DMM) are as defined by Hart (1988).

uniform $\delta^{18}\text{O}_{\text{SMOW}}$ (6.4~7.4‰) and $\delta^{13}\text{C}_{\text{PDB}}$ (−6.6~−7.0‰; Xu et al., 2002a) compositions of the carbonatites show that they have primary mantle stable isotope constitutions which have not been significantly affected by assimilation of crustal materials. Although Maoniuping carbonatites are distinguished by unusually higher initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.706074–0.706149), similar to the 60 my-old ferrocarbonatite complex of Amba Dongar in western India (Fig. 4D; Simonetti et al., 1995), the C and O isotope compositions of the Amba Dongar ferrocarbonatite are out of the “primary magmatic carbonatite box”. Simonetti et al. (1995) concluded that the Sr isotope ratios of the ferrocarbonatites were altered by low-temperature interaction with crustal materials.

(2) If crustal contamination occurred after segregation of the carbonatite magmas, this would also possibly lead to discrepancy of the Pb isotope ratios. Carbonatite in-

trusion post-dates that of silicate, a feature shared by most carbonatite complexes. It is imaginable that syenites should show higher $^{207}\text{Pb}/^{204}\text{Pb}$ ratios than carbonatites when syenites ascended, differentiated and interacted with radiogenic Pb of the crust. If so, the Sr and Nd isotope ratios of syenites should be more easily contaminated because syenites have much lower Sr (30.8 ppm–403 ppm) and Nd (57.4 ppm–132 ppm) contents than carbonatites (Sr: 10530 ppm–15017 ppm, Nd: 377 ppm–687 ppm; Xu et al., 2002a). But they show similar initial Sr and Nd isotope ratios. Moreover, the Maoniuping syenites display uniform primitive mantle-normalized trace element patterns (Xu et al., 2002a).

Thus, the more likely explanation is that the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio variations in Maoniuping syenites and carbonatites reflect the characteristic of their mantle sources, rather than crustal contamination. These sources are located in

a heterogeneous lithospheric mantle and were produced by depletion or enrichment processes at different times and degrees, as discussed in Kalt *et al.* (1997). The ϵ_{Sr} and ϵ_{Nd} values from carbonatites and syenites show narrow variation, while the Pb isotopes have large spread (Fig. 4). The Pb isotopes were decoupled from those of Sr and Nd during the melting processes (Bell, 1998). This appears to have happened in EM2 (and possibly also in EM1) type OIB, as well as in Indian Ocean MORB, which show no correlations between Sr (or Nd) and Pb isotopes (Hofmann, 1997). In addition, the $^{207}\text{Pb}/^{204}\text{Pb}$ ratios are more sensitive to differentiation processes than the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios (Kwon *et al.*, 1989; Tilton and Bell, 1994).

A striking feature for the 30-my-old Maoniuping carbonatites is their very negative ϵ_{Nd} , coupled with the high initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. For most isotopically analyzed carbonatites the Nd isotope ratios are greater than the bulk silicate Earth ratios (positive ϵ_{Nd}), as outlined in the summaries by Bell and Blenkinsop (1989) and Harmer and Gittins (1998). The remaining negative ϵ_{Nd} values are predominantly from East Africa, Brazil, India and Pakistan. In their original study of the East African Rift carbonatites with ages between 0 and 120 Ma, Bell and Blenkinsop (1987, 1989) found that six out of nine carbonatites gave negative ϵ_{Nd} values, and defined a line in an $\epsilon_{\text{Nd}}-\epsilon_{\text{Sr}}$ diagram that they called the East African Carbonatite Line (EACL), which tracks the present EM1-HIMU line. To explain the mixed EM1-HIMU type signature in the East African carbonatites, Bell and Simonetti (1996) suggested a two-stage model. First, fluid with a HIMU signature, generated from an upwelling mantle plume, metasomatized EM1 type sub-continental lithosphere. This was followed by variable degrees and discrete parting melting of the resulting heterogeneous, metasomatized sub-continental lithosphere to produce carbonated silicate melts.

A similar model can be envisaged in the case of the Maoniuping carbonatites and syenites. Their initial Sr and Nd isotope ratios deviate from the EACL, and plot near EM1 along the EM1 and EM2 line. In Fig. 4 the Pb-Pb isotope plots define a line and further suggest EM1-EM2 binary mixing processes. The mixture of EM1 with EM2 was also found from Kerguelen OIB in Indian Ocean (Hart, 1988).

Initially, Hart *et al.* (1986) sited EM1 in the sub-continental lithosphere. On the basis of the isotope systematics of carbonatites Bell and Simonetti (1996) further suggested that the principal storage area for EM1 might be the mantle lithosphere. For EM2, the generally accepted view regards it as a subducted and recycled continental crustal component for which long-term storage is contra-indicative (Hart, 1988). However, short-term storage in a mesosphere boundary is certainly a possibil-

ity. Geophysical data obtained by Zhang *et al.* (1988) show there exists an “anomalous mantle body” in the sub-continental lithosphere of the Panxi rift. Although the Maoniuping carbonatites occurred in the Panxi rift, they were emplaced during the Himalayan period when the Panxi rift closed (Zhang *et al.*, 1988). Due to collision between the Indian plate and the Yangtze plate, strong orogeny provided power for tectonic-magmatic mobilization. It may be speculated that fluid from the mesosphere boundary layer, with an EM2 signature, metasomatized the anomalous mantle body (EM1-like) stored in the Maoniuping sub-continental lithosphere.

Origin of REE ore-forming fluids

Fluorite of varied color and habit occurs in a variety of mineral deposit environments. The presence of fluorite is a common indicator of mineralization (Eppinger and Closs, 1990; Williams-Jones *et al.*, 2000). Previous isotopic investigations of fluorites, related to different types of ore deposits, have shown that initial Sr isotope ratios can serve as useful tracers of fluid sources, and the initial Nd ratios reflect the composition of the ore fluids (Ruiz and Kesler, 1985; Ruiz and Richardson, 1988; Chesley *et al.*, 1991, 1994; Galindo and Tornos, 1994).

The fluorites from the Maoniuping REE deposit have identical Sr and Nd isotope ratios to carbonatites and syenites, and differ from granites (Xu *et al.*, 2002b). In Fig. 3 the Pb isotope ratios from the galena, pyrite and fluorite samples also plot to between carbonatites and syenites. These indicate that the sources of REE ore-forming fluids are closely related with the carbonatites and syenites.

In order to establish the controls of REE deposition, it is necessary to understand the behavior of mineralizing species in aqueous solutions. The behavior of REE at elevated temperatures has been investigated theoretically by Wood (1990) and Haas *et al.* (1995). Based on chemistry of fluids and mineralogy of deposits, Wood (1990) and Haas *et al.* (1995) indicate that possible ligands involved in the transport of the REE are F^- , CO_3^{2-} , OH^- , Cl^- , SO_4^{2-} , and HCO_3^- . According to data presented by Wood (1990), F^- forms the strongest complex with REE. Salvi and Williams-Jones (1990) have suggested that REE mineral deposition occurred as a result of the decreased ligand concentration that accompanied massive fluorite deposition. Because of carbonatite intrusion post-dates that of the silicate rocks, the early fluid carrying REE fluoride mainly evolved from the syenite magma. This is also supported by the alkaline nature of the syenites. Fluorite, because of its extremely low solubility, would have started to precipitate immediately (at 400°C, the solubility product for fluorite is 3.8×10^{13} , calculated using SUPCRT92; Johnson *et al.*, 1991). As can be seen from Fig. 3a, the early fluorites (Sample No.: MNP-6, MNP-

135) show more radiogenic $^{207}\text{Pb}/^{204}\text{Pb}$ ratios than later fluorites and carbonatites (exception of sample MNP-16), and similar to syenites.

But low content of Ca in the syenites (0.2–0.6%; Xu *et al.*, 2002a) cannot lead to deposition of large quantities fluorites. We only found three early fluorites from 40 samples in the Maoniuping deposit. Williams-Jones *et al.* (2000) have pointed that Ca-free, REE fluoride-bearing fluids are an important ingredient for REE mineralization, that mixing of such fluids with Ca-, carbonate-bearing fluids or interaction with carbonate rocks is a major mechanism of REE-fluoro-carbonate mineral deposition. According to Richardson and Holland (1979), massive fluorites are precipitated either as a consequence of changes in temperature and pressure along the flow path of hydrothermal solutions or due to fluid mixing, or as the result of the interaction of hydrothermal solutions with wall rocks. Thus the mixture of F-rich, syenite-derived fluid with the later Ca-, CO_2 -bearing carbonatite-derived fluid caused deposition of REE minerals and later fluorites. The homogenization temperatures of vapor-liquid in bastnaesite are restricted from 116 to 196°C, similar to those of later fluorites, but lower than the those of early fluorites (494 to 502°C; Niu and Lin, 1995; Yuan *et al.*, 1995). The LREE have regular varieties from early to later fluorites by gradual decrease of (La/Nd)_n ratios (means of 1.98, 0.84, 0.46; Xu *et al.*, 2002b). These show that formation of bastnaesite was at late stage by a dissolution-reprecipitation process with a decrease of fluorine activity in the fluids.

The ore-forming fluids involved in the Maoniuping REE mineralization were not contaminated through interaction with ground water or the country rock fluids because (1) the fluorites show less radiogenic Pb isotopes, and the later fluorites have lower $^{207}\text{Pb}/^{204}\text{Pb}$ ratios than the early ones; (2) the δD and $\delta^{18}\text{O}$ values from Maoniuping quartzes range from –77 to –52‰, 7.8 to 9.4‰ (Xu *et al.*, 2002b), respectively, which shows characteristics of mantle-derived fluids.

CONCLUSIONS

The results of this study indicate the following:

1. The initial $^{207}\text{Pb}/^{204}\text{Pb}$ ratio variations between carbonatites and syenites were not affected by any crustal contamination. This implies heterogeneities in the mantle sources for Maoniuping carbonatite-syenite complex.
2. The Pb isotopes from the Maoniuping carbonatites and syenites prove the existence of Himalayan enriched mantle components. Due to orogeny, the rising fluid (EM2-like) from the deep mantle metasomatized the enriched mantle, with an EM1 signature, stored in Maoniuping sub-continental lithosphere.
3. The initial $^{207}\text{Pb}/^{204}\text{Pb}$ ratios from the Maoniuping

early fluorites are higher than those of later ones and carbonatites, but similar to those of syenites. It suggests that fluid involved deposition of early fluorites was mainly derived from syenites. But F-rich, syenite-derived fluid is not only factor to cause REE mineralization. Mixing of such fluid with Ca-, CO_2 -bearing (possibly small F, because F differentiated from syenite magma. If not, they would deposit fluorite early as disseminated crystals), carbonatite-derived fluid is very effective mechanism for depositions of REE minerals and later fluorites.

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