

THE SIGNIFICANCE OF PALEOPROTEROZOIC ZIRCON IN CARBONATITE DIKES ASSOCIATED WITH THE BAYAN OBO REE-Nb-Fe DEPOSIT

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ABSTRACT. Sensitive high resolution secondary ion mass spectrometry (SHRIMP II), laser ablation inductively coupled plasma mass spectrometry (ICP-MS) and laser Raman spectroscopy have been used to determine the ages in zircons from carbonatite dikes associated with the Bayan Obo giant REE-Nb-Fe deposit, Inner Mongolia, China. Analyses of small amounts of zircon extracted from large samples of three carbonatite dikes yield late Palaeoproterozoic $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 1894 ± 27 , 1944 ± 20 and 1956 ± 9 Ma. One sample also contained inherited grains with ages up to ~ 2.55 Ga. Zircon grains, even from a single rock, have a wide range of REE patterns, suggesting that they are probably inherited zircons trapped during magma genesis, not zircons crystallized from a single magma. None of the zircon grains has the extremely high Th/U characteristic of the Bayan Obo ore deposit or of the associated carbonatites. Further, mineral inclusions in the zircon identified by Raman spectroscopy are all silicate minerals (quartz and feldspars), consistent with crystallization of the zircon from silicate, not from carbonate, magmas. The Palaeoproterozoic zircons in the Bayan Obo carbonatite dikes did not crystallize from carbonatite magma at the time of dike emplacement, but were derived from wall rock contamination. The ages obtained from the zircons are consistent with ages measured on basement igneous rocks elsewhere in the Bayan Obo region.

INTRODUCTION

The giant Bayan Obo mineral deposit is the largest-known rare earth element (REE)-Nb-Fe deposit in the world, containing ~ 70 percent of the world's mineable light-REE reserves. Many different genetic models have been proposed to explain the extraordinary local concentration of REE, Nb and Fe at Bayan Obo, for example hydrothermal metasomatism (Chao and others, 1992, 1997; Yang and others, 2000a), metamorphism of sediments followed by hydrothermal metasomatism (Wang and Li, 1973), carbonatite intrusion (Le Bas and others, 1997; Zhang and others, 2001; Yang and others, 2003, Yang and Le Bas, 2004), and replacement of sediments by sea-floor carbonate or by the outpouring of coeval mantle-derived fluids (Tu, 1998).

The age of the mineralization is a matter of longstanding debate. Most researchers in China consider, based on Sm-Nd analyses, that the main mineralization occurred at ~ 1.2 Ga (Yuan and others, 1992; Cao and others, 1994; Ren and others, 1994; Zhang and others, 1994, 2001; Liu and others, 2005). The Sm-Nd ages fall into two groups, 1.66 to 1.50 Ga and 1.31 to 1.22 Ga, which have been interpreted as reflecting two related periods of carbonatite magmatism (Le Bas, 2006). However, no direct evidence for Mesoproterozoic magmatism has yet been found at Bayan Obo. Some U-Pb, Th-Pb and Re-Os dating of minerals considered to be closely related to mineralization has yielded early Palaeozoic ages (0.4 – 0.5 Ga) (Wang and others, 1994; Chao and others,

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1997; Qui, 1997; Liu and others, 2004). Although such ages, for example some Th-Pb ages of monazite, are similar to the ages measured on nearby granitoids, no genetic relationship between the Palaeozoic granites and mineralization has yet been demonstrated (Yang and others, 2000b).

The Bayan Obo deposit is very closely associated with carbonate (fig. 1). There are about 30 mapped carbonate dikes (or veins) with a range of mineral assemblages and chemical compositions in the vicinity of the Bayan Obo mine. The carbonate dikes have characteristically high MnO (> 0.50 wt.%) and SrO (> 0.15 wt.%) contents, typical of carbonatites (Yang and Le Bas, 2004). There is accumulating evidence that the genesis of the Bayan Obo deposit was related to carbonatite intrusions (Institute of Geochemistry Chinese Academy of Sciences, 1988; Le Bas and others, 1992; Bai and others, 1996; Yang and others, 2000a, 2000c), so determining the age of the carbonatitic magmatism has become central to understanding the formation of the deposit and its relationship to the regional geology.

Most previous estimates of the age of the carbonatites/ore bodies were obtained from Sm-Nd isochron ages published in the Chinese literature. Some of the principal results are those reported by Yuan and others, (1992): 1.59 ± 0.53 Ga from a 6-point whole rock (ore) isochron, Cao and others (1994): 1.70 ± 0.48 Ga from a 4-point REE mineral isochron, Zhang and others (1994): 1286 ± 91 Ma from a 13-point whole rock

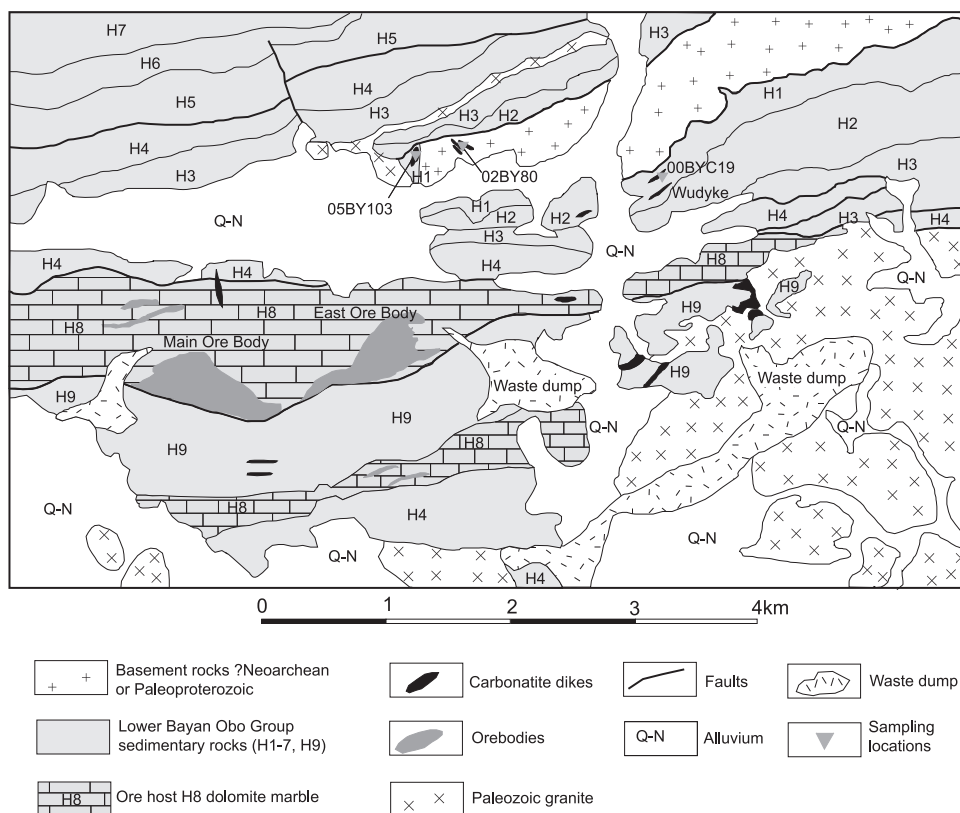


Fig. 1. Sketch map of the Bayan Obo deposit, based on the map in the Field Trip Guide, 30th International Geological Congress (Hou and Zhou, 1996), modified after advice from engineers Guowang Xiao and Tairong Zhang from the Bayan Obo Iron Mine Geological Surveying Department, and our field work.

isochron, Ren and others (1994): 1313 ± 41 Ma from a 7-point REE mineral isochron, and Zhang and others (2001): 1273 ± 100 Ma from a 16-point whole rock (dolomite) isochron and 1250 ± 210 Ma from a 9-point dolomite mineral isochron.

Because the Bayan Obo carbonatite dikes have been affected by later tectonic events (Yang and Le Bas, 2004) and are weathered, the geological significance of these ages remains unclear. Moreover, mineralization ages determined by other isotopic methods in some cases are very different. Qiu (1997), for example, reported SHRIMP U-Pb and Th-Pb ages of 1.00 to 0.40 Ga for monazite from the ore deposit. Similarly, monazite Th-Pb internal isochron ages of 555 to 400 Ma have been interpreted as the age of the main Bayan Obo mineralization by Wang and others (1994) and Chao and others (1997). A pyrite Re-Os age of 439 ± 86 Ma measured by Liu and others (2004), provides further evidence for early Palaeozoic mineralization. In contrast, Fan and others (2002), interpreted a zircon U-Pb age of ~ 2.0 Ga measured on a Bayan Obo carbonatite dike to be the age of carbonatite magmatism. This interpretation was questioned by Le Bas (2006), who suggested that ~ 2.0 Ga might be the age of the host rock. In response, Fan and others (2006) determined the ages of zircon from another dike (the Wudyke, fig. 1) previously described by Le Bas and others (1992) and Le Bas and others (1997). They found two main age groups, 1925 ± 8 Ma, which they interpreted as the age of the wall rocks, and 1416 ± 77 Ma, which was considered to be the age of the carbonatite. Neither interpretation was well constrained by direct evidence.

The present study was designed to test the applicability of zircon for dating carbonatite dike emplacement. Zircons from three Bayan Obo carbonatite dikes were dated by SHRIMP U-Th-Pb, then analyzed for trace elements and mineral inclusions, in order to determine the origin of the zircon and thus the significance of the measured ages.

GEOLOGY

The giant Bayan Obo REE-Nb-Fe deposit is located in Inner Mongolia, about 150 km north of Baotou city ($N41.7^\circ$, $E110.0^\circ$). It lies at the northern margin of the North China craton. In the vicinity of the mine, Palaeo- to Mesoproterozoic sediments of the Bayan Obo Group rest on basement rocks formerly called the Palaeoproterozoic Erdaowa Group or the Archaean Sertengshan Group (Wang and others, 2002).

The Bayan Obo Group consists of low grade metamorphic sandstones, siltstones, limestones and dolomites that vary in both lithology and facies along strike and down dip. The Bayan Obo Group has been divided into two parts (fig. 1), a lower regressive series (members H1–H10) and an upper transgressive series (members H11–H18), both of which have been affected by regional epimetamorphism and local contact metamorphism (Institute of Geochemistry, Chinese Academy of Sciences, 1988; Drew and others, 1990; Bai and others, 1996). The Lower Bayan Obo Group hosts the ore bodies. Igneous rocks in the mine area include Proterozoic anorogenic igneous rocks (Wang and others, 2003), Phanerozoic granite (Hou and Zhou, 1996), and a series of carbonatite dikes (Tao and others, 1998), the age of which is disputed (Fan and others, 2002, 2006; Le Bas, 2006).

The Bayan Obo ore bodies are located in the core of, and are shaped by, the Bayan syncline. The main body strikes WNW-ESE and dips 80 to 85° to the SSW. The eastern ore body strikes WSW-ESE and dips 70 to 85° to the SSE. There are 12 smaller ore bodies scattered over ~ 5 km along strike to the west. Mining is currently focused on the main and eastern bodies, which have a core of Fe ore, with REE ore in the hanging or footwalls, and modest enrichments in Nb. In contrast, the small western ore bodies are rich in all three commodities; Fe, REE and Nb (Institute of Geochemistry, Chinese Academy of Sciences, 1988).

METHODS

Sampling

About 20 kg of carbonate was collected from each of three carbonatite dikes for zircon analysis (fig. 1). Sample 00BYC19 (N41°49'05", E110°0'42") was collected from a dike ~ 2.5 km NE of the east ore body. The dike, hosted by H1 coarse sandstone of the Lower Bayan Obo Group, is less than 20 m long and 0.5 m wide. The sample was predominantly calcite, with minor amounts of magnetite and apatite.

Samples 02BY80 (N41°49'07", E109°59'34") and 05BY103 (N41°49'3", E109°59'10") were collected from dikes ~ 1.5 km N of the east ore body. Sample 02BY80 was taken from a strongly weathered dike less than 0.5 m wide and of unknown length. Sample 05BY103 was taken from a larger dike, more than 5 m wide and over 20 m long, consisting of dolomite with minor magnetite. Carbonatite dike 02BY80 intrudes rocks of the Paleoproterozoic (~2.0 Ga) basement complex (Wang and others, 2002), other small exposures of which consist of tonalite, syenite and small amounts of paragneiss. Carbonatite dike 05BY103 intrudes H1 coarse sandstone of the Bayan Obo Group.

The H1 member is the lowest unit of the Lower Bayan Obo Group regressive series. It consists of deltaic or littoral facies coarse sandstone and basal conglomerate, which rest unconformably on basement tonalite, syenite and paragneiss (Institute of Geochemistry Chinese Academy of Sciences, 1988; Bai and others, 1996). The age of the basement complex is predominantly ~ 2.0 Ga (Wang and others, 2002).

Analytical Techniques

Zircon was extracted from the carbonate samples using a procedure designed to minimize trace mineral cross-contamination. The rock samples were thoroughly cleaned of surface dust in the field, and then washed with purified water in the laboratory before being processed. Clean chips prepared with a jaw splitter were crushed to < 250 µm in a swing mill, then the heavy minerals concentrated using a Wilfley table. Strongly magnetic minerals were removed with a small hand magnet, then the weakly magnetic minerals using a model W72 isodynamic magnetic separator. Zircon was separated from the non-magnetic fraction by tetrabromoethane and methylene iodide, followed by hand picking. Zircon yields were very small, 25 to 30 grains from 00BYC19 and 02BY80, ~ 100 grains from 05BY103. Selected zircon grains were mounted in epoxy with reference zircon of known age and composition (Temora: $^{206}\text{Pb}/^{238}\text{U} = 0.06683$), then polished to half sections in preparation for analysis.

Prior to analysis, the zircon grains were studied under an optical microscope and their internal structures documented by cathodoluminescence (CL) imaging (fig. 2). The CL imaging was carried out at the Key Laboratory of Isotope Geochronology and Geochemistry at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, using a JEOL 8100 electron microprobe equipped with a Gatan Mono CL3 detector. The high REE contents suppressed the CL, so the microprobe was adjusted for maximum brightness; 15 kV accelerating voltage, 20 nA beam current and 11 mm working distance.

The zircon was dated using the sensitive high resolution ion microprobe (SHRIMP II) at the Beijing SHRIMP Center, Chinese Academy of Geological Sciences. Instrumental conditions and data acquisition procedures were similar to those described by Wan and others (2006) and Williams (1998). Working conditions were 10 kV primary beam of O_2^+ ions focused to a 25 µm diameter spot, 10 kV secondary ions mass analyzed at ~ R5000 by single electron multiplier using peak stepping. Common Pb was corrected using ^{204}Pb and a model Pb composition based on the inferred age of each grain. Ages were calculated using the decay constants recommended by the IUGS Subcommission on Geochronology (Steiger and Jäger, 1977).

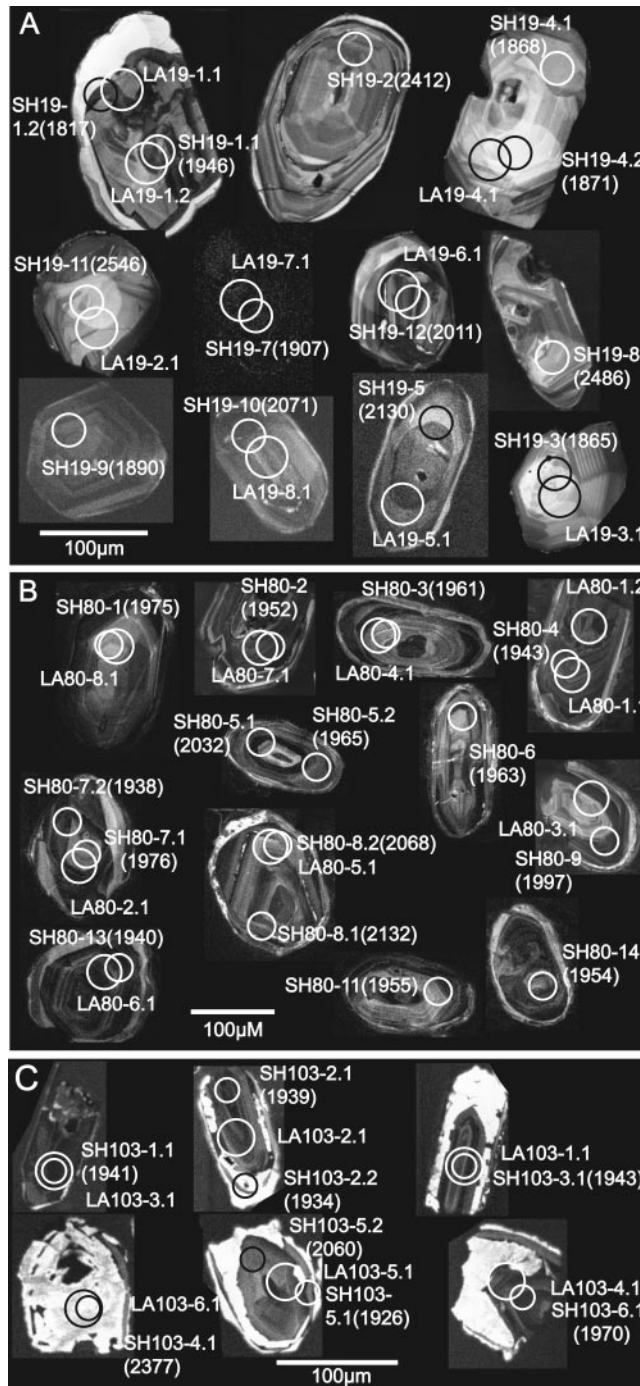


Fig. 2. CL images of analyzed zircon grains from Bayan Obo carbonatite dikes. Small circles (labeled SH**.*) are SHRIMP spots, larger circles (labeled LA**.*) are LA-ICP-MS spots. (A) 00BYC19. (B) 02BY80. (C) 05BY103. Ages are based on $^{207}\text{Pb}/^{206}\text{Pb}$.

The zircon was analyzed for trace elements at the State Key Laboratory of Continental Dynamics, Northwest University, Xi'an, China, using a Laser ICP-MS system consisting of an Agilent 7500a ICP-MS coupled to an ArF Lambda Physik Compex102 Excimer laser. The laser was operated at 200 mJ with a 30 μm diameter spot. Isotopes analyzed were: ^{29}Si , ^{139}La , ^{140}Ce , ^{141}Pr , ^{143}Nd , ^{147}Sm , ^{151}Eu , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{173}Yb , ^{175}Lu and ^{89}Y . NIST 610 glass (Pearce and others, 1997) and Temora zircon (Black and others, 2003) were used as external calibration standards. Instrumental conditions and data acquisition procedures for zircon have been described by Liu and others (2002) and Yuan and others (2006).

Mineral inclusions in the zircon were identified using a Laser Raman spectrometer at the Mineralogical Laboratory, the Guangzhou Institute of Geochemistry, Chinese Academy Sciences. The Raman scattering measurements were carried out at room temperature using a Renishaw RM2000 spectrometer (resolution better than 2 cm^{-1}) with a CCD detector attached to a Leica microscope. The samples were excited by a 20 mW 514.5 nm Argon ion laser. The diameter of the laser spot was $\sim 2 \mu\text{m}$.

RESULTS

Geochronology

The zircon grains dated by SHRIMP U-Th-Pb are illustrated in figure 2. The isotopic compositions are listed in table 1 and plotted on concordia diagrams in figure 3.

The zircon extracted from carbonatite 00BYC19 consisted of moderately coarse (70 – 120 μm diameter), clear, light brown, stubby, rounded prismatic grains with pitted surfaces and very few well-preserved crystal faces. CL imaging showed that most grains had a relatively simple growth texture, consisting either entirely of zircon with euhedral (probably igneous) oscillatory growth zoning, or of a euhedrally-zoned core surrounded by an overgrowth (fig. 2A). The cores were commonly crystal fragments. The overgrowths were mostly unzoned or weakly zoned, and ranged from weakly to strongly cathodoluminescent.

U-Th-Pb analyses of 13 spots on 11 zircon grains yielded a range of U concentrations (70 – 1000 ppm) and isotopic compositions. With one exception, the U-Pb analyses were concordant or nearly concordant within analytical error, but the $^{207}\text{Pb}/^{206}\text{Pb}$ apparent ages ranged from ~ 2.55 to ~ 1.82 Ga (fig. 3A). There was not a clear correlation between the measured ages and whether or not a core was sampled, some of the younger results coming from cores (for example analyses 3 and 4.2) and older results coming from outer parts of grains (for example analyses 5 and 8). The only cluster of ages was at the younger end of the distribution, where 6 spots had almost the same age within analytical uncertainty. Omitting the lowest analysis (1.2), which came from a spot overlapping a boundary between a core and overgrowth, the weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of the remainder (MSWD = 1.5) was 1894 ± 27 Ma (95% c.l.).

Less zircon was recovered from carbonatite 02BY80. Only 16 grains were mounted. These were very similar in appearance to the zircon from 00BYC19, moderately coarse (80 – 150 μm diameter), clear, pale brown and rounded with pitted surfaces and very few inclusions (none of the inclusions was accessible to identification using laser Raman). The grains also had similar growth textures, zircon with mostly simple oscillatory zoning forming whole grains or the cores of grains with thin unzoned overgrowths (fig. 2B).

Fifteen analyses of 12 grains yielded a slightly narrower range of U concentrations (180 – 1285 ppm) than the zircon from 00BYC19 and a different pattern of isotopic compositions. Although there was a narrower range of $^{207}\text{Pb}/^{206}\text{Pb}$ apparent ages (2.13 – 1.94 Ga), several of the analyses were significantly discordant, indicative of

TABLE 1
(continued)

Spot name	concentrations (ppm)				Isotopic ratios										Age (Ma)									
	U	Th	Pb*	Pb/U	$\frac{^{204}\text{Pb}}{^{206}\text{Pb}}$	$1\ \sigma$	$\frac{^{208}\text{Pb}}{^{206}\text{Pb}}$	$1\ \sigma$	$\frac{^{206}\text{Pb}^*}{^{238}\text{U}}$	$1\ \sigma$	$\frac{^{207}\text{Pb}^*}{^{235}\text{U}}$	$1\ \sigma$	$\frac{^{207}\text{Pb}^*}{^{206}\text{Pb}}$	$1\ \sigma$	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	$1\ \sigma$	$\frac{^{208}\text{Pb}^*}{^{232}\text{Th}}$	$1\ \sigma$	$\frac{^{207}\text{Pb}}{^{235}\text{U}}$	$1\ \sigma$	$\frac{^{208}\text{Pb}}{^{232}\text{Th}}$	$1\ \sigma$		
05BY103-1.1	1017	583	0.57	333	1.71E-03	6.35E-05	0.1164	0.0031	0.3080	0.0037	5.054	0.089	0.1190	0.0014	0.0625	0.0019	1731	18	1828	15	1941	21	1226	35
05BY103-2.1	936	435	0.47	293	8.50E-04	3.90E-05	0.0845	0.0017	0.3025	0.0023	4.956	0.060	0.1188	0.0010	0.0550	0.0012	1704	11	1812	10	1939	15	1082	23
05BY103-2.2	310	105	0.34	112	8.21E-04	6.49E-05	0.0833	0.0026	0.3505	0.0050	5.726	0.113	0.1185	0.0015	0.0866	0.0031	1937	24	1935	17	1934	22	1678	59
05BY103-3.1	523	112	0.21	174	5.43E-04	4.67E-05	0.0500	0.0018	0.3307	0.0039	5.431	0.085	0.1191	0.0011	0.0771	0.0029	1842	19	1890	14	1943	16	1501	55
05BY103-4.1	35	160	4.59	20	1.29E-02	8.18E-04	1.2169	0.0436	0.2840	0.0111	5.981	0.883	0.1527	0.0210	0.0753	0.0042	1612	56	1973	137	2377	256	1467	80
05BY103-5.1	294	90	0.30	107	1.15E-03	1.36E-04	0.0823	0.0051	0.3509	0.0041	5.710	0.136	0.1180	0.0023	0.0947	0.0060	1939	19	1933	21	1926	35	1829	110
05BY103-5.2	101	63	0.63	39	6.34E-03	5.05E-04	0.1906	0.0215	0.3394	0.0101	5.954	0.508	0.1272	0.0097	0.1032	0.0122	1884	49	1969	77	2060	141	1986	224
05BY103-6.1	377	126	0.33	140	4.67E-04	7.36E-05	0.0929	0.0029	0.3566	0.0032	5.946	0.090	0.1209	0.0013	0.0995	0.0033	1966	15	1968	13	1970	20	1917	61

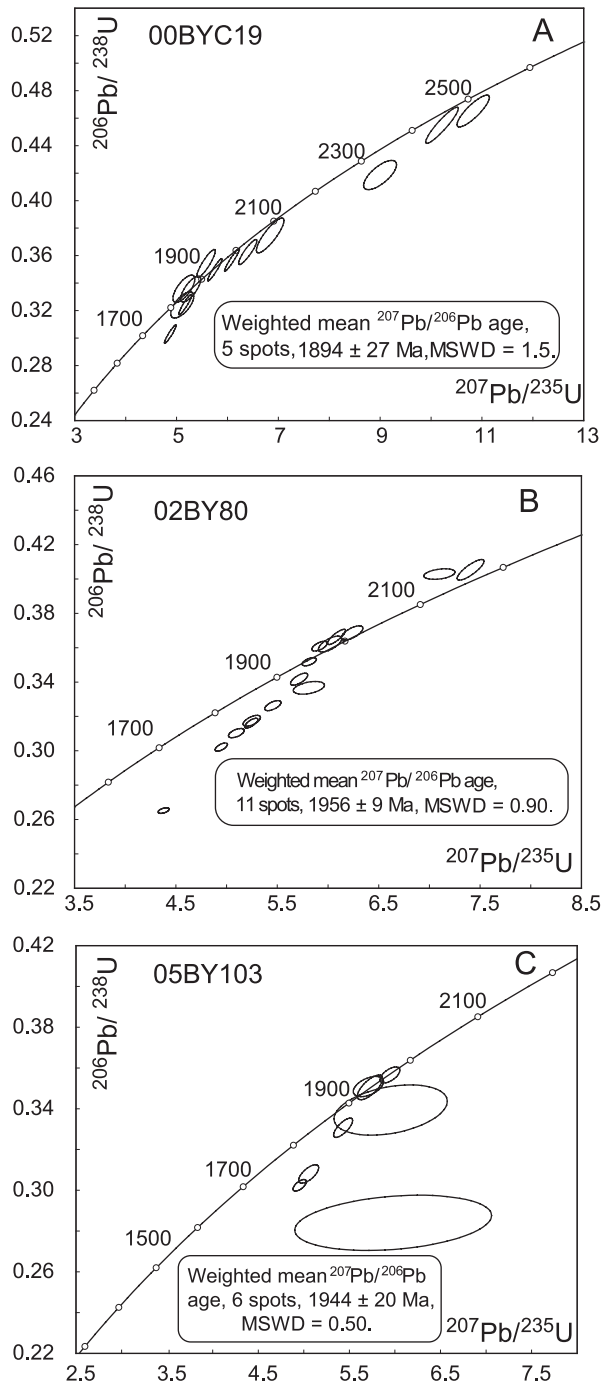


Fig. 3. U-Pb concordia diagrams showing SHRIMP analyses of zircon from Bayan Obo carbonatite dikes 00BYC19, 02BY80 and 15BY103. Error ellipses are 1σ .

radiogenic Pb loss (fig. 3B). Despite the discordance, however, 11 of the 15 analyses had the same radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ within analytical uncertainty (MSWD = 0.90), indicating that the Pb loss took place geologically recently. The weighted mean age of those spots was 1956 ± 9 Ma (95% c.l.). The two analyses with highest $^{207}\text{Pb}/^{206}\text{Pb}$ (8.1 and 8.2) came from the same grain, consistent with that grain being significantly older, ≥ 2.13 Ga.

The more abundant zircon recovered from carbonatite 05BY103 was finer grained (most 50 – 80 μm diameter) and different in appearance from the zircon in the other two samples. The crystals were mostly clear and colorless and, although generally of rounded prismatic shape, had distinctively rough surfaces. The very few exceptions were euhedral prismatic grains that made up less than 5 percent of the population. The explanation for the roughness was revealed by the CL imaging. More than 80 percent of the grains consisted of a core, commonly with oscillatory growth zoning, surrounded by a strongly luminescent overgrowth that appeared to be microcrystalline (fig. 2C). In some cases the strongly luminescent zircon occurred as patches within the grains, appearing to have replaced pre-existing zircon, possibly as a result of fluid-enhanced penetrative recrystallization. There was no strongly luminescent zircon in or on the euhedral prismatic grains.

Eight U-Th-Pb analyses of 6 grains gave a wide range of U concentrations (35 – 1017 ppm), the lowest values coming from the areas with strong luminescence. There was a very narrow range of isotopic compositions, however, all analyzed spots, despite a range of discordance (fig. 3C), having the same radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ within analytical uncertainty (MSWD = 0.8). Six of the analyses gave a well-defined mean $^{207}\text{Pb}/^{206}\text{Pb}$ age (MSWD = 0.5) of 1944 ± 20 Ma (95% c.l.). The other two (4.1 and 5.2), both from strongly luminescent areas, had very large analytical uncertainties but compositions that nevertheless indicated that the new growth and recrystallization took place very soon after the crystallization of the original host grains (fig. 3C).

REE Compositions

Trace element compositions measured on 26 zircon grains from the three carbonatite dike samples are listed in table 2 and the chondrite-normalized REE patterns are plotted in figure 4. In general, the domains with weak CL had higher REE concentrations than those with strong CL, consistent with previous observations that zircon CL tends to be suppressed by high levels of trace elements. All the REE patterns had the heavy-REE (HREE) enrichment typical of zircon, but there was significant variation in the relative abundances of the light REE (LREE) between crystal domains and between samples.

The HREE concentrations of all 10 analyzed spots from 00BYC19 zircon grains were very similar, but large differences in the abundances of the LREE, particularly La and Ce, meant that the patterns ranged from very steep to relatively flat (fig. 4A). All spots had similar, significant negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.11 - 0.35$), but there was a wide range of positive Ce anomalies from very large to very small ($\text{Ce}/\text{Ce}^* = 1.34 - 1.02$) (table 2). The Ce anomaly in one grain (analysis 2.1), on which a SHRIMP $^{207}\text{Pb}/^{206}\text{Pb}$ age of ~ 2.5 Ga was measured, was relatively high ($\text{Ce}/\text{Ce}^* = 12.11$). The anomalies in two strongly luminescent grains (~ 2.0 Ga) were extreme ($\text{Ce}/\text{Ce}^* = 126$ and 134).

The 10 analyzed spots from 02BY80 zircon grains had a slightly wider range in total REE concentration, but much less variety in REE pattern, the slopes being consistently shallow (fig. 4B). Eu anomalies were small and ranged from slightly negative to slightly positive ($\text{Eu}/\text{Eu}^* = 0.41-1.27$). Positive Ce anomalies were mostly small ($\text{Ce}/\text{Ce}^* = 1.0-5.2$).

The six analyzed spots from 05BY103 zircon grains had steeper REE patterns than the zircon from the nearby sample 02BY80. Two spots, one on a strongly luminescent

TABLE 2
LA-ICP-MS analyses of REE in zircon from three Bayan Obo carbonatite dikes

Spot name	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Ce*/CeN*	Eu*/EuN*
00BYC19-1.1	4.47	22.46	2.08	12.08	6.43	0.74	15.6	7.2	49.9	19.1	68.3	16.1	152.6	43.2	493.5	1.81	0.23
00BYC19-1.2	2.68	30.59	2.64	14.74	10.03	1.02	19.7	9.4	66.2	28.0	105.9	25.8	240.9	66.0	696.1	2.82	0.22
00BYC19-2.1	0.52	19.15	0.29	2.02	3.04	0.64	13.7	7.2	53.8	24.2	87.5	19.8	172.0	47.5	570.1	12.11	0.30
00BYC19-3.1	0.0072	13.68	0.10	1.51	2.65	0.26	12.7	6.9	51.8	24.3	89.6	20.7	180.4	50.7	518.7	126.27	0.14
00BYC19-4.1	<0.0072	10.36	0.05	0.99	1.84	0.23	9.3	5.0	36.3	17.2	61.3	14.7	129.8	37.5	364.9	134.43	0.17
00BYC19-5.1	2.54	33.1	1.78	11.56	8.24	0.62	28.1	16.6	114.1	55.0	197.3	47.3	410.1	123.4	1216.7	3.817	0.125
00BYC19-6.1	6.74	39.83	4.55	24.28	13.99	2.34	30.1	16.1	103.5	48.9	179.2	46.4	431.0	136.3	1142.0	1.76	0.35
00BYC19-7.1	14.86	333.67	18.61	105.49	65.32	8.68	104.8	47.6	208.6	74.7	223.5	53.1	456.3	143.2	1607.5	4.92	0.32
00BYC19-8.1	0.7	2.57	0.55	3.79	4.44	0.34	18.6	9.1	42.1	16.9	53.3	12.4	110.3	37.8	383.1	1.02	0.11
02BY80-1.1	7.94	60.61	8.70	54.32	59.01	34.32	133.1	51.1	417.4	117.2	428.6	88.8	799.0	146.1	2832.6	1.79	1.18
02BY80-1.2	17.91	251.68	29.91	187.67	194.93	107.32	341.7	125.2	895.7	208.5	657.9	135.1	1256.6	188.7	4434.6	2.67	1.27
02BY80-2.1	3.43	83.21	4.48	29.64	32.89	18.48	73.0	30.5	250.6	77.5	293.9	63.9	608.4	116.6	1879.9	5.20	1.15
02BY80-3.1	0.68	18.21	0.99	7.75	11.38	2.80	38.0	12.3	82.3	19.9	54.3	9.5	80.6	13.8	580.8	5.44	0.41
02BY80-4.1	16.58	225	19.58	106.66	70.33	22.12	106.9	43.0	368.1	125.2	476.9	109.9	1016.2	175.5	3117.9	3.06	0.78
02BY80-5.1	25.25	215.54	26.94	140.79	94.12	35.73	140.3	53.8	358.0	101.9	359.0	80.7	747.9	145.9	2494.5	2.03	0.95
02BY80-6.1	3.43	32.42	5.26	35.32	31.82	13.21	81.5	33.3	233.3	64.9	186.8	35.7	280.9	50.0	1677.5	1.87	0.79
02BY80-7.1	22.08	101.26	18.65	102.31	66.54	28.72	112.3	50.6	370.2	121.2	436.0	97.9	889.8	196.2	2890.5	1.22	1.01
02BY80-8.1	8.98	29.4	5.67	29.82	20.62	5.95	47.9	20.3	153.2	56.2	199.7	44.4	394.5	86.2	1370.7	1.01	0.58
05BY103-1.1	1.83	40.81	2.1	17.74	24.03	9.87	76.69	23.53	236.41	65.85	254.54	47.42	420.73	66.8	1889.07	5.10	0.70
05BY103-2.1	1.41	38.2	1.85	16.05	22.62	7.07	72.55	21.32	217.1	67.41	283.14	56.09	526.19	93.18	1929.51	5.80	0.53
05BY103-3.1	2.6	38.22	2.49	18.19	25.73	11.64	69.73	22.18	229.4	72.65	312.58	63.66	607.66	112.26	1956.5	3.68	0.84
05BY103-4.1	2.32	9.88	0.48	6.25	5.58	0.72	29.01	10.58	126.32	50.15	233.8	50.24	480.17	94.26	1398.54	2.30	0.17
05BY103-5.1	0.0204	3.5	0.059	1.28	2.92	0.31	17.54	6.63	74.88	29.05	126.54	27.03	258.06	51.47	814.71	24.73	0.13
05BY103.6-1	0.031	2.17	0.074	0.77	1.41	0.64	6.58	3.22	44.98	20.68	106.84	25.63	252.6	47.73	564.08	11.11	0.64

Ce and Eu anomalies are calculated after Sun and McDonough (1989).

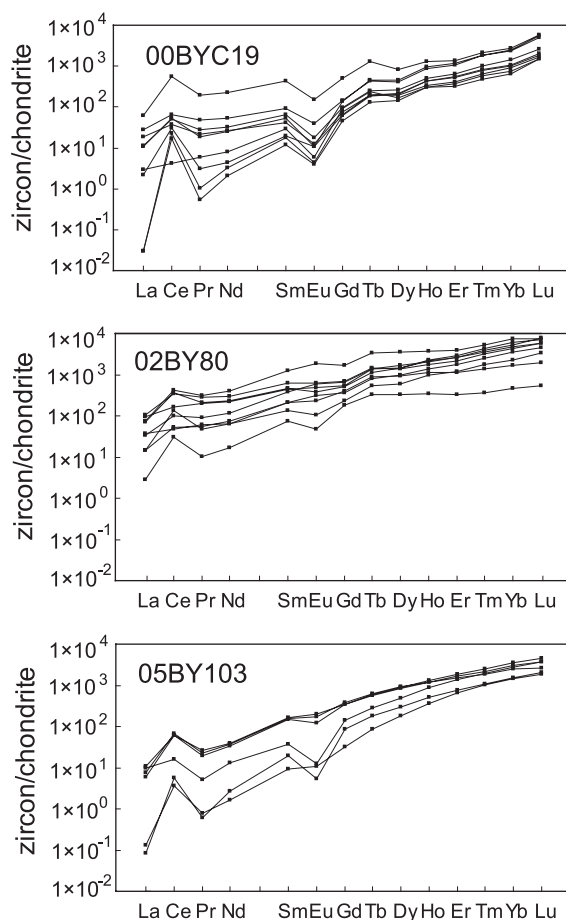


Fig. 4. Chondrite normalized REE patterns for zircon from Bayan Obo carbonatite dikes 00BYC19, 02BY80 and 15BY103. Normalization after (Sun and McDonough, 1989).

area and one not, had much lower LREE concentrations than the rest, but overall the patterns from all spots had similar characteristics, with moderate positive Ce anomalies ($\text{Ce}/\text{Ce}^* = 2.30\text{--}24.7$) and moderate to strong negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.13\text{--}0.84$) (table 2, fig. 2C).

Raman Spectrometry

Mineral inclusions in zircon provide direct evidence of the mineral phases present in the host rock at the time the zircon crystallized and thereby help to identify the host lithology. Zircon from the three carbonatite dike samples was therefore thoroughly searched for such inclusions. The zircon from samples 02BY80 and 15BY103 proved to be inclusion free, but more than 20 micro-inclusions were found exposed in the zircon from 00BYC19 using laser Raman and EMP analyses. Raman spectroscopy identified all the inclusions as quartz or feldspar.

Examples of the Raman spectra and the zircon grains from which they were obtained are illustrated in figure 5. Because the inclusions are transparent, all the spectra contain the peak at 1003 cm^{-1} characteristic of zircon. Peaks diagnostic of the inclusions themselves are clearly visible at $\sim 464\text{ cm}^{-1}$ (quartz) and $\sim 508\text{ cm}^{-1}$

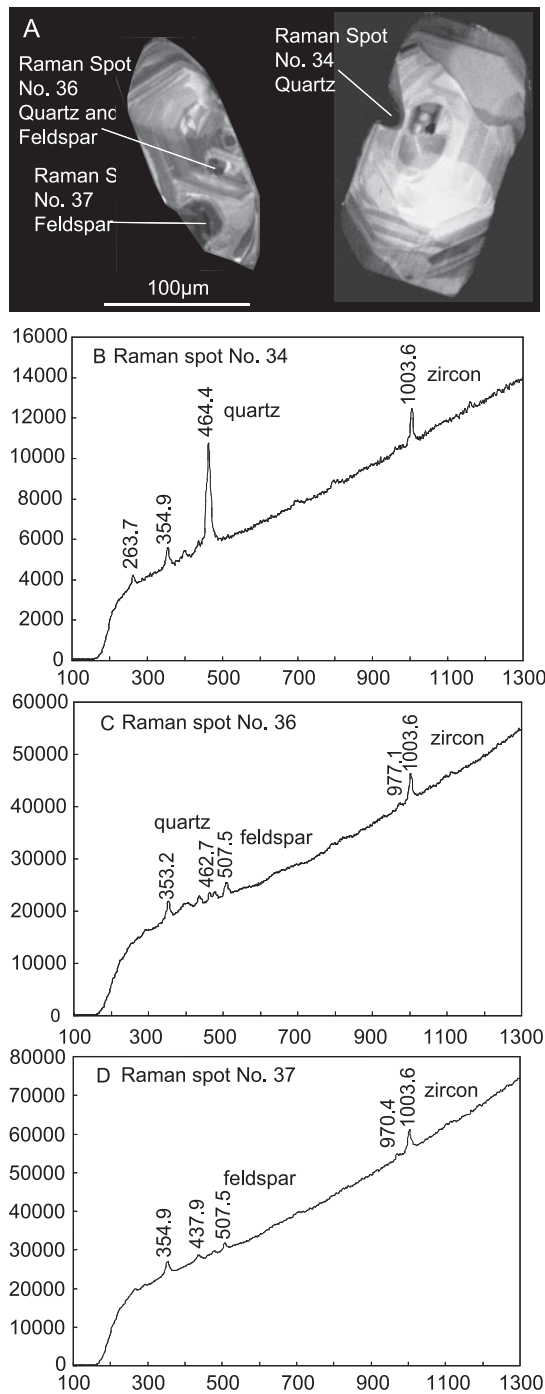


Fig. 5. Raman spectra of mineral inclusions in zircon from Bayan Obo carbonatite 00BYC19. (A) CL image of zircon containing inclusions. (B) Raman spectrum for spot 34 (quartz). (C) Raman spectrum for spot 36 (quartz and feldspar). (D) Raman spectrum for spot 37 (feldspar). The presence of silicate inclusions and absence of carbonate indicates that the zircon did not crystallize from a carbonatite magma.

(feldspar). None of the inclusions identified in any zircon was carbonate. The SHRIMP $^{207}\text{Pb}/^{206}\text{Pb}$ ages measured on the two illustrated grains were 1.87 and 2.49 Ga respectively, providing direct evidence that both the earlier and later generations of zircon growth identified by the geochronology originated from silicate rocks.

DISCUSSION

The Origin of the Zircon

Zircon from the three carbonatite dikes yielded mean population ages of 1894 ± 27 Ma for 00BYC19, 1956 ± 9 Ma for 02BY80 and 1944 ± 20 Ma for 05BY103, as well as apparent ages of ~ 2.41 , ~ 2.49 and ~ 2.55 Ga for three older zircon grains from sample 00BYC19. These population ages are close to the previously published U-Pb age of 2070 ± 33 Ma for zircon from a carbonatite dike that was at first interpreted as the intrusion age of the carbonatite (Fan and others, 2002). Considering that the zircon U-Pb age of 2070 Ma is much older than the Sm-Nd isochron ages, that zircon is not common in the Bayan Obo carbonatites, (and when present, is usually found near the margins of the intrusions), and that zircon in the carbonatites commonly occurs in the presence of sodic mafic silicate minerals, it has been argued that 2070 Ma is the age of the Wutai basement complex (dated elsewhere at 1.9 – 2.0 Ga), not the age of the host carbonatite dike (Le Bas, 2006). Fan and others (2006) subsequently obtained a concordant zircon age of 1925 ± 8 Ma and an upper intercept age of 1416 ± 77 Ma from a REE-rich carbonatite dike (the Wudyke, fig. 1) using U-Pb ID-TIMS. Taking the argument of Le Bas (2006) into consideration, the zircon age of 1925 ± 8 Ma was interpreted as the age of trapped wall rock, and the age of 1416 ± 77 Ma was interpreted as the intrusion age of the carbonatite (Fan and others, 2006). It is true that the Sm-Nd isotopic system is usually very resistant to later disturbance, however it can be reset during metamorphism in some circumstances (Li and others, 1996). More importantly, the Sm-Nd isochron age cannot be used as independent evidence for the geological significance of SHRIMP zircon ages. In addition, although zircon is very rare in carbonatite, it has been reported and studied in carbonatite from the Kola Peninsula (Claesson and others, 2000) and elsewhere (Heaman and others, 1990; Belousova and others, 2002). In these cases, the zircon mostly came from syenite closely associated with the carbonatites. In contrast to the small zircon crystals commonly found in silicate rocks, zircon crystals in carbonatites can sometimes be very large and well developed (Belousova and others, 2002). Therefore independent evidence is needed to understand the meaning of the SHRIMP U-Th-Pb ages of zircon from the Bayan Obo carbonatites.

The origin of zircon, and thus the geological significance of its SHRIMP age, can be constrained by its trace element patterns and mineral inclusions (Sun and others, 2002; Liu and others, 2006a, 2006b, 2006c). Both trace elements and mineral inclusions in zircon from the Bayan Obo carbonatite dikes have been examined for this study.

All the zircon grains from sample 00BYC19 had pronounced negative Eu anomalies, which is in contrast with the zircon from the Mud Tank carbonatite (Hoskin and Ireland, 2000; Belousova and others, 2002; Hoskin and Schaltegger, 2003), but similar to the zircon from the Phalaborwa complex carbonatite and silicate rocks (Hoskin and Ireland, 2000; Hoskin and Schaltegger, 2003). Interestingly, the LREE and Ce anomalies in the zircon from sample 00BYC19 are very different from grain to grain, suggesting that the zircon was not all formed by a single process. This conclusion is supported by the varied ages and the range of Th/U (0.12 – 0.75), which is far lower than typical Bayan Obo Th/U values (usually > 200 for whole rocks and up to > 10000 for monazite). Two grains analyzed had very large positive Ce anomalies ($\text{Ce}/\text{Ce}^* = 126$ and 134) and significant negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.14$ and 0.17), and

indistinguishable $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 1871 and 1865 Ma, respectively. These features are similar to those ascribed to zircon from evolved syenitic rocks by Belousova and others (2002). Zircon 7 has higher REE (particularly LREE) concentrations than the other zircon grains, indicating that that grain crystallized in a highly LREE enriched environment, for example a granitoid or syenite. Its moderate Th/U value is consistent with that origin. The weight of evidence is that these zircon grains did not crystallize in the carbonatite, but rather were derived from trapped wall rocks.

Significantly, mineral inclusions of quartz and feldspar have been identified in zircon grains of different ages from carbonatite sample 00BYC19, but no carbonate inclusions were found, indicating that those zircon grains did not crystallize from a carbonatite magma, but rather in silicate rocks. Syenite or other silicate rocks are usually closely associated with carbonatite magmas. If these zircons crystallized from syenite co-genetic with the carbonatite, then the age of the zircons should be close to that of the carbonatite magmatism. However, no syenite or other alkaline silicate rocks that might be co-genetic with the Bayan Obo carbonatite dikes have yet been reported (Institute of Geochemistry Chinese Academy of Sciences, 1988; Bai and others, 1996). Fenitization is common in both the carbonatite dikes and the ore bodies at Bayan Obo. The fenites, which consist mainly of riebeckite, albite and phlogopite, are of metasedimentary origin (Ni and others, 2003). No inclusions of those minerals were found in zircon samples studied. All these observations suggest that the zircon studied was not crystallized from carbonatite, but was trapped from wall rocks.

No mineral inclusions in the zircon from carbonatite samples 02BY80 and 05BY103 were identifiable. The REE patterns for the zircon from sample 02BY80 were very similar to those from Mud Tank carbonatite zircon, with weak positive Ce anomalies ($\text{Ce}/\text{Ce}^* = 0.97\text{--}5.20$) and no obvious Eu anomalies (Hoskin and Ireland, 2000; Belousova and others, 2002; Hoskin and Schaltegger, 2003). This kind of REE pattern is also seen in zircon from kimberlite and syenite (Hoskin and Ireland, 2000; Belousova and others, 2002; Hoskin and Schaltegger, 2003). The REE concentrations, however, range over two orders of magnitude, suggesting that these zircon grains were probably formed in different environments, not from a single magma series.

In contrast, the zircons from 05BY103 have positive Ce anomalies ($\text{Ce}/\text{Ce}^* = 2.3\text{--}24.7$) and negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.13\text{--}0.84$), which resemble those from zircon from the Phalaborwa complex carbonatite and silicate rocks (Hoskin and Ireland, 2000; Hoskin and Schaltegger, 2003). The LREE contents of the zircon from 05BY103 range over nearly two orders of magnitude, indicating that either these zircons are of different origin or, more likely given the recrystallization textures, there was a sharp drop in the LREE content of the crystallizing medium after the zircon initially formed.

The Th/U values of zircon from carbonatite 02BY80 are low to moderate, ranging from 0.18 to 0.36 (table 1), whereas those of 05BY103 are slightly higher, ranging from 0.21 to 0.63, with one exception (4.59 for spot 4.1). Although these Th/U values are within the range for igneous and some metamorphic zircon, they are much lower than those reported as typical of carbonatitic zircon, which are usually high (> 1) (Claesson and others, 2000) to extreme (> 1000) (Belousova and others, 2002).

A critical feature of the Bayan Obo REE-Nb-Fe deposit in this context is its very high Th/U (usually > 200 for whole rocks, and up to 10000 for monazite; Liu and others, unpublished data). None of the zircon compositions measured in any of the samples included in the present study have Th/U ratios consistent with crystallization in such a Th/U fractionated environment.

All the evidence assembled here points to the zircon grains from the three studied carbonatite dikes being derived from trapped wall rocks. Consequently, the SHRIMP U-Pb ages of 1894 ± 27 Ma, 1956 ± 9 Ma and 1944 ± 20 Ma represent the ages of

components within the basement rocks in the Bayan Obo region, consistent with Le Bas's prediction (Fan and others, 2006; Le Bas, 2006).

Geochronology and Regional Magmatism

The age of the Bayan Obo ore deposit and associated carbonatite dikes has been debated for about 20 years. The Sm-Nd ages for the Bayan Obo samples fall into two groups, 1.66 to 1.50 Ga and 1.31 to 1.22 Ga, which have been interpreted as reflecting two related periods of carbonatite magmatism (Le Bas, 2006). The ages of 1.66 to 1.50 Ga, however, are mostly Nd model ages, and are more relevant to the prehistory of the magmas than the age of the carbonatite dikes and/or mineralization. In contrast, the ages of 1.3 to 1.2 Ga are Sm-Nd isochron ages, which are much more likely to record the age of the dated minerals. Moreover, $^{40}\text{Ar}/^{39}\text{Ar}$ dating of riebeckite yields similar results. These ages have been interpreted as mineralization ages (Yuan and others, 1992; Cao and others, 1994; Ren and others, 1994; Zhang and others, 1994, 2001; Liu and others, 2005). This interpretation has been questioned, however, because no direct evidence for Mesoproterozoic magmatism has yet been found in Bayan Obo. Dating of minerals that are considered to be closely related to mineralization has yielded early Palaeozoic ages (0.5–0.4 Ga) (Wang and others, 1994; Chao and others, 1997; Qiu, 1997; Liu and others, 2004). The Re-Os isochron age of late-stage pyrite (439 ± 86 Ma) was interpreted recording an event that post-dated the major mineralization (Liu and others, 2004). Monazite Th-Pb ages of 555 to 400 Ma also have been interpreted as mineralization ages. Although the present work does not resolve the question of the age of the carbonatite dikes, it does show that previous interpretations of the dike zircon ages as the ages of dike intrusion (for example, Fan and others, 2002) were incorrect.

The wide variety of REE patterns in the zircon studied here implies that the magmatism in the Bayan Obo region at ~ 2.0 Ga involved magmas of a wide range of compositions. Further, there is now geochronological evidence for igneous events in the region ranging in age from Neoproterozoic (~ 2.5 Ga), through Paleoproterozoic (~ 2.0 Ga), Neoproterozoic (~ 0.9 Ga) and Paleozoic (450–500 Ma), to Mesozoic (Institute of Geochemistry Chinese Academy of Sciences, 1988; Wang and others, 1994; Bureau of Geology and Mineral Resources of Inner Mongolia Autonomous Region, 1991; Bai and others, 1996; Fan and others, 2002; Wang and others, 2002, 2003). The zircon age of 1894 ± 27 Ma is similar to that of anorogenic igneous rocks at Bayan Obo (Wang and others, 2003), and the age of 1944 ± 20 Ma is similar to that of the Shi'erfenzi K-feldspar granite (Bureau of Geology and Mineral Resources of Inner Mongolia Autonomous Region, 1991). It is possible that there was intensive magmatism in the western block of the North China craton associated with Paleoproterozoic rifting.

Bayan Obo is located on the north margin of the North China craton. The craton consists of Archean to Paleoproterozoic basement formed during four distinct tectonic cycles, which are called the Qianxi (> 3.0 Ga), Fuping (3.0–2.5 Ga), Wutai (2.5–2.4 Ga) and Lüliang (2.4–1.8 Ga) cycles respectively (Zhao and others, 2005). Rifting of the craton also occurred in the late Paleoproterozoic to early Mesoproterozoic. For example, continuous activity identified as the Zhongtiao-Xiong'er-Antao rifting (in the south of the North China craton) developed from 1.98 to 1.75 Ga, while the Miaoxiangshan-Chengde-Jixian rifting (in the North of the North China craton) took place from 1.90 to 1.63 Ga (Zhai and others, 2001). The zircon ages obtained here are consistent with this local geological background.

CONCLUSION

SHRIMP U-Pb dating of zircon from three carbonatite dikes from Bayan Obo yielded mean $^{207}\text{Pb}/^{206}\text{Pb}$ population ages of 1894 ± 27 Ma for 00BYC19, 1956 ± 9 Ma

for 02BY80 and 1944 ± 20 Ma for 05BY103. To understand the geological significance of these ages, trace element and mineral inclusions in zircon were studied using LA-ICP-MS and laser Raman spectroscopy, respectively. The presence of feldspar and quartz inclusions and the absence of carbonate in the zircon from sample 00BYC19 clearly indicate that it did not crystallize from a carbonatite magma, but rather is derived from trapped basement silicate rocks. The wide variety of REE patterns from the Bayan Obo carbonatite zircon is less diagnostic. Given that carbonatitic zircon commonly has high Th/U, and high Th/U is a characteristic of the Bayan Obo ore deposit, the low to moderate Th/U values in the studied zircon from the carbonatite dikes is inconsistent with crystallization from the carbonatite magmas, and the zircon is therefore considered to be unrelated to the Bayan Obo ore deposit.

The variety of REE patterns in the zircon is consistent with a variety of igneous activity in the Bayan Obo region at ~ 2.0 Ga. The zircon age of 1894 ± 27 Ma matches that of anorogenic igneous rocks at Bayan Obo (Wang and others, 2002, 2003), and the ages of 1956 ± 9 Ma and 1944 ± 20 Ma are similar to those of basement rocks and the Shi'erfenzi K-feldspar granite (Bureau of Geology and Mineral Resources of Inner Mongolia Autonomous Region, 1991). This magmatism was possibly related to local rifting.

ACKNOWLEDGMENTS

This work was supported by the Chinese Ministry of Science and Technology (2006CB403505) and the Nature Science Foundation of China (NSFC) (No. 40525010, No. 40573009). We thank Hua Tao (Beijing SHRIMP Center), Xiaoming Liu and Honglin Yuan (Northwest University, Xi'an, China) for helping with *in-situ* analyses, and Guowang Xiao and Tairong Zhang (Bayan Obo Iron Mine) for assistance in field work and mapping. Professor H. R. Fan and an anonymous referee are thanked for their careful reviews.

We respectfully dedicate this paper to Professor Dunyi Liu in appreciation of his lifetime contributions to, and fostering of, the science of isotope geochronology in China.

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