

Article

Post-Magmatic Fluids Dominate the Mineralization of Dolomite Carbonatitic Dykes Next to the Giant Bayan Obo REE Deposit, Northern China

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Abstract: The Bayan Obo rare earth element (REE) deposit in Inner Mongolia, northern China, is the largest REE deposit in the world, whose mineralization process remains controversial. There are dozens of carbonatite dykes that are tightly related to the deposit. Here we report the petrological and mineralogical characteristics of a typical dolomite carbonatite dyke near the deposit. The dolomite within the dyke experienced intense post-emplacement fluids metasomatism as evidenced by the widespread hydrothermal REE-bearing minerals occurring along the carbonate mineral grains. REE contents of bulk rocks and constituent dolomite minerals (>90 vol.%) are 1407–4184 ppm and 63–152 ppm, respectively, indicating that dolomite is not the dominant mineral controlling the REE budgets of the dyke. There are three types of apatite in the dyke: Type 1 apatite is the primary apatite and contains REE₂O₃ at 2.35–4.20 wt.% and SrO at 1.75–2.19 wt.%; Type 2 and Type 3 apatites are the products of replacement of primary apatite. The REE₂O₃ (6.10–8.21 wt.%) and SrO (2.83–3.63 wt.%) contents of Type 2 apatite are significantly elevated for overprinting of REE and Sr-rich fluids derived from the carbonatite. Conversely, Type 3 apatite has decreased REE₂O₃ (1.17–2.35 wt.%) and SrO (1.51–1.99 wt.%) contents, resulting from infiltration of fluids with low REE and Na concentrations. Our results on the dyke suggest that post-magmatic fluids expelled from the carbonatitic melts dominated the REE mineralization of the Bayan Obo deposit, and a significant fluid disturbance occurred but probably provided no extra REEs to the deposit.

Keywords: dolomite carbonatite dyke; petrology; mineralogy; metasomatism; REE mineralization; the Bayan Obo deposit

1. Introduction

The Bayan Obo rare earth element (REE) deposit, located in Inner Mongolia of northern China, is the largest REE deposit in the world. The deposit was originally generated at approximately 1.4–1.2 Ga as the product of mantle-derived carbonatitic magmas [1–5]. The REE-bearing minerals are mainly hosted in the dolomitic rocks. The debate about whether the ore-hosting rock is sedimentary [1,5–12] or igneous in origin [2–4,13–25] has lasted since the discovery of the deposit. Extensive application of advanced analytical techniques, such as in situ isotopic analysis, has demonstrated that the ore-hosting dolomitic rocks of the deposit are igneous in origin [26–28]. However, there are still details to be worked out to better understand the deposit formation processes. For example, which process played

a more important role in the REE enrichment of the deposit, carbonatite magmatism or post-magmatic hydrothermal alteration? Chronological studies showed two age clusters at 1.4–1.2 Ga and 0.5–0.4 Ga, respectively, in the deposit [5,11,23]. Does that mean the deposit experienced multiple stages of mineralization? As the deposit continued to evolve in response to protracted tectonic evolutions and complex geological processes [11,26], the answers to the questions above are not straightforward.

There are dozens of carbonatite dykes around the Bayan Obo deposit. These dykes are contemporaneous and genetically related to the formation of the deposit [12,14,20,21]. Compared with the ore-hosting rocks, these carbonatite dykes are small in scale and relatively simple in composition; effects of subsequent tectonic activities are thus limited or can be easily identified. Therefore, the study of these dykes is helpful to simplify the complicated problems associated with the Bayan Obo deposit. Based on the main constituent mineral, dykes in the Bayan Obo ore district can be classified into calcitic, dolomitic, and calcite-dolomitic carbonatites [21,29,30]. Apart from some studies (e.g., [21]) reporting the bulk rock geochemical characteristics of some dolomite carbonatite dykes (Dol-dykes), most previous research has concentrated on a calcite carbonatite dyke (Cal-dyke) named the Wu dyke in the northeast of East Orebody [12,18,30,31], as this dyke contains extremely high REE contents up to 20 wt.% [31] and caused prominent fenitization of its country rocks. However, rocks from Cal-dykes cannot be related directly to the ore-hosting dolomites as they may be in different evolution stages of carbonatitic magmas [21,28,29]. Therefore, it is necessary to further strengthen the research on Dol-dykes to provide a better comparison with the deposit.

In this paper, we conducted a detailed investigation of a typical Dol-dyke, including petrological, mineralogical, and geochemical analyses, to provide additional insights into the detailed mineralization processes of the Bayan Obo REE deposit.

The world-class Bayan Obo REE deposit in Inner Mongolia, China, occurs on the northern margin of the Northern China Craton. To its north is the Central Asian Orogenic Belt [32] (Figure 1a). Regional strata comprise the Archean–Paleoproterozoic crystalline basement complex and a Proterozoic cover. The former consists mainly of migmatite, gneiss, granulite, quartz schist, and amphibolite, with detrital zircon U–Pb ages of 2.6–1.9 Ga [33]; the latter is a sedimentary sequence of the Bayan Obo Group composed of coarse- to medium-grained low-grade metamorphic clastic and carbonate rocks [34]. The REE ore-hosting dolomite rocks have been traditionally regarded as part of the Bayan Obo group. The ore deposit consists of three orebodies, named the East, Main and West orebodies. The REE-bearing minerals in the deposit are mainly monazite and bastnaesite, which occur as massive, banded, and disseminated in the ore-hosting dolomites. There are many Permian granitic plutons southwest of the ore district as products of continent–continent collision between the North China plate and the Siberian plate [35,36], but these granitoids have been considered to have no contribution to the formation of the Bayan Obo deposit [36]. Random intrusion of carbonatite dykes into the Bayan Obo group and fenitization of country rocks, which is characterized by riebeckite-arfvedsonite, albite, and phlogopite mineral assemblages [31], occurred near most of the dykes. The dykes are generally 10 to 200 m long and 0.5 to 2.0 m wide. Most of the exposures are weathered, though some rocks beneath the surface are well preserved.

The Dol-dyke addressed in this study is located about 1500 m southeast of the East Orebody (Figure 1). It has an NWW trend and crosscuts the metamorphic quartz sandstones of the Bayan Obo group (Figure 2a). The dyke exposition is more than 100 m long and has an average width of about 2.0 m. The outcrop is yellow-brown with attached recrystallized carbonate shells on the surface (Figure 2b). Fenitization occurred at both sides of the dyke (Figure 2c). All samples for this study were collected at deep parts of the dyke aiming to avoid the effect of weathering.

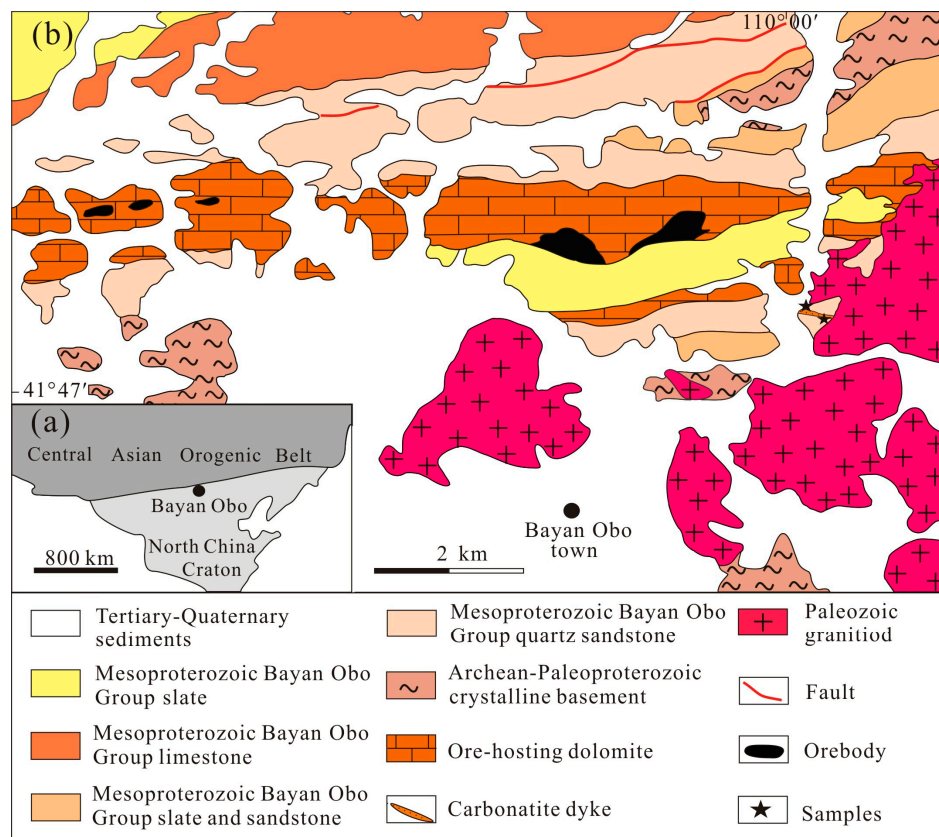


Figure 1. (a) Simplified map showing the tectonic location of the Bayan Obo deposit in the North China Craton (adapted from [21]); (b) Detailed geological map of the Bayan Obo rare earth element (REE) deposit (Modified from [1]).



Figure 2. (a) A segment of a typical Dol-dyke around the Bayan Obo deposit. (b) Outcrop of the Dol-dyke. (c). Fenitization of the country rocks near the Dol-dyke.

2. Analytical Methods

The detailed microscopic observations of thin sections and mineral separates using transmitted light, scanning electron microscope (SEM, Nova Nano SEM450, FEI, Hillsboro, OR, USA) and cathodoluminescence (CL) were carried out prior to further geochemical analysis. Major and trace element analysis of five dolomite rock samples were conducted at the Geoanalytical Center of Nuclear Industry, Beijing. The major elements were determined by X-ray fluorescence spectrometry (Axios mAX, PANalytical B.V., Almelo, Netherlands) with analytical precision better than 2%. Trace elements were determined using an inductively coupled plasma mass spectrometer (ICP-MS, NexION300D, PerkinElmer, Waltham, MA, USA) with analytical precision better than 5%. Before analysis, samples were dissolved in a mixture of HF + HNO₃ within a closed Teflon vessel on a hotplate at about 160 °C for 48 h and evaporated to dryness. After that, HClO₄ was added to the vessel and heated again to about 160 °C until the acid was completely evaporated. After cooling to room temperature, the dry sample was then dissolved in 1% HNO₃ to attain the solution for trace element determinations.

Major element compositions of apatite were determined by electron probe microanalyser (EPMA) using the Jeol JXA-8100 (Jeol Ltd., Tokyo, Japan) at Geoanalytical Center of Nuclear Industry, Beijing. An accelerating voltage of 15 kV, beam size of 10 µm, and beam current of 20 nA were adopted for the analysis. Natural and synthetic materials were used as standards that were previously tested for homogeneity before utilization for quantitative analysis. The standards used were BaF₂ for F, fluorapatite for Ca and P, and monazite for REEs. Matrix corrections were conducted by using the ZAF correction program supplied by the manufacturer.

Trace elements of dolomite were obtained using a New Wave UP 213 laser ablation system coupled to a Thermo-Finnigan Element II ICP-MS (Thermo Fisher Scientific, Waltham, MA, USA) at the National Research Center for Geoanalysis, Beijing. The laser was operated at a spot size of 40 µm in diameter and 12 J/cm² energy beam at 10 Hz. He was used as sweeping gas. Analyses of the standards (NIST610, GSE-1G, MACS-3) were conducted 3 times before and after each run of 10 sample analyses. The preferred values of element concentrations for the United States Geological Survey (USGS) reference glasses were taken from the GeoReM database (<http://georem.mpch-mainz.gwdg.de/>). The raw data were processed using Microsoft Excel 2007. The MACS-3 and NIST610 were used for external calibration and Ca ion signal intensities were employed as the internal standard to monitor instrumental drift [37]. The content (wt.%) of CaO was obtained using EPMA. The detection limit for most elements was considerably below 0.1 ppm.

3. Results

3.1. Petrography

The rock samples consist of predominantly (>90% Vol) subhedral medium-grained dolomite with sizes of ~500 µm, and accessory minerals (<5% Vol) including calcite, magnetite, and apatite. Primary monazite or bastnaesite intergrown with dolomite is rare. The magnetite occurs as irregular grains disseminated along dolomite grain boundaries (Figure 3b). Besides magnetite, dark anhedral minerals also occur as aggregates along the dolomite grain (Figure 3b,c) with fibrous or micro-granular textures, which are clearly the products of hydrothermal fluids after the crystallization of the dolomite. Energy dispersive spectrometry (EDS) analysis indicates that they are parasite and barite, as well as some Nb-, Fe-, Sr- and Ba-bearing minerals that cannot be identified (Figure 3d–f).

The apatite grains are euhedral with grain sizes of 100–200 µm. They commonly have smooth and flat contacts with surrounding dolomites (Figure 4a,b). BSE and CL images revealed that there are three types of apatite in the dyke rocks. Apart from apatite grains (Type 1) with relatively smooth surfaces and margins (Figure 4b,g), the others show severe alterations. Monazite occurs along Type 2 apatite grain boundaries or in internal fractures (Figure 4c–e), indicating that REE-rich metasomatic fluids post-dated this apatite generation. In some apatite grains (Type 3), lots of micro-pores can be observed (Figure 4f,h). These crosscutting pores are the relics of secondary fluid inclusions, which probably

represent other fluid activity. The CL images of Type 3 (Figure 4h) apatite separates are also darker than those of Type 1 apatite (Figure 4g).

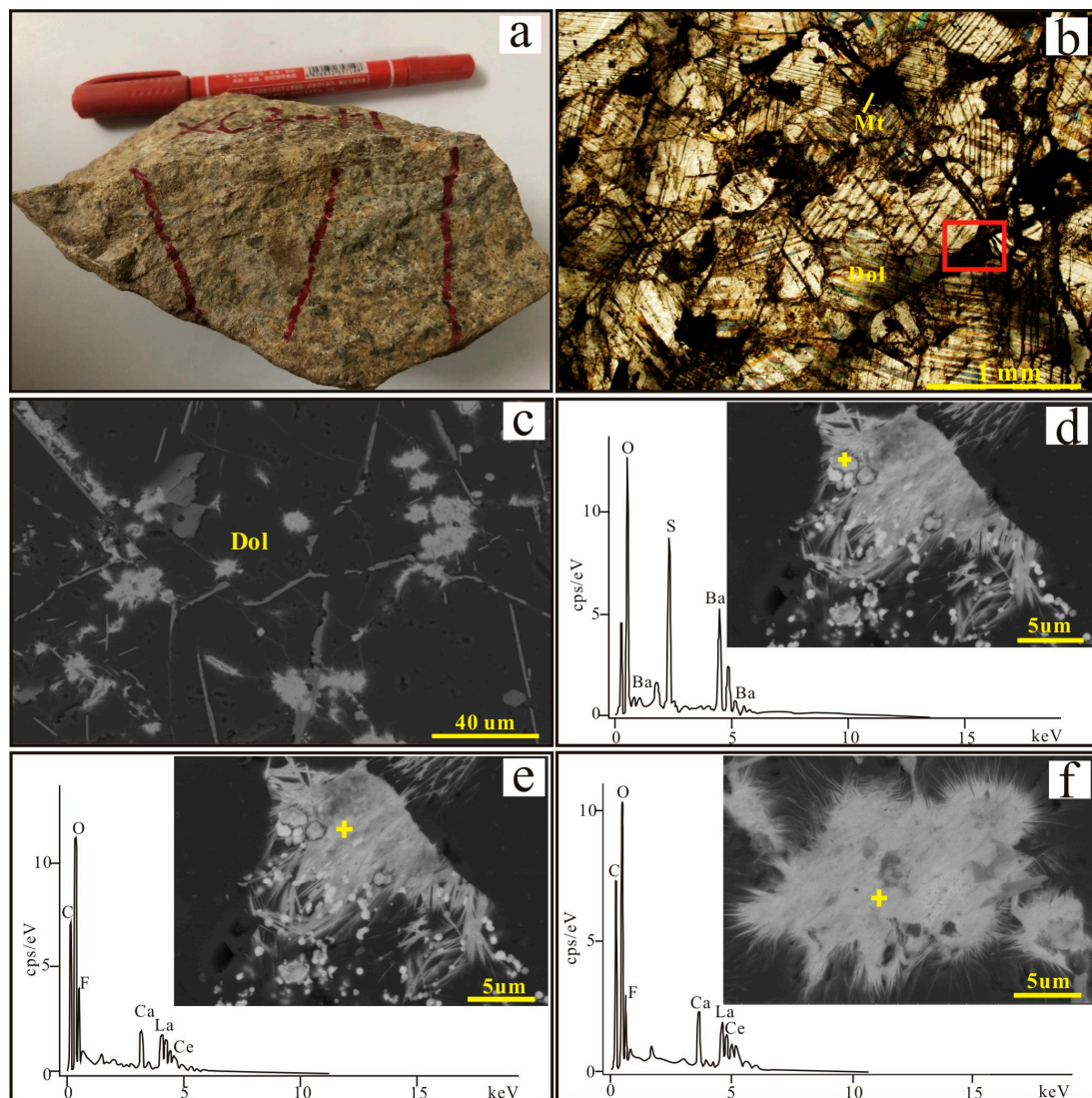


Figure 3. (a) Dolomite rock samples from the Dol-dyke. (b) Rock samples under microscope (cross-polarized light) showing constituent minerals of the rock and lots of hydrothermal minerals along the mineral boundaries. (c) Back-scattered-electron (BSE) image of the box area in Figure 3b. (d–f) are BSE images of detailed hydrothermal minerals with (EDS) of the marked area in each image, where baryte (e) and parisite (e,f) can be identified Abbreviations: Dol-dolomite, Ap-apatite.

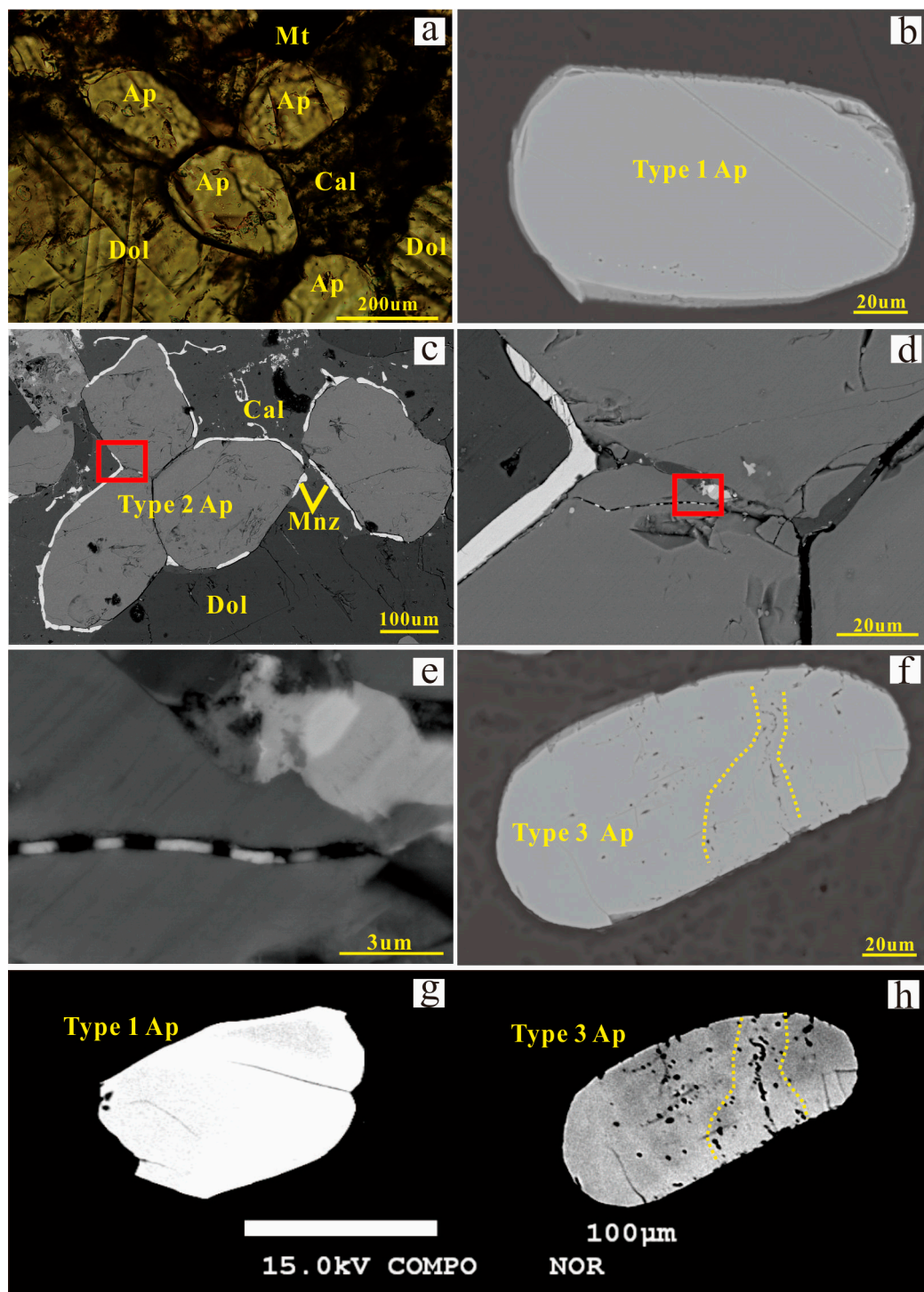


Figure 4. Representative photomicrographs of three types of apatite grains. (a) Apatite intergrown with dolomites (cross-polarized light). (b) BSE image of Type 1 apatite showing no obvious signs of alteration. (c) BSE image of Type 2 apatite. (d) Magnification of the box area in (c), showing details of intergranular boundary with monazite. (e) Magnification of the box area in (d), showing generation of monazite along the apatite internal fracture. (f) BSE image of Type 3 apatite, showing fluid veinlets crosscutting the grain. (g) CL image of Type 1 apatite showing a light and smooth surface. (h) CL image of Type 3 apatite, showing a dark surface with veinlets. Abbreviations: Mnz-monazite; others are the same as above.

3.2. Bulk Rock Geochemistry

Major and trace element compositions for five dolomite rock samples are listed in Table 1. These samples have CaO contents of 29.43–32.87 wt.% and MgO contents of 14.89–17.50 wt.%, with CaO/MgO ratios of 1.71–2.21. The total Fe₂O₃ + FeO + MnO contents are 7.34–11.17 wt.%. The relatively uniform major element contents indicate that the dyke consists of typical dolomite carbonatite (Figure 5). P₂O₅ contents are relatively low in these samples (0.08–0.37 wt.%). In addition, the samples have high Sr (13,800–18,400 ppm) and Ba (1198–5833 ppm) contents. Their primitive mantle-normalized trace element patterns show positive anomalies of Ba, Sr, and Nb and negative anomalies of Zr, Hf, Ta, and Pb (Figure 6a). The REE contents of these samples range from 1407 to 4184 ppm (2243 ppm on average) with (La/Yb)_N ratios of 243–1356. Their chondrite-normalized REE patterns display a strong enrichment in light rare earth element (LREE) and weak Eu negative anomalies (Figure 6b).

Table 1. Major element (wt.%) and trace element (ppm) concentrations of rock samples from the Dol-dyke.

Sample	XC3-1-1	XC3-1-2	XC3-1-3	XC3-1-4	XC3-1-5
SiO ₂	0.89	0.49	0.61	0.34	2.81
Al ₂ O ₃	0.06	0.03	0.06	0.02	0.03
Fe ₂ O ₃	6.36	6.62	4.66	6.32	8.51
FeO	1.97	2.07	1.98	2.11	2.05
MgO	14.89	16.90	16.21	17.50	15.45
CaO	32.87	30.59	32.44	29.96	29.43
NaO	bd	bd	bd	bd	bd
K ₂ O	0.01	0.01	0.01	0.01	0.01
MnO	0.80	0.90	0.70	0.91	0.61
TiO ₂	0.02	0.01	0.02	0.03	0.05
P ₂ O ₅	0.30	0.09	0.37	0.08	0.33
LOI	41.55	42.44	43.02	43.00	40.98
Sc	23.4	24.1	28.0	23.3	32.4
Pb	24.6	12.3	12.9	12.3	19.7
Rb	0.81	0.47	0.38	0.41	0.41
Ba	2005	1198	1533	1803	5833
Th	1.45	6.84	0.21	0.55	1.08
U	1.35	0.72	0.23	0.47	1.69
Nb	8.4	71.2	7.7	5.3	62.3
Ta	0.06	0.21	0.03	0.03	0.19
Zr	3.51	0.98	0.64	0.77	13.90
Hf	0.22	0.07	0.07	0.06	0.99
Sr	18,400	16,000	14,700	16,800	13,800
Y	13.7	14.5	30.8	13.6	18.3
La	1531	626	592	665	454
Ce	1936	900	771	941	654
Pr	164	82	72	87	62
Nd	451	234	216	248	182
Sm	33	21	23	21	18
Eu	6.5	4.4	5.5	4.6	4.7
Gd	49	24	26	26	21
Tb	2.8	1.8	2.3	1.8	1.7
Dy	6.2	4.8	7.6	4.6	5.3
Ho	0.53	0.52	1.03	0.48	0.65
Er	2.9	2.1	3.1	2.1	2.2
Tm	0.11	0.13	0.26	0.11	0.15
Yb	0.81	0.87	1.75	0.77	1.00
Lu	0.11	0.12	0.24	0.11	0.14

Note: bd denotes below detected limit.

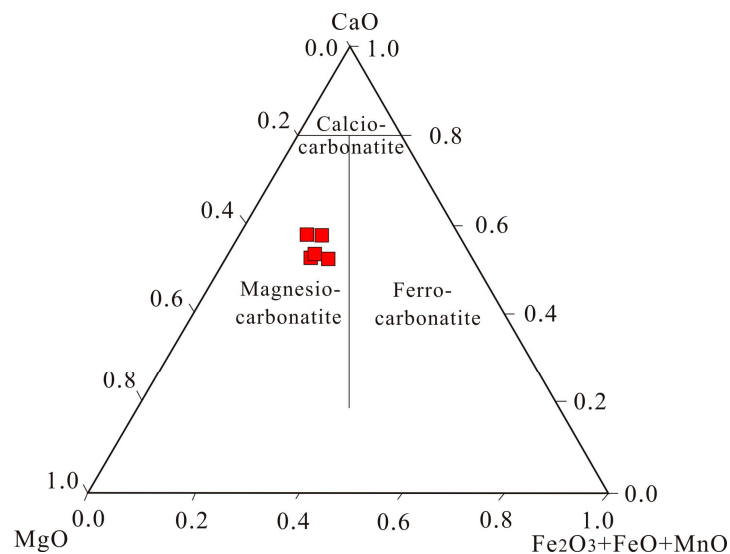


Figure 5. Classification diagram of CaO-MgO-(Fe₂O₃ + FeO + MnO) for samples from the Dol-dyke (after [38]).

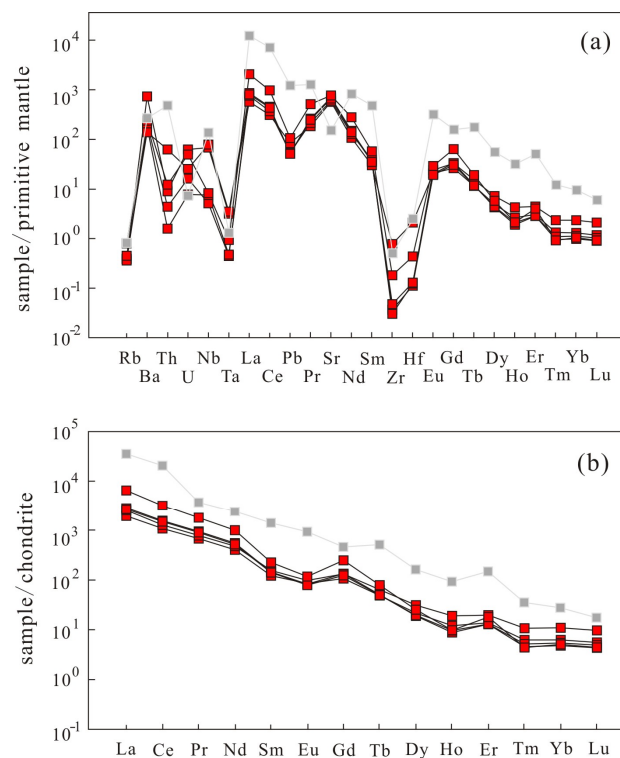


Figure 6. Primitive-mantle-normalized trace element (a) and chondrite-normalized REE patterns (b) for rock samples from the Dol-dyke. The gray lines are data of ore-hosting dolomites from the Bayan Obo deposit [26]. Data for normalisation according to [39].

3.3. Mineral Chemistry of Dolomite and Apatite

Trace element compositions for dolomite grains are listed in Table 2. As the major constituent mineral of the dyke, dolomite contains total REE contents of 62.8–152.2 ppm (100.3 ppm on average), which is much less than those of the bulk rock and the coarse-grained dolomite of the Bayan Obo ore-hosting rock reported by Chen et al. [26]. Their chondrite-normalized REE patterns are relatively flat (Figure 7) with (La/Yb)_N ratios range from 49 to 100. In addition, they have Sr and Ba contents of 5120–6036 ppm and 72–98 ppm, respectively.

Table 2. Trace element concentrations (ppm) of dolomite minerals from the Dol-dyke.

Sample	Sc	Ti	V	Cr	Mn	Rb	Ba	Th	U	Zr	Hf	Pb	Sr	Y
BY022-1	3.7	bd	0.18	7.28	4766	bd	82.7	0.003	0.050	bd	0.014	1.75	5727	2.54
BY022-2	4.8	0.77	0.34	5.69	4982	0.006	89.6	0.004	0.063	0.162	0.009	2.33	5927	3.79
BY022-3	3.2	0.02	0.22	5.15	4967	bd	90.0	0.003	0.142	bd	0.008	2.98	5597	3.66
BY022-5	2.0	0.10	0.15	4.78	4654	0.008	72.3	0.003	0.001	bd	0.004	0.79	5230	2.30
BY022-6	42.5	6.73	11.03	6.21	4847	0.022	76.1	0.005	0.176	0.002	0.065	2.73	5120	3.27
BY022-7	5.1	0.31	0.33	8.61	4912	0.005	97.9	0.011	1.380	bd	bd	1.29	5673	2.96
BY022-8	3.5	0.19	0.29	6.26	4793	bd	76.8	0.005	0.149	0.164	0.004	3.8	5957	3.23
BY022-9	4.7	0.12	0.32	7.07	4694	0.017	96	0.005	0.007	bd	bd	2.24	5418	3.32
BY022-10	5.9	0.42	0.52	6.18	5151	0.021	85.8	0.003	0.035	0.202	0.007	2.13	6036	4.79
Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
BY022-1	19.5	46.9	4.9	16.2	2.1	0.62	1.57	0.15	0.73	0.14	0.37	0.03	0.16	0.04
BY022-2	27.1	63.7	6.9	21.7	3.1	0.84	1.81	0.20	0.94	0.19	0.52	0.03	0.37	0.05
BY022-3	22.3	52.7	5.7	18.8	2.8	0.81	2.01	0.19	0.97	0.15	0.39	0.03	0.16	0.07
BY022-5	13.0	30.6	3.3	11.5	1.8	0.48	1.01	0.13	0.61	0.07	0.19	0.03	0.19	0.03
BY022-6	13.8	37.9	4.1	13.3	2.0	0.62	1.29	0.18	1.02	0.18	0.32	0.03	0.19	0.03
BY022-7	17.1	44.2	4.6	15.1	1.9	0.61	1.48	0.12	0.64	0.14	0.34	0.03	0.19	0.03
BY022-8	19.2	44.9	4.7	15.8	2.3	0.64	1.45	0.17	0.81	0.11	0.35	0.02	0.22	0.04
BY022-9	22.2	54.2	5.8	18.5	2.5	0.65	1.6	0.21	0.95	0.11	0.47	0.02	0.29	0.02
BY022-10	32.2	75.4	7.7	27.1	4.1	1.06	2.13	0.25	1.31	0.23	0.47	0.05	0.3	0.03

Note: bd denotes below detected limit.

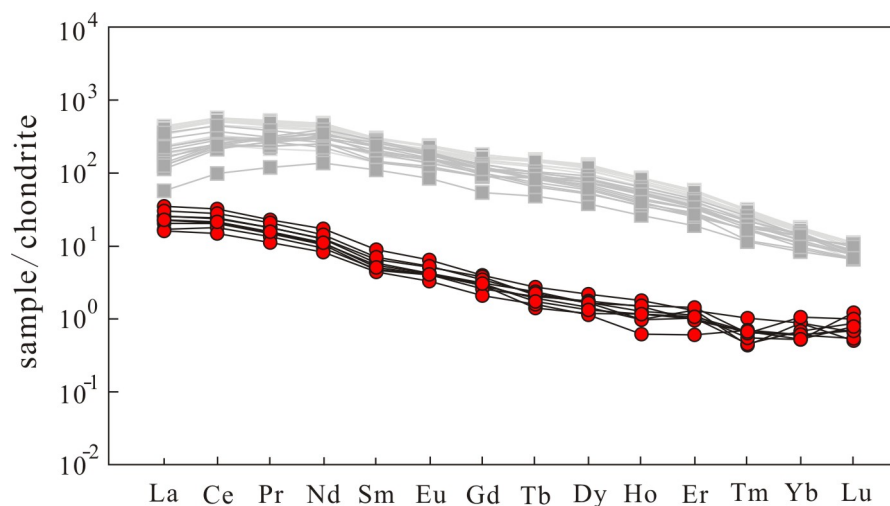


Figure 7. Chondrite-normalized REE patterns for dolomite mineral grains from the Dol-dyke. The gray lines are data of coarse-grained dolomite from the Bayan Obo deposit [26]. Data for normalization according to [39].

The major element compositions for apatite are listed in Table 3. All apatite grains can be classified as fluorapatite with similar F and P_2O_5 contents that are 2.30–3.64 wt.% and 41.14–42.37 wt.% for Type 1 apatite, 1.80–3.34 wt.% and 41.20–42.20 wt.% for Type 2, and 2.30–3.53 wt.% and 41.50–43.15 wt.% for Type 3, respectively. They all have SiO_2 below the detection limit (0.01 wt.%) and negligible Cl (<0.05 wt.%). The three types of apatite differ in terms of CaO and Na₂O contents. Type 1 apatite contains CaO contents ranging from 48.99 to 50.96 wt.%, and Na₂O from 0.59 to 1.09 wt.%. Type 2 has lower CaO contents (42.89–44.94 wt.%) and the highest Na₂O (1.36–1.76 wt.%) contents. In contrast, Type 3 has the highest CaO (50.76–52.31 wt.%) and the lowest Na₂O (0.45–0.66 wt.%) contents. All types of apatite have high LREE₂O₃ (La–Nd) and SrO contents. Type 1 apatite has LREE₂O₃ contents of 2.35–4.20 wt.% and SrO contents of 1.75–2.19 wt.%. Type 2 apatite contains much higher LREE₂O₃ (6.10–8.21 wt.%) and SrO (2.83–3.63 wt.%) contents than type 1. In contrast, Type 3 apatite has slightly lower LREE₂O₃ (1.17–2.35 wt.%) and SrO (1.51–1.99 wt.%) contents than Type 1.

Table 3. Major element concentrations (wt.%) of the three types of apatite in the Dol-dyke.

Element	P ₂ O ₅	SiO ₂	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	CaO	SrO	Na ₂ O	F	Cl	Total
Type 1 apatite												
BY22-1	41.83	bd	1.93	3.72	0.38	1.06	44.94	2.83	1.50	1.80	bd	99.28
BY22-2	42.32	bd	1.10	3.61	0.45	0.94	44.73	2.89	1.53	2.25	bd	98.88
BY22-3	42.07	bd	2.24	3.72	0.49	1.04	44.84	2.96	1.55	2.01	0.05	100.21
BY22-4	41.50	bd	2.40	4.28	0.59	0.94	43.19	3.63	1.76	2.18	0.02	99.57
BY22-5	42.34	bd	1.78	4.13	0.53	0.79	44.18	3.32	1.73	2.24	0.04	100.14
BY22-6	41.51	bd	2.26	3.75	0.51	0.91	43.88	3.45	1.66	2.55	0.04	99.45
BY22-7	41.94	bd	1.76	4.22	0.47	1.15	43.89	3.54	1.58	2.32	bd	99.98
BY22-8	41.14	bd	2.62	3.72	0.47	0.87	44.79	3.46	1.72	2.68	0.02	100.36
BY22-9	42.37	bd	2.00	3.77	0.49	1.12	42.89	3.04	1.57	3.34	bd	99.19
BY22-10	42.03	bd	2.22	4.03	0.59	1.05	43.13	3.47	1.69	2.37	0.03	99.61
BY22-11	41.90	bd	2.55	4.11	0.57	0.69	43.58	3.60	1.55	2.17	bd	99.81
BY22-12	41.68	bd	2.15	4.24	0.37	0.81	43.87	3.23	1.74	3.00	0.04	99.99
BY22-13	41.88	bd	1.84	4.17	0.50	1.02	44.13	3.29	1.63	2.68	0.02	100.03
BY22-14	41.68	bd	2.20	4.44	0.53	0.76	42.92	3.50	1.54	3.22	bd	99.44
BY22-15	42.39	bd	1.60	3.74	0.40	1.09	42.98	3.59	1.36	2.88	bd	98.89
BY22-16	42.33	bd	2.11	3.79	0.46	0.97	44.28	3.33	1.58	2.12	0.03	100.11
BY22-17	41.49	bd	2.09	3.74	0.69	0.79	43.50	3.50	1.66	2.68	bd	99.01
BY22-18	42.20	bd	1.70	4.45	0.50	1.25	43.15	3.35	1.71	2.40	0.03	99.73
BY22-19	42.26	bd	2.09	4.10	0.44	0.84	44.13	3.25	1.51	3.02	bd	100.37
Type 2 apatite												
XC3-4	41.3	bd	0.63	1.74	0.26	0.48	48.99	2.19	0.91	3.17	0.02	98.40
XC3-5	41.86	bd	1.19	1.94	0.17	0.44	49.59	1.92	1.09	3.55	0.02	100.33
XC3-6	42.07	bd	1.24	1.11	0.23	0.40	49.77	1.86	0.83	2.51	0.02	99.03
XC3-7	41.20	bd	0.92	1.20	0.18	0.31	49.63	1.97	1.05	3.64	0.01	98.65
XC3-8	41.60	bd	0.96	1.44	0.25	0.35	50.41	1.76	0.77	3.09	0.02	99.38
XC3-9	41.56	bd	1.03	1.96	0.16	0.47	49.59	1.83	0.93	3.01	0.01	99.35
XC3-10	42.04	bd	0.70	1.58	0.14	0.31	50.43	1.84	0.8	2.35	0.02	99.22
XC3-11	42.20	bd	0.79	1.71	0.23	0.42	49.55	1.92	0.92	3.00	bd	99.58
XC3-12	41.71	bd	1.28	2.00	0.30	0.62	49.20	2.09	1.07	2.88	bd	100.01
XC3-16	42.05	bd	1.09	1.73	0.29	0.35	49.27	1.87	0.89	2.42	0.01	98.99
XC3-17	41.59	bd	0.98	1.56	0.19	0.36	50.23	1.81	0.78	2.30	0.01	98.88
XC3-19	41.79	bd	0.74	1.15	0.13	0.47	50.21	1.79	0.79	3.01	0.01	98.83
XC3-21	42.05	bd	1.02	1.69	0.30	0.40	50.33	2.05	0.88	2.76	bd	100.32
XC3-22	41.75	bd	0.51	1.73	0.16	0.35	50.04	2.00	0.80	2.98	0.01	99.12
XC3-33	42.14	bd	0.72	1.38	0.08	0.26	49.99	1.88	0.90	2.96	bd	99.13
XC3-34	41.63	bd	0.63	1.79	0.23	0.30	49.89	1.87	0.87	2.72	0.01	98.80
XC3-36	41.95	bd	0.84	0.98	0.22	0.31	50.96	1.75	0.59	2.62	0.01	99.22

Table 3. Cont.

Element	P ₂ O ₅	SiO ₂	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	CaO	SrO	Na ₂ O	F	Cl	Total
Type 3 apatite												
XC3-1	42.51	bd	0.71	0.88	0.09	0.36	51.10	1.51	0.59	3.12	0.01	99.61
XC3-2	42.20	bd	0.52	0.86	0.11	0.30	51.75	1.88	0.52	3.08	0.01	99.97
XC3-3	42.18	bd	0.45	0.89	0.21	0.37	50.79	1.71	0.63	2.61	0.02	98.79
XC3-13	42.28	bd	0.70	0.82	0.11	0.32	51.34	1.77	0.53	3.04	bd	99.71
XC3-14	42.29	bd	0.38	0.91	0.18	0.27	51.60	1.67	0.51	3.53	0.01	99.92
XC3-15	43.15	bd	0.72	0.80	0.15	0.31	51.73	1.66	0.55	2.30	0.02	100.48
XC3-18	42.89	bd	0.58	0.52	0.08	0.35	52.29	1.79	0.41	2.62	0.03	100.53
XC3-20	42.62	bd	0.86	0.73	0.19	0.31	51.18	1.77	0.53	2.43	0.01	99.65
XC3-24	42.17	bd	0.21	0.62	0.09	0.26	51.4	1.79	0.56	2.32	0.01	98.51
XC3-25	42.44	bd	0.23	0.57	0.09	0.28	52.31	1.82	0.46	2.94	0.01	99.92
XC3-26	42.04	bd	0.23	1.00	0.13	0.21	51.28	1.79	0.66	3.43	0.01	99.38
XC3-27	42.07	bd	0.63	0.65	0.08	0.22	51.54	1.72	0.49	2.66	0.01	98.95
XC3-28	41.99	bd	0.70	1.13	0.15	0.37	50.76	1.63	0.71	2.89	0.03	99.15
XC3-29	42.22	bd	0.35	0.88	0.06	0.22	51.02	1.64	0.42	3.26	0.01	98.71
XC3-30	42.45	bd	0.33	0.88	0.16	0.44	51.66	1.51	0.74	3.38	0.01	100.20
XC3-31	41.50	bd	0.28	1.02	0.10	0.21	51.65	1.83	0.64	2.63	0.02	98.78
XC3-32	41.96	bd	0.23	0.95	0.10	0.30	51.30	1.78	0.54	2.67	bd	98.78
XC3-35	42.08	bd	0.33	0.58	0.06	0.26	51.86	1.99	0.45	3.16	0.01	99.55

Note: bd denotes below detected lim.

4. Discussion

4.1. Formation of the Three Types of Apatite

As mentioned earlier, the three types of apatite show similar textures, grain sizes, and P_2O_5 and F contents, indicating that they were originally a batch of crystallized products from carbonatitic melts. And for all types of apatite in the dyke, CaO contents display negative correlations with $LREE_2O_3 + Na_2O$ and SrO contents, and there is a significant positive correlation between $LREE_2O_3$ and Na_2O contents (Figure 8). These indicate that for all apatite grains in the dyke, the REE and Sr go in and out of the apatite mainly via the coupled substitution $Na^+ + REE^{3+} = 2Ca^{2+}$ and $Sr^{2+} = Ca^{2+}$. Among the mineral constituents of the rock samples, apatite seems to be the main gauge of fluid interaction. REE and Sr in apatite can be easily affected by hydrothermal alteration processes [40–43]. Therefore, tracing these element variations in apatite is a good way to understand the crystallization and overprinted subsequent processes. In this study, the three types of apatite exhibit distinctly different REE and Sr contents. As shown in Figure 9, Type 1 apatite has $LREE_2O_3$ contents comparable to primary apatite in other Dol-dykes [44] from the Bayan Obo ore district. BSE and CL images of Type 1 display no reaction textures, indicating that it was not affected or was little affected by post-crystallization alteration. Therefore, it can represent the primary apatite crystallized from carbonatitic melts.

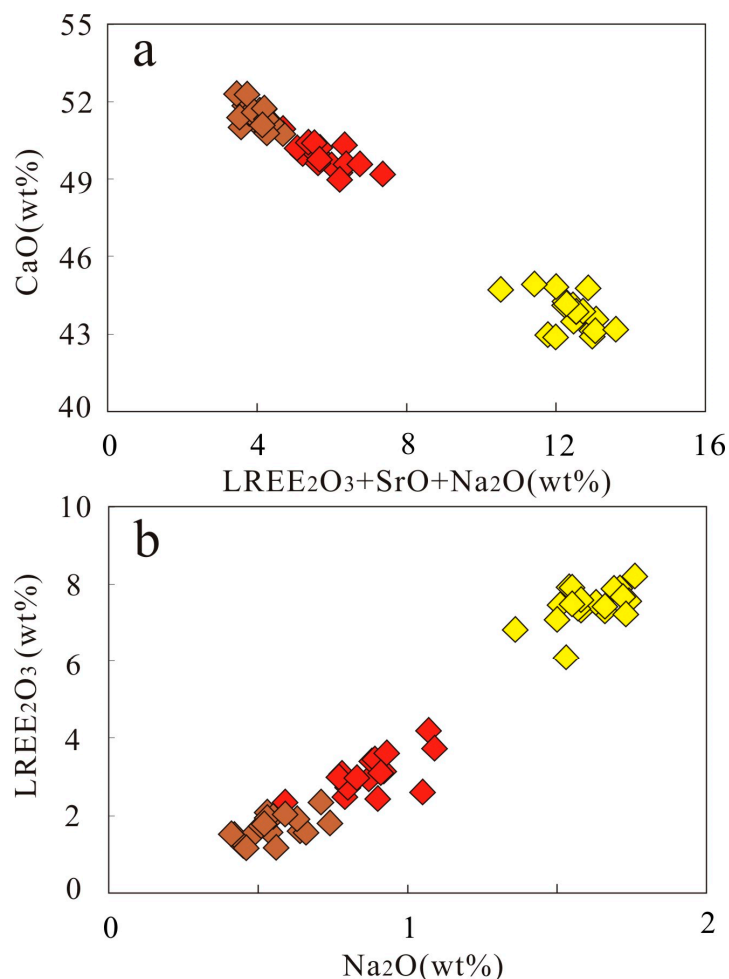


Figure 8. Plots of (a) CaO vs. ($LREE_2O_3 + SrO + Na_2O$) and (b) Na_2O vs. $LREE_2O_3$ for the three types of apatite.

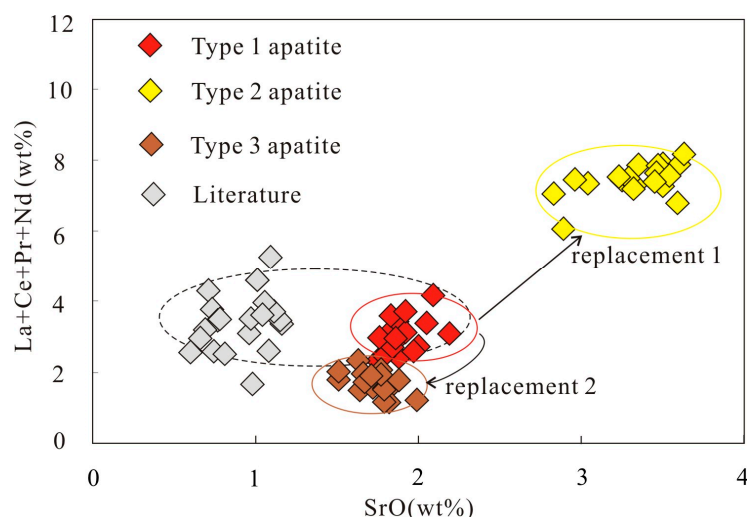


Figure 9. Plots of LREE_2O_3 vs. SrO for the three types of apatite. The dashed line shows the LREE_2O_3 of primary apatite of the Dol-dykes. Literature data are from other Dol-dykes in the ore district [44].

According to reaction textures and compositional changes, Type 2 and Type 3 are the products of replacement of the primary apatite (Type 1 apatite). Compared with Type 1 apatite, Type 2 apatite has a sharp increase in contents of LREE_2O_3 , Na_2O , and SrO . In fact, Type 2 apatite contains the highest REE contents found so far in the Bayan Obo ore district. This, in conjunction with the monazite replacements at the Type 2 apatite grain boundaries or internal fractures, indicates an interaction between primary apatite and LREE-, Na-, and Sr-rich fluids. The process can be represented by Reaction (1): Type 1 apatite + (LREE^{3+} , Na^+ , Sr^{2+}) in fluids = Type 2 apatite + monazite + Ca^{2+} in fluids. The X-ray element scanning images (Figure 10) show that the Type 2 apatite is relatively homogeneous in Ca, P, and Sr compositions, which means a complete re-equilibration between Type 2 apatite and the extensive fluids. The formation of metasomatic monazites along the apatite grain boundaries or interior fractures indicates that phosphate probably had an important role in the precipitation of REE in fluids.

Type 3 apatite shows dark CL images as compared with the bright CL images of Type 1 apatite (Figure 4g,h). This luminescent intensity difference can be explained by the REE variation [45]. Under the same conditions, apatite that has been metasomatized by fluids and consequently lost LREEs appears dark in CL images [46]. In this study, Type 3 apatite contains lower total LREE_2O_3 , Na_2O , and SrO contents than Type 1 apatite. The veinlets in Type 3 apatite are the main argument that this is an overprinted apatite and not a primary apatite, and they are also direct evidence for the mobility of hydrothermal fluids. Therefore, it is obvious that the leaching of LREE from primary apatite occurred. The migration of LREE out of apatite can be expressed by Reaction (2): Type 1 apatite + Ca^{2+} in fluids = Type 3 apatite + LREE^{3+} , Sr^{2+} and Na^+ in fluids.

Reaction (2) can be regarded as the reverse of reaction (1), so the nature of the fluids in Reaction (2) should be completely different from that of fluids in Reaction (1). Besides having low LREE and Sr concentrations to impel the leaching process, the fluids in Reaction (2) were also supposed to be poor in Na or Si contents, because these elements can freely enter the apatite lattices to maintain an electrovalent balance, thereby inhibiting the removal of REE from apatite [47,48].

In conclusion, primary apatite in the dyke was affected by fluids at two separate stages: a first metasomatic stage represented by the formation of Type 2 apatite, driven by post-magmatic fluids with fairly high LREE, Na, and Sr contents derived from evolved carbonatitic magmas, and a second stage of metasomatic modification caused LREEs leaching from the primary apatite and formed Type 3 apatite.

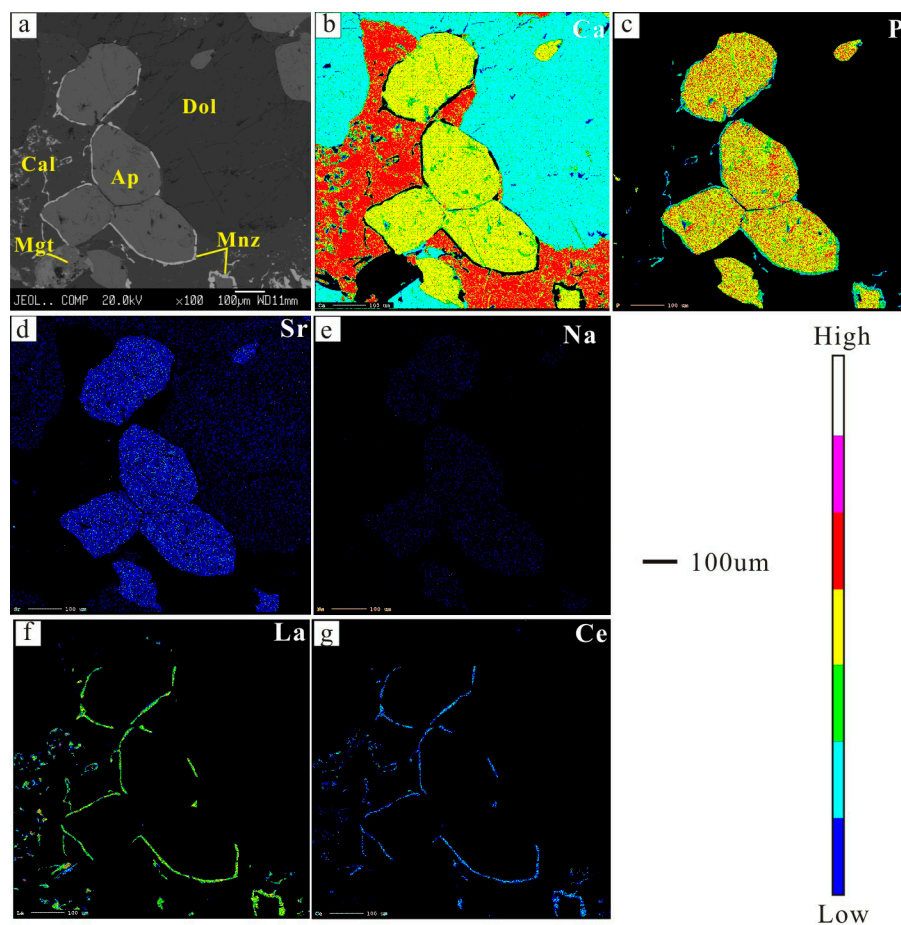


Figure 10. Backscattered electron and X-ray element mapping images of Type 2 apatite. Legend to the right refers to element concentrations from low to high, but not to scale. (a) BSE image of Type 2 apatite. (b) X-ray element mapping image of calcium. (c) X-ray element mapping image of phosphorus. (d) X-ray element mapping image of strontium. (e) X-ray element mapping image of sodium. (f) X-ray element mapping image of lanthanum. (g) X-ray element mapping image of cerium. Abbreviations are the same as above.

4.2. The REE Mineralization of the Dol-Dyke

As noted earlier, dolomite mineral comprises more than 90% of the sample's volume but contains very low REE contents (62.8–152.2 ppm). Hence, it contributes little to the whole-rock REE budget (1407–4184 ppm) of the dyke. Due to the lack of primary monazite or bastnaesite, the main primary REE-bearing mineral in the dyke is apatite. However, the low P_2O_5 content (0.23 wt.% on average) of the rock samples indicates that apatite only comprises a very small proportion. Therefore, the primary of apatite role in controlling the whole-rock REE budget can be excluded. As a result, the REE contents of the dyke come from the hydrothermal REE-bearing minerals. That is, hydrothermal fluids dominate the REE mineralization of the dyke. The fluids shall be the same as the post-magmatic fluids responsible for the formation of Type 2 apatite mentioned above.

Bulk rock REE contents of other carbonatite dykes in the ore district have also been reported in previous studies, and the data vary greatly between different types of dykes, different dykes of the same type, or different zones of the same dyke. For example, REE contents of rock samples from different Dol-dykes range from ~100 ppm [21] to >15,000 ppm [8]. As field observations show that a Cal-dyke crosscut, a Dol-dyke, and a Cal-dyke have higher REE contents and $(La/Yb)_N$ ratios, a magnesio-ferro-carbonatite to calcio-carbonatite evolution sequence is thus established [21,28,29]. Liu et al. [25] proposed that calcio-carbonatites represented residual melts of evolved carbonatite magma and are rich in LREE, Sr, and Ba. However, this magmatic evolution process is not consistent

with the evolution trend of most carbonatites in the world [49] and also cannot explain the heterogeneous REE mineralization of the carbonatite dykes in the ore district. Alternatively, our study results highlight that late-stage fluids expelled from the carbonatitic magmas dominate the REE mineralization of most dykes. The fluids interacted with dykes and wall rocks, causing heterogeneous REE mineralization of the dykes, transformation of some primary magmatic minerals, and different degrees of fenitization of wall rocks.

4.3. Implication for the Formation of the Bayan Obo Deposit

There are fine-grained and coarse-grained dolomite rocks in the Bayan Obo REE deposit according to the sizes of constituent minerals. The fine-grained dolomite rocks host more intense REE mineralization compared to the coarse-grained rocks [7,17]. Due to experiencing limited metasomatism and deformation, the coarse-grained dolomite rock is believed to be closer to the protolith before mineralization [25,26]. The total REE contents in coarse-grained dolomite mineral grains (Figure 7) are far lower than those of the whole rock (Figure 6b), similar to the case in the Dol-dyke mentioned above. Theoretically, carbonate minerals are supposed to have high capacity to incorporate REE for the substitution of Ca by REEs. However, if REEs in carbonatitic magmas can eventually form ore deposit, then REEs should be concentrated in the evolved melts or fluids rather than be dispersed in early formed carbonate minerals. Xu et al. [50] studied the Miaoya carbonatites and found that REE contents of calcite are only 100–260 ppm, far lower than those of the whole rocks. However, precisely because of the crystallization of these calcites, the REEs were able to concentrate in the residual melts and finally formed Miaoya REE ore deposit. Similarly, in the Bayan Obo ore district, dolomite grains from the Dol-dyke and ore-hosting dolomites contain low REE contents, indicating that early crystallized dolomite minerals consume little REE during carbonatitic melt evolution. Petrographic studies on the Dol-dyke in this study and ore-hosting dolomites in previous studies [25,44] reveal that REE-bearing minerals mainly occurred along dolomite grain boundaries or as late-stage veins in the dolomite rocks, implying that REE mineralization occurred later than the formation of dolomite minerals and was controlled by hydrothermal fluids. Therefore, it is highly possible that fluids derived from the evolved carbonatitic magmas controlled the REE mineralization of the deposit. The role of post-magmatic hydrothermal overprint in REE mineralization of carbonatites has also been proved and highlighted by many research studies worldwide [43,51,52]. Considering that the physicochemical conditions of REE mineralization were poorly constrained in the Bayan Obo deposit, it is important to conduct further studies on related fluid inclusions.

The ages of the deposit and carbonatite dykes have been dated by various testing methods, and the results cluster in periods at 1.4–1.3 Ga and 0.5–0.4 Ga [3,5,11,23]. Campbell et al. [53] reported SHRIMP ^{232}Th - ^{208}Pb ages for a single zircon from the East orebody of 1325 ± 60 Ma in the zircon core and 455.6 ± 28 Ma at the rim. All these studies concluded that the deposit originally formed in the Mesoproterozoic and was subsequently influenced by hydrothermal fluids. Song et al. [27] found that in situ Th-Pb ages for monazite from the deposit range from 361 Ma to 913 Ma and interpreted these ages as results of subsequent thermal perturbations. In addition, in situ analysis of other minerals indicate that the deposit underwent significant modification events after its formation, as evidenced by the addition of radiogenic Sr and Pb in dolomite and apatite [26,27] and abrupt changes in apatite compositions [44,54]. In this study, the presence of the Type 3 apatite in the dyke directly proves the occurrence of such a distinct hydrothermal activity in the Bayan Obo area. Although it is hard to tell the exact time of the disturbance, the fluids, according to the forming mechanism for Type 3 apatite, contain low contents of REE, Na, and Si contents. That is to say, the most outstanding disturbing fluids that occurred in the area probably provided no extra REEs to the Bayan Obo carbonatites.

5. Conclusions

(1) There are three types of apatite in the Dol-dyke. Type 1 apatite represents the primary apatite, which survived subsequent modification. After crystallization, the primary apatite in the dyke

interacted with fluids of two separate stages: the first stage of metasomatism by post-magmatic fluids with fairly high LREE, Na, and Sr contents derived from evolved carbonatitic magmas, followed by a second stage of fluid infiltration that caused leaching of LREE and Sr from the primary apatite.

(2) The REE contents of the Dol-dyke in this study were controlled by hydrothermal fluids expelled from the carbonatitic magmas as demonstrated by widespread REE-bearing hydrothermal minerals as well as fluid-induced REE-rich Type 2 apatite.

(3) The studying results on the Dol-dyke of this study suggest that post-magmatic fluids derived from the evolved carbonatite melts played a key role in the REE mineralization of the Bayan Obo carbonatites, and a significant fluid disturbance occurred but provided no extra REEs for the carbonatites.

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References

1. Drew, L.J.; Meng, Q.R.; Sun, W.J. The Bayan Obo iron rare-earth niobium deposits, Inner-Mongolia, China. *Lithos* **1990**, *26*, 43–65. [\[CrossRef\]](#)
2. Le Bas, M.J.; Keller, J.; Tao, K.; Wall, F.; William, C.T.; Zhang, P.S. Carbonatite dykes at Bayan Obo, Inner Mongolia, China. *Miner. Petrol.* **1992**, *46*, 195–228. [\[CrossRef\]](#)
3. Zhu, X.K.; Sun, J.; Pan, C.X. Sm-Nd isotopic constraints on rare-earth mineralization in the Bayan Obo ore deposit, Inner Mongolia, China. *Ore Geol. Rev.* **2015**, *64*, 543–553. [\[CrossRef\]](#)
4. Zhang, S.H.; Zhao, Y.; Liu, Y. A precise zircon Th-Pb age of carbonatite sills from the world's largest Bayan Obo deposit: Implications for timing and genesis of REE-Nb mineralization. *Precambrian Res.* **2017**, *291*, 202–219. [\[CrossRef\]](#)
5. Yang, X.Y.; Lai, X.D.; Pirajno, F.; Liu, Y.L.; Ling, M.X.; Sun, W.D. Genesis of the Bayan Obo Fe-REE-Nb formation in Inner Mongolia, North China Craton: A perspective review. *Precambrian Res.* **2017**, *288*, 39–71. [\[CrossRef\]](#)
6. Chao, E.C.T.; Back, J.M.; Minkin, J.A.; Tasumoto, M.; Wang, J.W.; Conrad, J.E.; Mckee, E.H. *The Sedimentary Carbonate-Hosted Giant Bayan Obo REE-Fe-Nb Ore Deposit of Inner Mongolia, China: Cornerstone Examples for Giant Polymetallic Ore Deposits of Hydrothermal Origin*; Bulletin 2143; United States Government Publishing Office: Washington, DC, USA, 1997; p. 65.
7. Lai, X.D.; Yang, X.Y.; Sun, W.D. Geochemical constraints on genesis of dolomite marble in the Bayan Obo REE-Nb-Fe deposit, Inner Mongolia: Implications for REE mineralization. *J. Asian Earth Sci.* **2012**, *57*, 90–102. [\[CrossRef\]](#)
8. Lai, X.D.; Yang, X.D. Geochemical characteristics of the Bayan Obo giant REE Nb-Fe deposit and constraints on its genesis. *J. S. Am. Earth Sci.* **2013**, *41*, 99–112. [\[CrossRef\]](#)
9. Lai, X.D.; Yang, X.Y.; Santosh, M.; Liu, Y.L.; Ling, M.X. New data of the Bayan Obo Fe-REE-Nb deposit, Inner Mongolia: Implications for ore genesis. *Precambrian Res.* **2015**, *263*, 108–122. [\[CrossRef\]](#)
10. Ling, M.X.; Liu, Y.L.; Williams, I.S.; Teng, F.Z.; Yang, X.Y.; Ding, X.; Wei, G.J.; Xie, L.H.; Deng, W.F.; Sun, W.D. Formation of the world's largest REE deposit through protracted fluxing of carbonatite by subduction-derived fluids. *Sci. Rep.* **2013**, *3*, 1776–1783. [\[CrossRef\]](#)
11. Smith, M.P.; Campbell, L.S.; Kynicky, J. A review of the genesis of the world class Bayan Obo Fe-REE-Nb deposits, Inner Mongolia, China: Multistage processes and outstanding questions. *Ore Geol. Rev.* **2015**, *64*, 459–476. [\[CrossRef\]](#)

12. Liu, Y.L.; Ling, M.X.; Williams, I.S.; Yang, X.Y.; Wang, C.Y.; Sun, W.D. The formation of the giant Bayan Obo REE-Nb-Fe deposit, North China, Mesoproterozoic carbonatite and overprinted Paleozoic dolomitization. *Ore Geol. Rev.* **2018**, *92*, 73–83. [\[CrossRef\]](#)
13. Le Bas, M.J.; Spiro, B.; Yang, X.M. Oxygen carbon and strontium isotope study of the carbonatitic dolomite host of the Bayan Obo Fe-Nb-REE deposit, Inner Mongolia, N. China. *Mineral. Mag.* **1997**, *61*, 531–541. [\[CrossRef\]](#)
14. Le Bas, M.J.; Yang, X.M.; Taylor, R.N.; Spiro, B.; Milton, J.A.; Zhang, P.S. New evidence for the magmatic origin of the Bayan Obo ore-bearing dolomite marble, Inner Mongolia, China, from a calcite-dolomite carbonatite dyke. *Miner. Petrol.* **2007**, *90*, 223–248. [\[CrossRef\]](#)
15. Yuan, Z.X.; Bai, G.; Zhang, Z.Q. Trachytic rock and associated fenitization in the Bayan Obo ore deposit, Inner Mongolia, China: Evidence for magmatic–hydrothermal mineralization related to a carbonatitic complex. *Acta Geol. Sin. Engl. Ed.* **2000**, *74*, 148–153.
16. Hao, Z.G.; Wang, X.B.; Li, Z.; Xiao, G.; Zhang, T.R. The carbonatitic type REE-Nb-Fe ore deposit-A rare case of Middle Proterozoic Paleo-volcanogenic mineralization in Bayan Obo, Inner Mongolia. *Acta Geol. Sin. Engl. Ed.* **2002**, *76*, 525–540.
17. Yang, X.M.; Le Bas, M.J. Chemical compositions of carbonate minerals from Bayan Obo, Inner Mongolia, China: Implications for petrogenesis. *Lithos* **2004**, *72*, 97–116. [\[CrossRef\]](#)
18. Wang, K.Y.; Zhang, J.E.; Yu, L.J.; Fang, A.M.; Dong, C.; Hu, F.Y. Fenitized wall rock geochemistry of the first carbonatite dyke at Bayan Obo, Inner Mongolia, China. *Acta Geol. Sin. Engl. Ed.* **2018**, *92*, 180–193. [\[CrossRef\]](#)
19. Wang, K.Y.; Fang, A.M.; Zhang, J.E.; Yu, L.J.; Dong, C.; Zan, J.F.; Hao, M.Z.; Hu, F.Y. Genetic relationship between fenitized ores and hosting dolomite carbonatite of the Bayan Obo REE deposit, Inner Mongolia, China. *J. Asian Earth Sci.* **2019**, *174*, 189–204. [\[CrossRef\]](#)
20. Yang, K.F.; Fan, H.R.; Santosh, M.; Hu, F.F.; Wang, K.Y. Mesoproterozoic mafic and carbonatitic dykes from the northern margin of the North China Craton: Implications for the final breakup of Columbia supercontinent. *Tectonophysics* **2011**, *498*, 1–10. [\[CrossRef\]](#)
21. Yang, K.F.; Fan, H.R.; Santosh, M.; Wang, K.Y. Mesoproterozoic carbonatitic magmatism in the Bayan Obo deposit, Inner Mongolia, North China: Constraints for the mechanism of super accumulation of rare earth elements. *Ore Geol. Rev.* **2011**, *40*, 122–131. [\[CrossRef\]](#)
22. Sun, J.; Zhu, X.; Chen, Y.; Fang, N. Iron isotopic constraints on the genesis of Bayan Obo ore deposit, Inner Mongolia, China. *Precambrian Res.* **2013**, *235*, 88–106. [\[CrossRef\]](#)
23. Fan, H.R.; Yang, K.F.; Hu, F.F.; Liu, S.; Wang, K.Y. The giant Bayan Obo Re-Nb-Fe deposit, China: Ccontroversy and ore genesis. *Geosci. Front.* **2016**, *7*, 335–344. [\[CrossRef\]](#)
24. Xie, Y.L.; Qu, Y.W.; Yang, Z.F.; Liang, P.; Zhong, R.C.; Wang, Q.W.; Xie, J.M.; Li, B.C. Giant Bayan Obo Fe-Nb-REE deposit: Progresses, Controversaries and new understandings. *Miner. Depos.* **2019**, *38*, 983–1003, (In Chinese with English abstract).
25. Liu, S.; Fan, H.R.; Groves, D.I.; Yang, K.F.; Yang, Z.F.; Wang, Q.W. Multiphase carbonatite-related magmatic and metasomatic processes in the genesis of the ore-hosting dolomite in the giant Bayan Obo REE-Nb-Fe deposit. *Lithos* **2020**, *354–355*, 105359. [\[CrossRef\]](#)
26. Chen, W.; Liu, H.Y.; Lu, J.; Jiang, S.Y.; Simonetti, A.; Xu, C.; Zhang, W. The formation of the ore-hosting dolomite marble from the giant Bayan Obo REE-Nb-Fe deposit, Inner Mongolia: Insights from micron-scale geochemical data. *Miner. Depos.* **2020**, *55*, 131–146. [\[CrossRef\]](#)
27. Song, W.L.; Xu, C.; Smith, M.P.; Chakhmouradian, A.R.; Brenna, M.; Kynicky, J.; Chen, W.; Yang, Y.H.; Deng, M.; Tang, H.Y. Genesis of the world's largest rare earth element deposit, Bayan Obo, China: Protracted mineralization evolution over 1 b.y. *Geology* **2018**, *46*, 323–326. [\[CrossRef\]](#)
28. Yang, K.F.; Fan, H.R.; Pirajno, F.; Li, X.C. The Bayan Obo (China) giant REE accumulation conundrum elucidated by intense magmatic differentiation of carbonatite. *Geology* **2019**, *47*, 1198–1202. [\[CrossRef\]](#)
29. Wang, K.Y.; Fan, H.R.; Xie, Y.H. Geochemistry of REE and other trace elements of the carbonatite dykes at Bayan Obo, implication for its formation. *Acta Petrol. Sin.* **2002**, *18*, 340–348, (In Chinese with English abstract).
30. Fan, H.R.; Hu, F.F.; Yang, K.F.; Pirajno, F.; Liu, X.; Wang, K.Y. Integrated U-Pb and Sm-Nd geochronology for a REE-rich carbonatite dyke at the giant Bayan Obo REE deposit, Northern China. *Ore Geol. Rev.* **2014**, *63*, 510–519. [\[CrossRef\]](#)
31. Yang, X.M.; Yang, X.Y.; Zheng, Y.F.; Le Bas, M.J. A rare earth element-rich carbonatite dyke at Bayan Obo, Inner Mongolia, North China. *Miner. Petrol.* **2003**, *78*, 93–110. [\[CrossRef\]](#)

32. Xiao, W.J.; Windley, B.F.; Hao, J.; Zhai, M.G. Accretion leading to collision and the Permian Solonker suture, Inner Mongolia, China: Termination of the central Asian orogenic belt. *Tectonics* **2003**, *22*, 1–20. [\[CrossRef\]](#)
33. Fan, H.R.; Yang, K.F.; Hu, F.F.; Wang, K.Y.; Zhai, M.G. Zircon geochronology of basement rocks from the Bayan Obo area, Inner Mongolia, and tectonic implications. *Acta Petrol. Sin.* **2010**, *26*, 1342–1350. (In Chinese)
34. Bai, G.; Yuan, Z.X.; Wu, C.Y.; Zhang, Z.Q.; Zheng, L. *Demonstration on the Geological Features and Genesis of the Bayan Obo Ore Deposit*; Geological Publishing House: Beijing, China, 1996. (In Chinese)
35. Qiu, Y.Z.; Wen, H.J.; Qin, C.J. Precise determination of the age of Hercynian granitoids and discovery of Yanshanian granitoids. *Acta Miner. Sin.* **2011**, *31*, 631–632, (In Chinese with English abstract).
36. Ling, M.X.; Zhang, H.; Li, H.; Liu, Y.L.; Liu, J.; Li, L.Q.; Li, Y.C.; Yang, X.Y.; Sun, W.D. The Permian-Triassic granitoids in Bayan Obo, North China Craton: A geochemical and geochronological study. *Lithos* **2014**, *190–191*, 430–439. [\[CrossRef\]](#)
37. Hu, Z.C.; Gao, S.; Liu, Y.S.; Hu, S.H.; Chen, H.H.; Yuan, H.L. Signal enhancement in laser ablation ICP-MS by addition of nitrogen in the central channel gas. *J. Anal. At. Spectrom.* **2008**, *23*, 1093–1101. [\[CrossRef\]](#)
38. Woolley, A.R.; Kempe, D.R.C. Carbonatites: Nomenclature, average chemical compositions, and element distribution. In *Carbonatites: Genesis and Evolution*; Bell, K., Ed.; Unwin Hyman: London, UK, 1989; pp. 1–14.
39. Sun, S.S.; McDonough, W.F. Chemical and isotopic systematics of oceanic basalt: Implications for mantle compositions and processes. In *Magmatism in the Ocean Basins*; Saunders, A.D., Norry, M.J., Eds.; Geological Society of London Special Publication: London, UK, 1989; Volume 42, pp. 313–314.
40. Zirner, A.L.K.; Marks, M.A.W.; Wenzel, T.; Jacob, D.E.; Markl, G. Rare earth elements in apatite as a monitor of magmatic and metasomatic processes: The Ilímaussaq complex, South Greenland. *Lithos* **2015**, *228–229*, 12–22. [\[CrossRef\]](#)
41. Li, X.C.; Zhou, M.F. Multiple stages of hydrothermal REE remobilization recorded in fluorapatite in the Paleoproterozoic Yinchang Fe–Cu–(REE) deposit, Southwest China. *Geochim. Cosmochim. Acta* **2015**, *166*, 53–73. [\[CrossRef\]](#)
42. Harlov, D.E. Apatite: A fingerprint for metasomatic processes. *Elements* **2015**, *11*, 171–176. [\[CrossRef\]](#)
43. Broomfendley, S.; Styles, M.T.; Appleton, J.D.; Gunn, G.; Wall, F. Evidence for dissolution-reprecipitation of apatite and preferential LREE mobility in carbonatite-derived late-stage hydrothermal processes. *Am. Mineral.* **2016**, *101*, 596–611. [\[CrossRef\]](#)
44. Hu, L.; Li, Y.K.; Wu, Z.J.; Bai, Y.; Wang, A.J. Two metasomatic events recorded in apatite from the ore-hosting dolomite marble and implications for genesis of the giant Bayan Obo REE deposit, Inner Mongolia, Northern China. *J. Asian Earth Sci.* **2019**, *172*, 56–65. [\[CrossRef\]](#)
45. Roeder, P.L.; MacArthur, D.; Ma, X.-P.; Palmer, G.R.; Mariano, A.N. Cathodoluminescence and microprobe study of rare-earth elements in apatite. *Am. Mineral.* **1987**, *72*, 801–811.
46. Xing, C.M.; Wang, C.Y. Cathodoluminescence images and trace element compositions of fluorapatite from the Hongge layered intrusion in SW China: A record of prolonged crystallization and overprinted fluid metasomatism. *Am. Mineral.* **2017**, *102*, 1390–1401. [\[CrossRef\]](#)
47. Betkowski, W.B.; Harlov, D.E.; Rakovan, J.F. Hydrothermal mineral replacement reactions for an apatite-monazite assemblage in alkali-rich fluids at 300–600 °C and 100 Mpa. *Am. Mineral.* **2016**, *101*, 2620–2637. [\[CrossRef\]](#)
48. Harlov, D.E.; Wirth, R.; Förster, H.J. An experimental study of dissolution–reprecipitation in fluorapatite: Fluid infiltration and the formation of monazite. *Contrib. Mineral. Petrol.* **2005**, *150*, 268–286. [\[CrossRef\]](#)
49. Trofanenko, J. The nature and origin of the REE mineralization in the Wicheeda carbonatite, British Columbia, Canada. *Econ. Geol.* **2016**, *111*, 199–223. [\[CrossRef\]](#)
50. Xu, C.; Kynicky, J.; Chakhmouradian, A.N.; Campbell, I.H.; Allen, C.M. Trace-element modeling of the magmatic evolution of rare-earth-rich carbonatite from the Miaoya deposit, Central China. *Lithos* **2010**, *118*, 145–155. [\[CrossRef\]](#)
51. Prokopyev, I.R.; Borisenko, A.S.; Borovikov, A.A.; Pavlova, G.G. Origin of REE-rich ferrocarbonatites in southern Siberia (Russia): Implications based on melt and fluid inclusions. *Mineral. Petrol.* **2016**, *110*, 845–859. [\[CrossRef\]](#)
52. Zheng, X.; Liu, Y. Mechanisms of element precipitation in carbonatite-related rare-earth element deposits: Evidence from fluid inclusions in the Maoniuping deposit, Sichuan Province, southwestern China. *Ore Geol. Rev.* **2019**, *107*, 218–238. [\[CrossRef\]](#)

53. Campbell, L.S.; Compston, W.; Sircombe, K.N.; Wilkinson, C.C. Zircon from the East Orebody of the Bayan Obo Fe–Nb–REE deposit, China, and SHRIMP ages for carbonatite-related magmatism and REE mineralization events. *Contrib. Mineral. Petrol.* **2014**, *168*, 1040–1062. [[CrossRef](#)]
54. Ren, Y.; Yang, X.; Wang, S.; Öztürk, H. Mineralogical and geochemical study of apatite and dolomite from the Bayan Obo giant Fe-REE-Nb deposit in Inner Mongolia: New evidences for genesis. *Ore Geol. Rev.* **2019**, *109*, 381–406. [[CrossRef](#)]

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