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A rare earth element-rich carbonatite dyke at Bayan Obo, Inner Mongolia, North China

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Summary

A carbonatite dyke, extremely enriched in rare earth elements (REE), is reported from Bayan Obo, Inner Mongolia, North China. The REE content in the dyke varies from 1 wt% to up to 20 wt%. The light REEs are enriched and highly fractionated relative to the heavy REEs, and there is no Eu anomaly. Although carbon isotope δ^{13}C (PDB) values of the carbonatites (-7.3 to -4.7‰) are within the range of normal mantle (-5 ± 2‰), oxygen isotope δ^{18}O (SMOW) (11.9 to 17.7‰) ratios apparently are higher than those of the mantle (5.7 ± 1.0‰), indicating varying degrees of exchange with hydrothermal fluids during or after magmatic crystallization. The carbonatite is the result of partial melting followed by fractional crystallization. Primary carbonatite melt was formed by less than 1% partial melting of enriched mantle, leaving a garnet-bearing residue. The melt then rose to a crustal magma chamber and underwent fractional crystallization, producing further REE enrichment. The REE and trace element distribution patterns of the carbonatites are similar to those of fine-grained dolomite marble, the ore-host rock of the Bayan Obo REE–Nb–Fe giant mineral deposit. This fact may indicate a petrogenetic link between the dykes described here and the Bayan Obo mineral deposit.

Introduction

Since the discovery of carbonatite dykes (*Le Bas* et al., 1992) at Bayan Obo, Inner Mongolia, North China, evidence is accumulating that the ore-bearing dolomite marble of the Bayan Obo giant REE–Nb–Fe mineral deposit, the world's largest known REE ore deposit, is carbonatitic in origin (*Yuan* et al., 1992;

Le Bas et al., 1996, 1997; *Yang* et al., 1994, 1998a, b, 2000a, b). Although the origin of the ore deposit is under continued dispute, there is no doubt that detailed studies of the carbonatite dykes will provide valuable clues as to the genesis of the ore deposit. Geological mapping showed that there are more than thirty carbonatite dykes occurring within 0–3.5 km north-east of the East ore body of the deposit. The dykes cut across a thrust inlier of the Wutai group granitic gneiss and Archean migmatites in the Kuangou anticline and its southern limb, consisting of Middle Proterozoic metasediments of the Bayan Obo group. New zircon U–Pb ages (1.9–2.0 Ga) for the Wutai group gneiss suggest a Paleoproterozoic (*Wang* et al., 2002) rather than Archaean age. Since the gneiss is tonalitic to syenitic in composition, *Wang* et al. (2002) suggest that it is more appropriate to term it a basement complex. There are also several carbonatite dykes recently discovered in the southern limb of the secondary Bayan Obo syncline. It is significant that these dykes have metasomatised the country rocks on both sides of the contact zones, producing fenites characterized by the presence of sodic amphiboles and albite (*Le Bas* et al., 1992; *Yang* et al., 1994, 2000b). X-ray fluorescence spectrometry (XRF) shows that most of the carbonatite dykes are calcic in composition, and three are also enriched in REE; only two analyses are magnesio-carbonatitic according to the nomenclature of *Woolley* et al. (1989).

This paper describes the Wu carbonatite dyke, named after its discoverer, the mining geologist Mr. Zhan-Jiang Wu. It discusses the processes of REE enrichment and compares the dyke with the REE-enriched dolomite marble of the Bayan Obo deposit.

Petrological features of the carbonatite dyke

The Wu carbonatite dyke is located at Dulahala, 2 km NNE of the East ore body of the Bayan Obo ore deposit (Fig. 1). The dyke is 1.1–1.5 m wide and well exposed for 60 m. It strikes north 20° east and dips to the northwest with an angle of $\sim 85°$. It is emplaced along a fault that separates H1 coarse quartz sandstone from H3 shale, both members of the Middle Proterozoic Bayan Obo group. The bedding planes of both sandstone and shale are almost at right angles to the dyke. Contacts with both wall rocks are sharp. The wall rocks are fenitized to a width of 10 to 20 cm on both sides, and the fenites are characterized by the assemblage of riebeckite–arfvedsonite, albite, and phlogopite. This alkaline mineralization sometimes extends along fractures and joints into the sandstone wall rocks, for up to 30 metres away from the contact zones.

Although the carbonatite is generally even-textured, it locally contains xenocrysts of strained quartz and xenoliths of quartzite and fenite with sodic amphibole from the wall rock. The carbonatite is fine-grained with occasional large calcite crystals. The dyke was affected by later tectonism and is strongly deformed and sheared sub-parallel to the dyke walls, with strong alignments of the mafic minerals. In thin section, one observes curved cleavage and wavy extinction of the larger calcite crystals. These larger crystals appear to be relicts from the original carbonatite before it was deformed and recrystallized. The bulk of the calcite occurs as euhedral to subhedral grains 0.2–0.4 mm across, locally with a few calcite phenocrysts up 7 mm in diameter. The calcite forms interlocking grains producing a

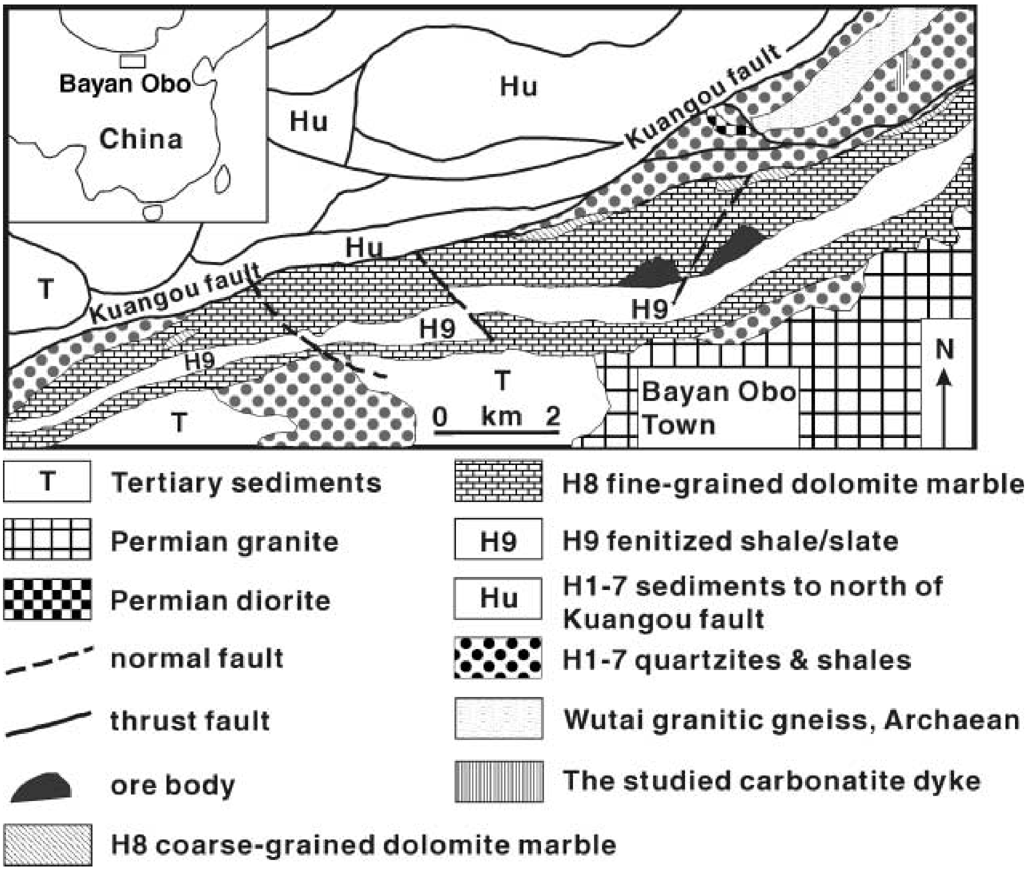

Fig. 1. Geological sketch map of the Bayan Obo region, North China, modified from *Drew* et al. (1990) and *Le Bas* et al. (1997). The carbonatite dyke cuts across H1 coarse-grained quartz sandstone and H3 shale of the Middle Proterozoic Bayan Obo group

mosaic texture with some triple junctions, typical in both igneous carbonatites and recrystallized carbonate rocks. The calcite is high in Sr and Mn, but REE could not be detected by electron microprobe analysis (EMPA) (*Yang* et al., 1998a). The carbonatite includes variable contents of bastnaesite [$(Ce, La)(CO_3)F$] and parisite [$(Ce, La)_2Ca(CO_3)_3F_2$], most of which are euhedral to subhedral, 0.01–0.07 mm across, but with some larger grains up to 0.5 mm in diameter. Many of the finer grains occur in aggregates interlocked with calcite (Fig. 2), indicating that they crystallized in equilibrium with calcite crystals (*Yang* et al., 1998b). Under polarized light, bastnaesite and parisite are light brown to light yellow and weakly pleochroic, as well as having high relief and higher-order interference colors. In addition, the dyke contains cebaite [$Ba_3Ce_2(CO_3)_5F_2$], cordylite [$CaBa(Ce,La)_2(CO_3)_4F_2$], huanghoite [$BaCe(CO_3)_2F$], magnesio–riebeckite, apatite, hematite, magnetite, monazite, allanite, quartz, fluorite, dolomite, and barite (*Yang* et al., 2000a). Being fine-grained, the carbonatite could be termed an alvikite. Interestingly, Ba–REE and Ca–REE fluorcarbonate series minerals are also important in the REE–Nb–Fe giant ore body at Bayan Obo (*Institute of Geochemistry*, *Chinese*

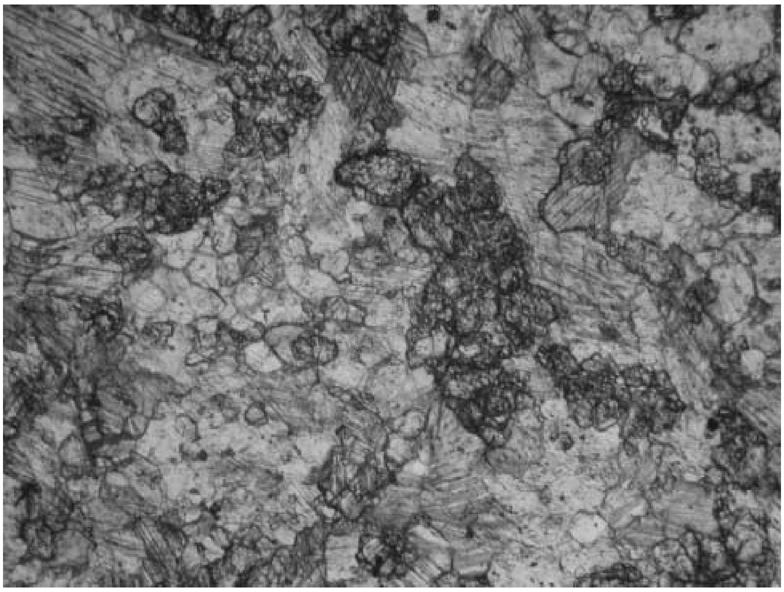

Fig. 2. Photomicrograph of fine-grained carbonatite (sample 93/149) from the Wu dyke. Many fine bastnaesite [(Ce, La)(CO_3)F] and parisite [$(Ce, La)_2Ca(CO_3)_3F_2$] (darker brown and higher relief) grains occur interlocked with calcite, indicating that they crystallized in equilibrium with the calcite crystals. Plain-polarized light; field of view 2 mm

Academy of Sciences, 1988; *Yuan* et al., 1992; *Zhang* et al., 1995; *Chao* et al., 1997; *Yang* et al., 2000a).

Analytical procedures

About 500 g chips for each sample were washed with distilled water at room temperature then dried at 100 °C. The chip samples were ground to – 200 mesh with an agate mill. Whole-rock X-ray fluorescence spectrometry (XRF) and inductively coupled plasma-emission spectrometry (ICP-ES) analyses were performed at the Geology Department of Leicester University, U.K., following analytical procedures described by *Le Bas* et al. (1992, 1997). To overcome problems of extreme trace element enrichment and to match matrices, trace elements in the samples were calibrated against certified carbonatite reference standards, following *Hodgeson* (1985) and *Clarke* et al. (1994). Accuracy and precision for major elements were estimated to be better than 1 to 3% relative standard deviation (RSD), except for SiO_2 that may be around 5% RSD, and all trace elements including rare earth elements (REE) better than 10% RSD. Instrumental detection limits (3 sigma) by XRF for trace elements are (in ppm): Sc (4), V (4), Cr (1), Co (3), Ni (3), Cu (2), Zn (1), Rb (0.5), Sr (0.6), Y (0.3), Zr (0.7), Nb (0.4), Ba (24), Th (2). Instrumental detection limits (3 sigma) by ICP–ES for REE are (in ppm): La (3), Ce (3), Pr (5), Nd (5), Sm (2), Eu (0.3), Gd (3), Tb (15), Dy (1), Ho (3), Er (3), Yb (0.2), Lu (0.2). ICP-ES and XRF results are presented in Tables 1 and 2.

Carbon and oxygen isotope compositions of the carbonatites were obtained by reacting the samples with pure H_3PO_4 at 25 °C following *McCrea* (1950).

Table 1. *REE contents (ppm) of carbonatites from Bayan Obo, and comparison with associated fenites as well as fine-grained ore-hosted dolomite marble from the Bayan Obo ore deposit*

Sample No.	90/39	90/43	90/44	90/48	93/149	93/151	90/49	90/51	90/58	90/64	B230	B256
Rock type	D	D	D	D	D	D	F	F	f	f	f	f
La	5082	59295	33280	5925	94810	7207	29	33	8854	10360	3855	13522
Ce	7021	75535	42834	7656	90630	10370	56	68	13070	17603	17140	26526
Pr	510	5835	3457	603	5392	936	6	7	1161	1526	1955	2282
Nd	1592	16418	9439	1702	6538	2066	15	59	3888	4726	7813	8519
Sm	110	1147	797	143	492	240	4	3	356	386	330	399
Eu	22.8	236.5	155.0	37.1	49	77	0.4	0.6	78.8	85.5	56.0	60.1
Gd	53	513	346	94	458	212	3	3	164	164	168	44
Tb	na	na	na	na	52	26	na	na	na	na	na	na
Dy	29	338	217	66	566	111	1	2	84	94	95	40
Ho	na	na	na	na	40	23	na	na	na	na	na	na
Er	36	395	268	57	80	55	0.8	0.4	74	88	84	15
Tm	na	na	na	na	7.0	6.0	na	na	na	na	na	na
Yb	3	52	35	14	36	35	0.4	0.4	10	10	26	17
Lu	0.5	8.0	10.0	2.5	5.1	4.6	<0.3	<0.3	1.4	1.4	6.4	2.1
ΣREE	14458	159771	90835	16299	199154	21368	115	175	27740	35042	31529	51427

Note: *D* carbonatite from Wu dyke; *F* fenite from Wu dyke; *f* fine grained dolomite marble from ore-host rock for the Bayan Obo deposit; *na* not analyzed

Table 2. *The major element (wt%) and trace element (ppm) content of carbonatites from Bayan Obo, and comparison with associated fenites as well as fine-grained ore-hosted dolomite marble from the Bayan Obo ore deposit*

Sample No.	90/39	90/42	90/43	90/44	90/45	90/52	93/149	90/40	90/46	90/55	90/56	90/58	90/64	B230	B256
Rock type	D	D	D	D	D	D	D	F	F	F	F	f	f	f	f
SiO_2	10.06	13.79	8.61	3.63	22.21	16.50	1.63	60.79	64.65	61.52	58.07	0.38	0.44	1.10	1.64
TiO_2	0.04	0.05	0.02	0.02	0.26	0.27	0.03	0.12	0.59	0.03	0.69	0.03	0.04	0.09	0.30
Al_2O_3	0.30	0.38	0.22	0.21	1.20	0.25	0.31	14.48	14.15	16.92	15.82	0.15	0.15	0.21	0.29
Fe_2O_3	5.78	5.25	1.29	1.23	6.78	7.19	1.42	4.73	6.30	0.94	5.82	8.72	9.09	14.63	11.78
MnO	1.28	1.91	0.49	0.52	1.37	1.52	0.56	0.10	0.14	0.03	0.11	1.35	1.30	2.36	1.58
MgO	2.16	3.39	0.32	0.44	3.01	2.63	0.43	bd	1.65	0.2	2.5	15.04	12.95	9.16	9.23
CaO	31.9	39.65	20.34	24.5	28.63	31.53	43.91	0.27	0.52	0.48	0.34	29.52	27.62	26.58	23.92
Na_2O	0.93	0.69	0.19	0.15	0.56	0.77	0.05	2.25	5.99	7.60	5.81	bd	0.01	0.05	0.02
K_2O	0.44	0.41	0.01	0.04	1.31	0.19	0.20	11.94	5.18	5.05	5.90	0.01	0.01	0.17	0.09
P_2O_5	0.69	0.26	0.08	0.06	0.92	0.33	0.16	0.15	0.25	0.12	0.22	0.07	0.52	0.20	0.26
Sc	54	42	45	33	40	55	30	47	13	6	18	40	43	50	53
V	8	18	5	10	11	81	10	82	74	17	84	bd	21	58	44
Cr	1	1	3	2	2	1	6	64	62	19	108	bd	bd	37	5
Co	36	9	12	1	19	14	2	9	19	2	23	bd	9	32	37
Ni	31	10	22	21	22	32	28	4	35	1	45	5	5	1	5
Cu	119	36	154	83	55	328	84	11	9	6	8	12	11	15	13
Zn	422	239	576	403	506	1107	52	111	287	73	340	229	109	106	81
Rb	1	1	1	1	2	1	34	119	61	54	196	4	3	5	5
Sr	18093	12413	8759	9496	10925	16371	12529	68	138	148	209	1550	1681	2406	1621
Y	187	188	269	260	285	463	166	12	38	14	20	77	112	78	132
Zr	13	53	6	14	79	37	5	63	649	16	317	4	bd	3	1
Nb	273	90	219	86	723	3379	52	84	57	56	23	611	68	652	340
Ba	42951	13087	28718	18513	43917	41717	37771	1113	996	1630	2349	204	385	2421	1089
La	5082	5885	59295	33280	9264	5852	90505	80	35	17	37	8854	10360	3855	13522
Ce	7021	8506	75535	42833	13755	8645	110671	131	76	15	59	13070	17602	17140	26526
Nd	1592	1998	16418	9439	3661	1980	23292	47	36	1	19	3888	4726	7813	8519
Th	181	301	1436	1193	906	691	887	15	16	20	14	83	20	94	129

Note: The symbols for rock type is the same as Table 1; *bd* below detection

Table 3. *Carbon and oxygen isotope composition* (‰) *of carbonatites from Bayan Obo*

Samples	Rock type	$\delta^{13}C_{Cc}$	$\delta^{13}C_{Dol}$	$\delta^{18}O_{Cc}$	$\delta^{18}O_{Dol}$
90/39	carbonatite	– 5.4	na	14.0	na
90/43	carbonatite	– 5.4	na	16.4	na
90/44	carbonatite	– 4.6	na	17.7	na
90/45	carbonatite	– 6.6	na	11.9	na
BY177	carbonatite	– 5.6	−7.2	13.8	11.9
BY180	carbonatite	– 6.6	−7.3	16.4	14.2
BY181	carbonatite	– 5.7	−6.5	13.9	12.8
BY184	carbonatite	– 4.7	−6.7	15.1	12.7

Notes: *Cc* calcite; *Dol* dolomite; *na* not analysed

The released CO_2 was analyzed with a Finnigan Delta + mass spectrometer at the Department of Earth and Space Sciences, University of Science and Technology, China. Since the samples contained both calcite and dolomite they were analyzed using the double extraction technique of *Al-Asam* et al. (1990). Results are reported relative to PDB and SMOW with an overall analytical precision of ± 0.2 per mil for both $\delta^{13}C$ and $\delta^{18}O$. The C and O isotope analytical results are tabulated in Table 3.

The geochemistry of the carbonatite dyke

As shown in Table 1, the whole-rock carbonatite samples are extremely enriched in REE with a large range from 1 to 20 wt%, averaging 8 wt%. The chondrite-normalized REE patterns for carbonatites show strong LREE enrichment without a Eu anomaly (Fig. 3a), a feature typical of carbonatites worldwide (*Nelson* et al., 1988; *Woolley* et al., 1989; *Zaitsev* et al., 1998; *Le Bas*, 1999). $(La/Yb)_N$ ranges from 139 to 1776 with an average of 814, indicating that La and Yb experienced extreme fractionation during carbonatite evolution. $(Ce/Yb)_N$ also varies markedly from 77 to 673, with an average of 373. Variation in these parameters reflects that LREE and HREE are extremely differentiated in the carbonatite dyke. In addition, total REE contents differ by 14 times among samples, revealing that the distribution of REE phases is highly heterogeneous. This agrees with thin section observations that bastnaesite is locally concentrated up to 30 vol%. Calcites from the dyke have high SrO and MnO contents, again typical of carbonatites (*Yang* et al., 1998a). However, REE in the calcites could not be detected by means of EMPA, indicating that the REE reside in discrete REE phases such as bastnaesite and parisite. It is interesting that the REE patterns of the Wu dyke are similar to those of the ore-bearing, fine-grained dolomite marble (H_{8f}) of the Bayan Obo giant REE–Nb–Fe ore deposit (Fig. 3b).

REE patterns of associated fenites are different from those of carbonatites, with overall lower REE contents and a negative Eu anomaly (Fig. 3a). Even though the CI-normalized HREE of the fenites remain relatively uniform, their LREE content were obviously enriched and the negative Eu anomaly somewhat moderated, compared with the primary sedimentary quartz sandstones (*Institute of Geochemistry*,

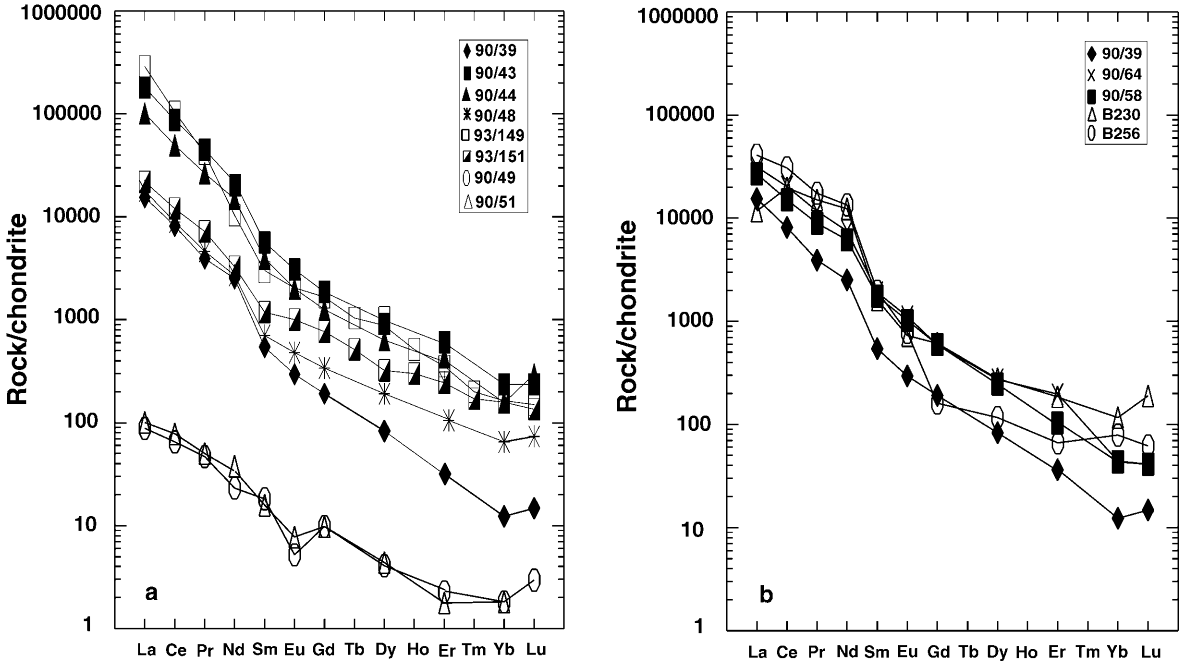

Fig. 3. Chondrite-normalized REE patterns of the samples in Table 1. **a** Carbonatites and fenites from the Wu carbonatite dyke. **b** Fine-grained dolomite marble of the Bayan Obo Fe–Nb–REE ore deposit. Chondrite data from *Boynton* (1984)

The Chinese Academy of Science, 1988). These characteristics reflect sodic metasomatism (i.e. fenitization) of wall rocks caused by intrusion of the carbonatite dyke.

Figure 4a presents mantle-normalized trace element spidergrams for carbonatites and related fenites. The diagrams show that the carbonatites are rich in Ba, Th, LREE, and Sr, variable with respect to Nb and P, and relatively low in Rb, K, and Ti. Although Zr contents are low, there is no obvious Zr anomaly. The spidergrams for the carbonatites are identical to those of alvikites elsewhere in the world (*Nelson* et al., 1988; *Woolley* et al., 1989; *Le Bas*, 1999). It is worth noting that they almost overlap the trace element spidergrams of the dolomite marble (H_{8f}) of the Bayan Obo giant REE–Nb–Fe ore deposit (Fig. 4b). These trace element and REE similarities imply that there could be a genetic link between the carbonatite dyke and the dolomite marble.

Compared with sedimentary quartz sandstones (*Institute of Geochemistry*, *The Chinese Academy of Science*, 1988) SiO_2 contents of fenites are depleted, whereas Na_2O and Fe_2O_3 are enriched, indicating net addition of Na and Fe during fenitization and net loss in silica. In addition, the spidergrams for fenites show relatively high Rb, K, and Zr (Fig. 4a), reflecting a tendency for fenites to retain to some extent the geochemical signature of their sedimentary quartz sandstone protoliths. The notable positive Zr anomaly may reflect a detrital zircon component in the metasediment that survived fenitization. However, Ba, La, Ce, Nd, and Sr are apparently enriched (Fig. 4a), which is a signature imposed by fenitization. Therefore, fenitizing fluids emanated from the carbonatite magma were rich in Na, Fe, LREE, Ba, and

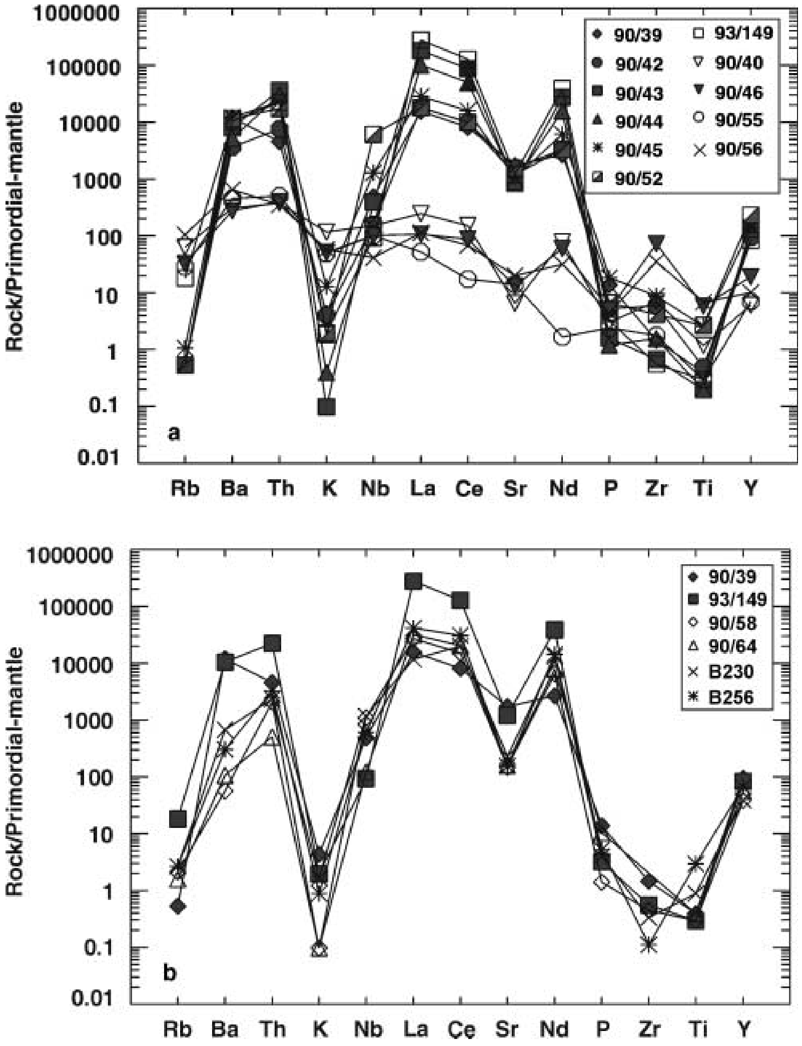

Fig. 4. Mantle-normalized trace element spidergrams for the samples in Table 2. **a** Carbonatites and fenites from the Wu carbonatite dyke. **b** Fine-grained dolomite marble hosting the Bayan Obo Fe–Nb–REE ore deposit. Primordial mantle data from *Wood* et al. (1979)

Sr, but relatively depleted in silica. Since fluorite is ubiquitous in both the carbonatite and fenite, fluorine may have been high in the fenitizing fluids.

$\delta^{18}O_{SMOW}$ ratios of both calcite and dolomite from the Wu carbonatite dyke (11.9 to 17.7‰; Table 3) are higher than those in unaltered carbonatites (5.7 ± 1.0‰; *Le Bas*, 1981; *Deines*, 1989). $\delta^{18}O_{SMOW}$ ratios of the calcite are higher than those of coexisting dolomite (Table 3). However, the $\delta^{13}C_{PDB}$ ratios (− 4.6 to − 7.3‰; Table 3) of calcite and dolomite from the dyke remain within the range normal for carbonatite (− 4 to − 7‰; *Deines*, 1989), with the $\delta^{13}C_{PDB}$ of calcites also higher than those of the coexisting dolomites. $\delta^{18}O_{SMOW}$ and $\delta^{13}C_{PDB}$ ratios of calcite–dolomite pairs reveal that in terms of these isotopes, the two minerals are not in equilibrium with each other, indicating varying degrees of exchange with hydrothermal fluids either during or after magmatic crystallization. Again, the $\delta^{18}O_{SMOW}$ values of the carbonatites are within the range of the dolomite marble ($H8_f$) of the Bayan Obo ore deposit (*Le Bas* et al., 1997).

Whole-rock Sm–Nd isotope age and initial Nd isotope ratio of the carbonatite dyke (*Zhang* et al., 1994) are 1223 ± 65 (2σ) Ma, $I_{Nd} = 0.510926 \pm 35$ (2σ) (εNd (t) $= -2.63 \pm 0.68$). Within error, this age is identical to the Sm–Nd age of REE ores from the Bayan Obo deposit. Initial $^{143}Nd/^{144}Nd$ ratios are also very close to each other (*Zhang* et al., 1994). A magnesio–riebeckite sample collected from the Wu dyke yielded a $^{40}Ar/^{39}Ar$ plateau age of 1288 ± 12 Ma (*Ren* et al., 1994). These ages suggest that the carbonatite magmatism at Bayan Obo took place in the Mid-Proterozoic. *Yang* et al. (1994) suggested that fenites formed at almost the same time as, or slightly later than, the carbonatites. A mineral internal isochron of Rb–Sr isotopes, based on three points (i.e. albite, riebeckite and fenite whole rock), yielded an age of 343 ± 7 (2σ) Ma (*Yang* et al., 1994). This age is unlikely to represent the emplacement age of the fenite because the Rb–Sr system was reset during the Caledonian orogeny (*Chao* et al., 1992, 1993, 1997) followed by extensive intrusion of Permian granites (Fig. 1). In conclusion, the whole-rock Sm–Nd ages of the fenite and carbonatites (*Zhang* et al., 1994) are considered more reliable because the Sm–Nd isotope system has a higher closure temperature.

Discussion

Two models are commonly proposed to explain the origin of carbonatites: (1) immiscible carbonate melt exsolved from parental CO_2-bearing nephelinitic or melilititic melts derived from the mantle (*Le Bas*, 1977, 1981; *Wyllie* et al., 1996); and (2) primary carbonate melts derived by partial mantle melting (*Gittins*, 1989; *Bell* et al., 1998). An interesting model recently proposed by *Lentz* (1998, 1999) suggests that intrusion-induced syntexis of limestone through volatile fluxing could generate carbonate melts; carbonatitic dykes or veins formed in this manner are not associated with the cogenetic peralkaline magmatic rocks in the intrusion-related skarn systems. However, the geochemical features and the mineral parageneses of the Wu carbonatite dyke and associated fenites as well as the Middle Proterozoic age rule out a genetic link with Permian granite intrusion (Fig. 1). The present study shows that the Wu carbonatite dyke at Bayan Obo may be formed by fractional crystallization of primary carbonatite magma derived by low degrees of partial melting of enriched mantle.

REE carbonatites from the Wu dyke at Bayan Obo possibly constitute the richest REE occurrence in the world. REE mainly reside in bastnaesite and parisite. The REE minerals are interlocked with calcite, producing a mosaic texture with triple junctions (Fig. 2) as is typical of carbonatites elsewhere, indicating that they are primary minerals that crystallized directly from carbonatite magma (*Yang* et al., 1998b, 2000a). This type of fabric was also found in REE-rich carbonatites at Mountain Pass, California, USA (*Mariano*, 1989). It is worth noting that the compositions of REE phases in the carbonatite dyke are identical to those of the dolomite marble in the Bayan Obo ore deposit (*Yang* et al., 1998b, 2000a). Trace element patterns (Fig. 4a and b) and formation ages are also the same within error

(*Yuan* et al., 1992; *Zhang* et al., 1994; *Ren* et al., 1994). These geochemical signatures demonstrate that there could be a genetic link between the carbonatite dyke and the Bayan Obo ore deposit. The results from O, C and Sr isotopic studies (*Le Bas* et al., 1996, 1997) support this conclusion.

Both the carbonatite dyke and the ore-hosted dolomite marble are deformed and sheared, reflecting that tectonism postdating the carbonatitic magmatism is intensified in the Bayan Obo region, which may be associated with Caledonian subduction (*Chao* et al., 1992, 1993, 1997) and extensive intrusion of Permian granites (Fig. 1). However, other authors argued that the dolomite marble may belong to the metasedimentary H8 dolostone marble of the Middle Proterozoic Bayan Obo group (*Chao* et al., 1992, 1993, 1997; *Wang* et al., 1994). Although this debate is still ongoing, evidence is increasing that carbonatites may play a key role in REE mineralization at Bayan Obo. *Campbell* and *Henderson* (1997) studied apatite parageneses in the ore deposit and suggested a model for ore formation, involving mineralizing fluids derived from unexposed carbonatite intrusives reacting with a sedimentary host, the Proterozoic H8 marble of the Bayan Obo group. *Drew* et al. (1990) also attributed the formation of the deposit to carbonatitic fluids. Evidence from mineral parageneses, REE fractionation, and fluid inclusions in the ore deposit imply that the mineralizing fluids could have been carbonatitic (*Smith* et al., 1999, 2000a, b).

Calcite in the REE carbonatite from the Wu dyke is rich in Sr and Mn, and the relationship of these two elements are inversely correlated (Fig. 5). This trend reveals that the melt may have undergone fractional crystallization (*Clark* et al., 1994; *Yang* et al., 1998a). Figure 3 and Fig. 4 also indicate that the carbonatite evolved by fractional crystallization. Hence, it could be deduced that calcite fractionation might result in REE enrichment in the residual magma. This kind of REE enrichment process is very similar to that of carbonatites from Mountain Pass, California, USA (*Wyllie* et al., 1996). These authors argued that REE concentration takes places by fractional crystallization in the crust but requires high initial REE contents in the carbonatite melt derived from the mantle. Otherwise, REE would enter carbonate minerals and other phases, preventing the formation of discrete REE minerals (*Wyllie* et al., 1996). If the REE content of a carbonatite exceeds a

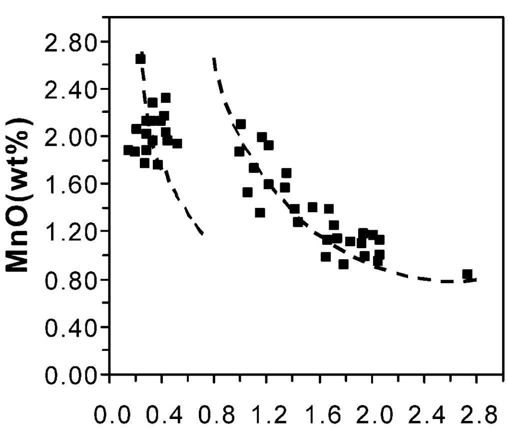

Fig. 5. SrO–MnO variation for calcite from the Wu carbonatite dyke. EMPA data from *Yang* et al. (1998a)

certain value (e.g. 1000 ppm), the most important minerals to prevent enrichment of REE would be monazite, apatite, and perovskite, i.e. minerals that crystallize relatively early from a carbonatitic melt. As a result, a common apatite-magnetite type carbonatite would form (*Le Bas*, 1977; *Wyllie* et al., 1996).

Since there are no known silica-undersaturated peralkaline igneous rocks associated with carbonatites in the Bayan Obo area, it is difficult to consider that the Wu carbonatite dyke was formed by liquid immiscibility of a nephelinitic magma under upper crustal conditions, following its derivation by very low degree partial melting of enriched mantle. In the Middle Proterozoic, Bayan Obo was located in a continental rift on the northern margin of the North China platform (*Drew* et al., 1990). This tectonic situation favored the formation of peralkaline igneous rocks and associated carbonatites, such as those in eastern Africa (*Le Bas*, 1977). However, although it cannot be discounted that liquid immiscibility occurred at depth within the crust, there would not have been significant enrichment of REE in the immiscible carbonatite melt (*Wyllie* et al., 1996). This discovery is consistent with experimental results (*Hamilton* et al., 1989) especially under low pressure (0.2 to 0.3 GPa). Recent experimental data confirm that the REE partition coefficients between immiscible carbonate and silicate melt are close to unity and even tend to fall with increasing pressure to 1 GPa, discounting significant enrichment of REE in carbonatite melt by liquid immiscibility (*Jones* et al., 1995). Under pressures and temperatures of the upper mantle, LREE seem to prefer carbonatite melt in any carbonate/silicate immiscible pair of liquids, by a factor of about ten or greater (*Hamilton* et al., 1989). However, there is no geological evidence for liquid immiscibility under high-pressure conditions. Hence, this mechanism for REE enrichment through liquid immiscibility, either at low or high pressures, is not supported here because there are no peralkaline magmatic rock found in the Bayan Obo area.

A number of experimental investigations showed that primary carbonatite melt may be produced by partial melting of mantle lherzolite between 2.1 and 3.1 GPa and 930° to 1080 °C (*Wallace* and *Green*, 1988; *Bailey*, 1993; *Sweeney*, 1994; *Yaxley* and *Green*, 1996). Using mineral/carbonatite melt partition coefficients of clinopyroxene, orthopyroxene, olivine (*Brenan* and *Watson*, 1991), garnet, and amphibole (*Sweeney* et al., 1992), the phase relations established by *Wallace* and *Green* (1988), *Sweeney* (1994), and *Yaxley* and *Green* (1996) and a batch melting model (*Hanson*, 1978) render it possible that carbonatite may form by partial melting within the upper mantle. The computed results (Fig. 6a) show that less than one percent partial melting of a metasomatized mantle source 10 to 20 times more enriched than primitive mantle (*McDonough* and *Sun*, 1995) could produce an initial carbonatite melt with Ce of up to 1000 ppm and $(Ce/Yb)_N$ of 30. Garnet in the residual mantle would be around 20%. This process may account for about 10 to 15% enrichment of REE observed in the Wu dike. Note that a mantle source more enriched than assumed would contribute more to the enrichment of REE than the computed results in Fig. 6a. If such a primary carbonatite melt undergoes further fractional crystallization within a magma chamber and/or during ascent, its REE will be further enriched since most rock-forming minerals have Ce partition coefficients lower than 0.01 (*Brenan* and *Watson*, 1991; *Rollinson*, 1993). A simple fractional crystallization model is described below.

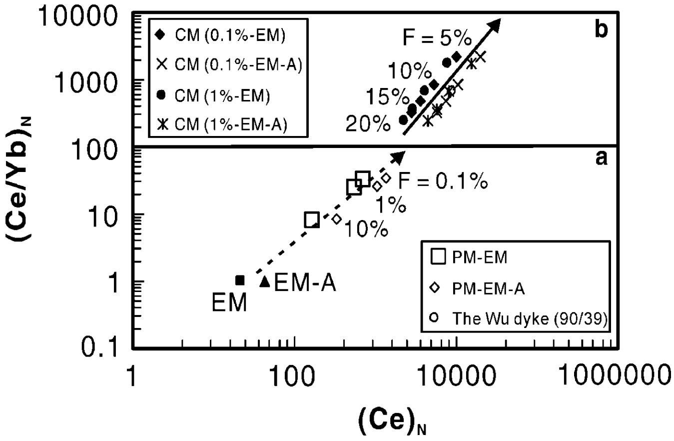

Fig. 6. Numerical modeling results of REE enrichment by partial mantle melting and fractional crystallization. **a** (Ce)$_N$–(Ce/Yb)$_N$ variations in carbonatite melts generated through very low degree partial melting of enriched mantle (EM); chondrite-normalizing data as in Fig. 3a. EM-enriched mantle with Ce and Yb ten times higher than primitive mantle (*McDonough* and *Sun*, 1995). EM-A-enriched mantle with Ce and Yb twenty times higher than primitive mantle. Arrow denotes enrichment of REE by various degrees of partial melting (F) of EM, using a batch melting equation of *Hanson* (1978). Open squares are partial melts of EM and open diamonds are melts from EM-A. The residual mineral assemblage is assumed to be 40% olivine, 25% garnet, 15% orthopyroxene, 15% clinopyroxene, and 5% amphibole, based on experimental data by *Wallace* and *Green* (1988), *Sweeney* (1994), and *Yaxley* and *Green* (1996). Mineral/carbonate melt Ce and Yb partition coefficients use data from *Sweeney* et al. (1992) and *Brenan* and *Watson* (1991). **b** (Ce)$_N$–(Ce/Yb)$_N$ variations of residual carbonatite melts produced by Rayleigh fractional crystallization (*Rollinson*, 1993) of primary carbonatite mantle melts generated in Fig. 6a. F (5 to 20%) denote residual melt fraction. Four sets of data are calculated using the 0.1% and 1% partial melts generated in Fig. 6a: Asterisk-CM (1%-EM-A)-residual melts after fractional crystallization of 1% partial melts of EM-A; solid circle-CM (1%-EM)-residual melts after fractional crystallization of 1% partial melts of EM; cross-CM (0.1%-EM-A)-residual melts after fractional crystallization of 0.1% partial melts of EM-A; solid diamond-CM (0.1%-EM)-residual melts after fractional crystallization of 0.1% partial melts of EM. The open circle is sample 90/39 from the Wu carbonatite dyke, thought to represent the least evolved sample for the Wu dyke

Studies show that carbonatite melt has extremely low density (2.0 to 2.2 g/cm^3, see *Trieman* and *Schedl*, 1983; *Wolf*, 1994) and low viscosity ($5 * 10^{-4}$ to $5 * 10^{-2}$ poise, see *Trieman* and *Schedl*, 1983; *Norton* and *Pinkerson*, 1997), permitting a high degree of mobility and fractional crystallization at high levels in the crust, or even eruption to the surface such as the Oldoinyo Lengai natrocarbonatite in Tanzania. Recent experimental data demonstrate that fractional crystallization of silicate phases (i.e. nepheline, melanite, melilite, clinopyroxene) from silicate-bearing natrocarbonatite magma could occur at pressures as low as ca. 20 MPa. Subsequent evolution of the magma could be dominated by carbonate crystallization and separation (*Petibon* et al., 1998). Since no REE were detected in calcite from the Wu dyke with EPMA, the calcite/melt REE partition coefficient could be very low. If we assume a bulk Ce partition coefficient of 0.04, then 85–90% Rayleigh fractionation of a carbonatite magma derived from low degree (0.1–1%) partial melting of enriched mantle may lead to Ce concentrations of up to 9434 ppm, which is 10 times higher than in the original melt (Fig. 6b). As shown by experimental results (*Petibon* et al., 1998), melanite occurs as a major fractionating phase during crystallization of carbonatite magma. It is reasonable to suppose a bulk Yb partition coefficient (D_{Yb}) of 1.5, compared with the garnet partition coefficient data for mineral/carbonate-melt system (*Sweeney* et al., 1992) with those for mineral/basaltic melt systems (see *Brenan* and *Watson*, 1991; *Rollinson*, 1993). This would yield $(Ce/Yb)_N$ ratio of 758 in the residual carbonatite magma, equivalent to that of the sample 90/39 from the Wu dyke (Fig. 6b) which is considered to represent the least evolved melt (Fig. 3a and Fig. 4a). Therefore, fractional crystallization of REE-enriched carbonatite melt (Fig. 6b) could result in the formation of REE carbonatites as the Wu dyke at Bayan Obo (Fig. 6b).

Most models involving fractional crystallization of carbonatite magma placed the process in a magma chamber (*Wyllie* et al., 1996; *Petibon* et al., 1998) even though it could happen during ascent. At Bayan Obo, one should pay attention to alkaline metasomatic rocks in the footwall and the hanging wall of the ore deposit. The footwall is characterized by sodic alteration involving albite and magnesioriebeckite, whereas the hanging wall experienced potassic alteration with microcline and phlogopite (*Drew* et al., 1990; *Yuan* et al., 1992; *Yang* et al., 1994, 2000b). These alkaline metasomatic rocks are similar to fenites associated with carbonatite dykes distributed within the area of 0 ~ 3.5 km north-east of the East ore body of the Bayan Obo deposit, and also similar to fenites elsewhere (*Le Bas*, 1977, 1981). The existence of fenites suggests that the primary carbonatite magma may have been more alkaline, consistent with experimental results (*Wallace* and *Green*, 1988; *Sweeney*, 1994; *Yaxley* and *Green*, 1996) and Oldoinyo Lengai; furthermore a magma chamber may have existed where fractional crystallization took place and where meteoric water may have leached the alkalines from the carbonatites, resulting in the low alkaline contents and C and O isotope signatures in the present carbonatite samples.

Conclusions

The Wu dyke at Bayan Obo is an extremely REE-rich carbonatite dyke with typical fenite envelopes but without associated silica-undersaturated peralkaline igneous rocks. It may constitute an example for carbonatite melt directly derived from enriched mantle by very small degrees of partial melting. The magma underwent fractional crystallization in a crustal magma chamber, resulting in further REE enrichment. The REE and trace element distribution patterns, as well as carbon and oxygen isotopic compositions of dyke samples are similar to those of the fine-grained dolomite marble of the Bayan Obo REE–Nb–Fe giant mineral deposit, suggesting that there may be a petrogenetic link between the two. Both the dyke and the Bayan Obo deposit may have had a common mantle source for REEs and associated trace elements. Although the nature of the ore-bearing dolomite marble is still under debate, the present study suggests it is carbonatitic in origin.

The nature of alkaline metasomatism, potassic in the hanging wall and sodic in the footwall, may provide important clues to the genesis of the ore-bearing dolomite marble. Furthermore, a detailed investigation of stable isotopes of REE minerals (i.e., Ca–REE fluorcarbonate series and Ba-fluorcarbonate series minerals, monazite) may provide further information.

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