

Short Communication

Scandium-Bearing Minerals in the Bayan Obo Nb-REE-Fe Deposit, Inner Mongolia, China

Hidehiko SHIMAZAKI¹, Zhuming YANG², Ritsuro MIYAWAKI¹ and Masako SHIGEOKA¹

¹Department of Geology and Paleontology, National Museum of Nature and Science, Hyakunincho, Shinjuku, Tokyo, Japan and

²Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China

Abstract

Aegirine, “perrierite-(Ce)”, and ferrocolumbite, occurring in the Bayan Obo Nb-REE-Fe deposit in Inner Mongolia, China, contain appreciable amounts of scandium. The Sc₂O₃ content in aegirine (sample TS-15) was 0.34–1.81 wt% (with one exceptionally high value of 3.45%) with an average value of 1.19%. The Sc₂O₃ content of “perrierite-(Ce)” (TS-20) was 2.82–3.64% with an average value of 3.26%. In the ferrocolumbite samples (TS-16, TS-23), the Sc₂O₃ content was 0.20–0.25% with an average value of 0.22% in sample TS-16, and 0.56–1.04% with an average value of 0.67% in sample TS-23. These data provide the basic information for future possible recovery of scandium as a by-product from the deposit.

Keywords: Aegirine, Bayan Obo, ferrocolumbite, “perrierite-(Ce)”, scandium.

1. Introduction

1.1. Bayan Obo deposit

The Bayan Obo ore deposit is a famous, world-class, giant Nb-REE-Fe deposit located in Inner Mongolia, China, situated approximately 80 km south of the border between China and Mongolia, at 109°57'E and 41°46'N. The deposit is contained within the sediments of the Proterozoic Bayan Obo Group, which consist predominantly of sandstones and slates, with the exception of the H8 dolomite marble unit, which hosts the vast majority of the ore. The paragenesis of the deposit is extremely complex, from deposition, through metamorphism and mineralization, to the intrusion of Hercynian granitoids to the south of the deposit (e.g. Chao *et al.*, 1997). It is suggested that four metallogenetic periods in the entire mineralizing process of the deposit exist, as follows: (i) Middle Protero-

zoic (1600–1200 Ma); (ii) Late Proterozoic (800–600 Ma); (iii) Caledonian (500–400 Ma); and (iv) Hercynian (340–270 Ma) (Ren *et al.*, 1994; Zhang *et al.*, 1994; Bai *et al.*, 1996).

The size of the deposit is approximately 18 km long from east to west, and 0.5–5 km wide from north to south. It includes several orebodies, among which the East orebody and the Main orebody are the two major Nb-REE-Fe orebodies. Based on the mineralization characteristics, all the ores can be classified into three main types: Nb-REE-Fe ore, Nb-REE ore, and Nb ore. More than 190 mineral species have been identified from the Bayan Obo deposit. The complicated mineralogy of the deposit has been described in detail by previous workers (e.g. Zhang & Tao, 1986). The main economic minerals include magnetite, hematite, bastnäsite-(Ce), monazite-(Ce), and pyrochlore.

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Corresponding author: H. SHIMAZAKI, Department of Geology and Paleontology, National Museum of Nature and Science, Hyakunincho 3-23-1, Shinjuku, Tokyo 169-0073, Japan. Email: caw40120@pop21.odn.ne.jp

1.2. Scandium in the deposit

Besides the elements presently exploited, such as Nb, rare earth elements (REE), and Fe, scandium and thorium have been considered as possible by-products from this deposit (Wang, 2004; Che *et al.*, 2006). Scandium is the lightest REE, and has a high price. It has recently attracted the interest of those engaged in the mineral industry (e.g. Ishihara, 2006). The crustal abundance of scandium is 22 ppm (Rudnick & Fountain, 1995). According to Wang (2004), various types of ore in the Bayan Obo deposit have Sc_2O_3 contents between 40 and 169 ppm. In the REE ore tailing, the Sc_2O_3 content reaches 250 ppm. The main minerals occurring in the deposit, including magnetite, hematite, bastnäsite-(Ce), parisite-(Ce), monazite-(Ce), riebeckite, aegirine, phlogopite, biotite, and apatite, contain Sc_2O_3 contents between 100 and 500 ppm, and two minerals, magbasite and ilmenorutile, are known to have an Sc_2O_3 content of 21,000 and 1540 ppm, respectively. Magbasite is an Sc-bearing mineral that was first reported from the Bayan Obo deposit (Semenov *et al.*, 1965; cited in Fleischer, 1966).

From investigations into 29 rock and ore samples collected by one of the authors (RM) in 2004, electron microprobe analysis of aegirine, Ce-member of chevkinite-perrierite group, and ferrocolumbite, has newly found appreciable amounts of Sc_2O_3 within these three minerals. Sc-bearing aegirine was found in sample TS-15, Sc-bearing Ce-member of chevkinite-perrierite group in sample TS-20, and Sc-bearing ferrocolumbite in sample TS-16 and TS-23. All four samples were collected in the East orebody.

This paper presents a brief description of the occurrence and chemical composition of these Sc-bearing minerals. It is of significance for further studies into the distribution and recovery of scandium from various ores and tailings in the Bayan Obo deposit.

2. Analytical methods

A preliminary study of thin sections of collected samples was carried out for qualitative and semi-quantitative analysis of the constituent minerals using an electron microscope equipped with an energy dispersive spectrometer (JEOL 5400 with fully quantitative Link Systems model QX2000) with an operating voltage of 15 kV and Faraday cup current of 1 nA at National Museum of Nature and Science, Tokyo, Japan. Consequent quantitative analysis was performed using an electron-probe microanalyzer equipped with a wavelength spectrometer (JXA 8800

of JEOL) with an operating voltage of 15 kV and a current of 20 nA, with a beam diameter of approximately 2 μm , at National Museum of Nature and Science, Tokyo, Japan. The following synthetic materials were used as standards: CaSiO_3 for Si and Ca; TiO_2 for Ti; Al_2SiO_5 for Al; Mg_2SiO_4 for Mg; Fe_2SiO_4 for Fe; (Ca, Mn) $\text{Mn}_4\text{Si}_5\text{O}_{15}$ for Mn; $\text{NaAlSi}_3\text{O}_8$ for Na; CaF_2 for F; $\text{ScP}_5\text{O}_{14}$ for Sc; YP_5O_{14} for Y; SnSe for Sn; ThO_2 for Th; FeNb_2O_6 for Nb; MnTa_2O_6 for Ta; $\text{LaP}_5\text{O}_{14}$ for La; $\text{CeP}_5\text{O}_{14}$ for Ce; $\text{PrP}_5\text{O}_{14}$ for Pr; $\text{NdP}_5\text{O}_{14}$ for Nd; $\text{SmP}_5\text{O}_{14}$ for Sm; $\text{GdP}_5\text{O}_{14}$ for Gd; and $\text{DyP}_5\text{O}_{14}$ for Dy.

3. Aegirine

3.1. Sample description

Aegirine is a common silicate mineral in the Bayan Obo deposit. It is frequently associated with fluorite, magnetite, barite, apatite, pyrochlore, and monazite-(Ce), and is the main constituent of aegirine-type Nb, REE, and Fe ores in some parts of the deposit. But in the present study no appreciable amount of scandium was detected in the aegirine of this type of occurrence. An exception is the aegirine associated with phlogopite and bastnäsite-(Ce), occurring in a banded fluorite-bastnäsite-(Ce) rock (sample TS-15). The aegirine grains exhibit a short prismatic shape of approximately $50 \times 20 \mu\text{m}$ (Fig. 1a, b), and are rare in the thin section studied. Electron microprobe analysis indicated that scandium presents in the grains. Besides the minerals mentioned here, the sample contained monazite-(Ce), apatite, magnetite, sphalerite, pyrite, and pyrochlore.

3.2. Analytical results

The analysis of Sc-bearing aegirine is shown in Table 1. The Sc_2O_3 content ranged from 0.34 to 1.81 wt% with one exceptionally high value of 3.45 wt%. For comparison, the analytical result of Sc-free aegirine from an aegirine rock (sample TS-5) is also shown in Table 2. As shown in Table 1, in the Sc-bearing aegirine a slight excess in the occupancy of the tetrahedral site is present, whereas a slight deficiency in the octahedral site occurs. Aegirines from typical aegirine rocks (sample no. TS-5 and TS-6) also have a similar tendency, as demonstrated in Table 2.

3.3. Discussion

According to Wang (2004), aegirine-type Nb, REE, and Fe ores have the highest Sc_2O_3 content of 169 ppm among the various types of ores in the Bayan Obo

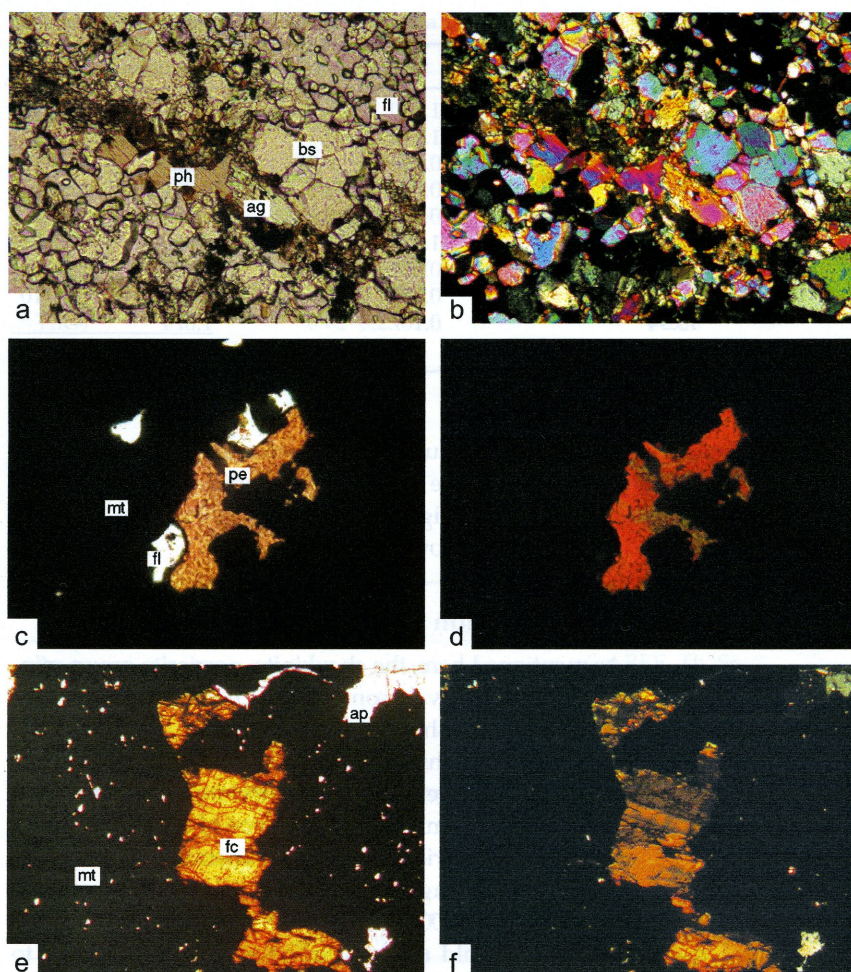


Fig. 1 Photomicrographs of Sc-bearing minerals. (a, b) Aegirine (ag) with bastnaesite-(Ce) (bs), phlogopite (ph), and fluorite (fl) (sample TS-15; open and crossed polars; width of photomicrograph, approx. 250 μm); (c, d) "perrierite-(Ce)" (pe) with magnetite (mt) and fluorite (fl) (sample TS-20; open and crossed polars; width of photomicrograph, approx. 250 μm); (e, f) ferrocolumbite (fc) with magnetite (mt) and apatite (ap) (sample TS-16; open and crossed polars; width of photomicrograph, approx. 2 mm).

deposit. Although, as stated here, the aegirine in this type of occurrence does not show any appreciable amount of scandium in the present study (Table 2), trace amounts of scandium contained in the aegirine is thought to contribute to the high Sc_2O_3 content of aegirine-type ores, because aegirine, a species in parti-

cular called acmite, is well known to concentrate Ce and other REE in their crystal structure (Deer *et al.*, 1963). As demonstrated by the Sc-bearing aegirine in sample TS-15, it is reasonable to consider that aegirine played an important role as an absorber of scandium during the formation of the Bayan Obo deposit.

Table 1 Sc-bearing aegirine (TS-15; 21 analyses)

	Range (wt%)	Average	SD	No. of atoms (O=6)	
SiO_2	50.49–55.16	53.69	1.052	2.146	2.15
TiO_2	0.00–0.24	0.05	0.061	0.001	
Al_2O_3	0.38–4.45	1.48	0.950	0.070	
Sc_2O_3	0.34–3.45	1.19	0.947	0.041	0.77
MgO	0.01–2.94	0.49	0.873	0.029	
$\Sigma\text{Fe}_2\text{O}_3$	25.81–31.70	29.69	1.850	0.631	
MnO	0.00–0.05	0.02	0.018	0.001	
CaO	0.04–5.48	1.01	1.639	0.043	1.08
Na_2O	10.94–14.15	13.42	0.947	1.038	
Total		101.04		4.000	

Table 2 Sc-free aegirine (TS-5; six analyses)

	Range (wt%)	Average	SD	No. of atoms (O=6)	
SiO ₂	51.47–55.02	53.51	1.300	2.131	2.13
TiO ₂	0.16–3.50	1.84	1.210	0.055	
Al ₂ O ₃	0.26–0.74	0.5	0.190	0.023	
Sc ₂ O ₃	0.00–0.04	0.02	0.016	0.001	0.79
MgO	0.30–1.58	0.91	0.488	0.054	
ΣFe ₂ O ₃	27.68–32.95	30.68	1.871	0.650	
MnO	0.02–0.15	0.07	0.051	0.002	
CaO	0.34–0.86	0.55	0.184	0.023	1.10
Na ₂ O	13.77–14.12	13.94	0.107	1.074	
Total		102.02		4.013	

Some phlogopites from the Bayan Obo deposit have an excess of silica and a deficiency of alumina (H. Shimazaki, unpubl. data, 2007). But the phlogopite associated with Sc-bearing aegirine in sample TS-15 had a normal composition very close to $K(\text{Mg,Fe})_3\text{AlSi}_3\text{O}_{10}(\text{F,OH})_2$, and neither an excess of silica nor a deficiency in alumina were observed.

4. Ce-member of chevkinite-perrierite group

4.1. Sample description

Chevkinite-perrierite group minerals are relatively rare in the Bayan Obo deposit. Sc-bearing Ce-member of this group is rarely found in a weakly banded apatite-magnetite-fluorite rock (sample TS-20). Under the microscope the grains have an elongated shape with dimensions of $60 \times 20 \mu\text{m}$, are brown in color, and are surrounded by magnetite (Fig. 1c, d). Besides apatite, magnetite, fluorite, and “perrierite-(Ce)”, the sample also contained calcite, hematite, monazite-(Ce), barite, bastnäsite-(Ce), aeschynite-(Ce), and parisite-(Ce).

4.2. Analytical results

The analytical results are given in Table 3. The Sc_2O_3 content ranged from 2.82 to 3.64 wt% with an average of 3.26%. The total of average weight percent of the components reaches only approximately 97.5 wt%, and some heavy elements are possibly overlooked. Some iron is possibly in the ferric form, but all the iron is calculated as being ferrous in Table 3 due to the difficulty of exact assignment.

The chevkinite-perrierite group minerals have a relatively complicated chemical compositions, with a general formula of $\text{A}_4\text{BC}_4(\text{Si}_2\text{O}_7)_2\text{O}_8$. Scandium is an REE. However, partly because the A site for the REE

has an excess number of atoms, and partly because scandium has the smallest ionic radius among the REE, scandium is assigned to the C site in Table 3, along with Al, Ti, and other elements.

4.3. Discussion

As mentioned here, the chevkinite-perrierite group minerals have a relatively complicated chemical composition, and the relationship between chevkinite and perrierite, whether dimorphs or not, has been controversial for a long time. A single crystal diffraction study represents the conclusive determination of the type of crystal structure, chevkinite or perrierite, for these minerals (e.g. the crystal structure of rengerite with the perrierite structure; Miyawaki *et al.*, 2002). In the present study, although X-ray diffraction could not be applied to the material due to its scarcity and fine grain size, the discrimination diagram proposed by Macdonald and Belkin (2002) suggested the present Sc-bearing Ce-member to be perrierite-(Ce). According to this diagram the relative abundance of CaO and FeO^* is a good criterion for distinguishing between the two minerals; that is, as shown in Table 3, the relatively high CaO content and low FeO^* content is a consequence of the nature of perrierite. In contrast, in the present study another Ce-member with relatively low CaO and high FeO^* was recognized in a massive calcite-phlogopite rock (sample TS-12). The analytical results (Table 4) indicate this mineral to be chevkinite according to the discrimination diagram of Macdonald and Belkin (2002). Only a small amount of CaO was present in this mineral, and no scandium was detected.

These two minerals from the Bayan Obo deposit were also identified in previous studies. Zhang and Tao (1986) identified an example of chevkinite-(Ce) and reported chemical composition and X-ray diffraction data. The relative abundance of ferrous and ferric iron in the mineral relative to CaO clearly demonstrated

Table 3 "Perrierite-(Ce)" (TS-20; 10 analyses)

	Range (wt%)	Average	SD	No. of atoms (O=22)	
SiO ₂	20.50–21.75	21.14	0.453	4.215	4.22
La ₂ O ₃	7.19–9.11	8.31	0.696	0.610	
Ce ₂ O ₃	18.89–20.61	19.81	0.483	1.445	
Pr ₂ O ₃	1.97–2.51	2.27	0.166	0.165	
Nd ₂ O ₃	6.83–7.79	7.20	0.289	0.513	
Sm ₂ O ₃	0.22–0.64	0.40	0.116	0.028	4.07
Gd ₂ O ₃	0.00–0.45	0.15	0.135	0.010	
Dy ₂ O ₃	0.00–0.17	0.05	0.061	0.003	
ThO ₂	0.01–0.25	0.08	0.079	0.004	
CaO	3.95–5.19	4.73	0.407	1.010	
SrO	1.87–2.68	2.41	0.245	0.277	
ΣFeO	5.23–8.61	6.68	0.925	1.000	1.00
				0.110	
TiO ₂	17.01–18.34	17.70	0.061	2.647	
Nb ₂ O ₅	0.16–0.92	0.49	0.220	0.044	3.84
Sc ₂ O ₃	2.82–3.64	3.26	0.255	0.565	
Al ₂ O ₃	1.30–2.59	2.03	0.356	0.476	
Total		96.71		13.122	
A ₄ BC ₄ (Si ₂ O ₇) ₂ O ₈				No. of atoms	
A		Ca, REE, Th, Sr		4.07	
B		Fe		1.00	
C		Al, Ti, Fe, Sc, Nb		3.84	
Si				4.22	
		Total		13.13	

Table 4 "Chevkinite-(Ce)" (TS-12; four analyses)

	Range (wt%)	Average	SD	No. of atoms (O=22)	
SiO ₂	19.57–20.98	20.38	0.512	4.285	4.29
Y ₂ O ₃	0.00–0.12	0.05	0.052	0.006	
La ₂ O ₃	13.74–18.02	15.90	1.881	1.231	
Ce ₂ O ₃	23.47–25.97	24.64	0.885	1.895	
Pr ₂ O ₃	1.81–2.45	2.18	0.238	0.167	
Nd ₂ O ₃	6.07–7.53	7.05	0.969	0.529	3.99
Sm ₂ O ₃	0.05–0.51	0.31	0.168	0.022	
Gd ₂ O ₃	0.00–0.21	0.07	0.086	0.005	
Dy ₂ O ₃	0.00–0.20	0.07	0.081	0.005	
ThO ₂	0.00–0.20	0.07	0.082	0.003	
CaO	0.39–0.91	0.57	0.208	0.128	
ΣFeO	8.98–9.78	9.48	0.310	1.000	1.00
				0.661	
TiO ₂	14.56–15.73	15.00	0.439	2.365	4.17
Al ₂ O ₃	0.38–2.29	1.70	0.771	0.421	
MgO	1.45–1.61	1.53	0.057	0.722	
Total		99.00		13.445	
A ₄ BC ₄ (Si ₂ O ₇) ₂ O ₈				No. of atoms	
A		REE, Ca, Y, Th		3.99	
B		Fe		1.00	
C		Al, Ti, Fe, Mg		4.17	
Si				4.29	
		Total		13.45	

Table 5 Sc-bearing ferrocolumbites (TS-16, three analyses; TS-23, 15 analyses)

Sample	TS-16					TS-23				
	Range (wt%)	Average	SD	No. of atoms (O=6)		Range (wt%)	Average	SD	No. of atoms (O=6)	
Nb ₂ O ₅	68.99–72.88	70.56	1.647	1.749	2.04	68.89–78.19	71.73	2.221	1.795	2.05
TiO ₂	5.04–8.51	7.08	1.481	0.292		2.96–7.91	6.08	1.426	0.253	
Ta ₂ O ₅	0.00–0.02	0.01	0.010	0.000		0.00–0.30	0.12	0.093	0.002	
ΣFeO	16.52–17.00	16.69	0.220	0.764	1.03	16.07–18.22	16.76	0.603	0.775	0.98
MnO	4.61–5.09	4.92	0.220	0.229		2.77–3.32	3.03	0.148	0.142	
MgO	0.12–0.13	0.12	0.005	0.010		0.08–0.17	0.13	0.023	0.011	
Sc ₂ O ₃	0.20–0.25	0.22	0.021	0.011		0.56–1.04	0.67	0.129	0.032	
Y ₂ O ₃	0.25–0.69	0.43	0.188	0.013		0.14–0.36	0.22	0.058	0.007	
SnO ₂	0.10–0.15	0.12	0.021	0.003		0.14–0.66	0.38	0.127	0.008	
Total		100.15		3.071			99.12		3.025	

that the mineral fell in the chevkinite region in the discrimination diagram of Macdonald and Belkin (2002). The occurrence of perrierite-(Ce) in the Bayan Obo deposit was described by Zhang *et al.* (1995), and confirmed using X-ray diffraction data. It is known that the mineral perrierite-(Ce) can contain appreciable amounts of Sc₂O₃, up to 4.13 wt%, as cited in the textbook on mineralogy by Gaines *et al.* (1997), and thus it is reasonable to assign the Sc-bearing chevkinite-perrierite group mineral in the present study to perrierite-(Ce).

5. Ferrocolumbite

5.1. Sample description

Ferrocolumbite, FeNb₂O₆, is another relatively uncommon accessory mineral in Bayan Obo ores. Sc-bearing ferrocolumbite was found in two samples (sample TS-16 and TS-23) in the present study. Sample TS-16 was a banded fluorite-bastnäsitate-(Ce)-magnetite rock. Under the microscope ferrocolumbite was observed as brown-colored grains, 0.5 mm in size, surrounded by magnetite (Fig. 1e, f). Other minerals in the sample included apatite, barite, monazite-(Ce), parisite-(Ce), pyrochlore, aeschynite-(Ce), calcite, dolomite, ilmenorutile, and pyrite.

Sample TS-23 is a massive magnetite rock with fluorite, monazite-(Ce), and apatite. Under the microscope ferrocolumbite occurs as small, reddish brown grains with a size of less than several tens of microns, and is associated with magnetite and fluorite. Small amounts of barite, bastnäsitate-(Ce), parisite-(Ce), calcite, dolomite-ankerite, quartz, ilmenorutile, and ilmenite are present in the sample.

5.2. Analytical results

The analytical results of Sc-bearing ferrocolumbites are shown in Table 5. The Sc₂O₃ content ranged from 0.20 to 0.25 wt% with an average of 0.22% for sample TS-16, and 0.56 to 1.04% with an average of 0.67% for sample TS-23. Very small amounts of tantalum, yttrium, and tin are identified. A marked variation in TiO₂ content is also identified.

5.3. Discussion

As mentioned here, Wang (2004) reported an Sc₂O₃ content in ilmenorutile from the Bayan Obo deposit of 1540 ppm. In the present study niobian rutile to ilmenorutile is recognized in samples TS-5, TS-16, and TS-23. These samples also include some ferrocolumbite and, as discussed here, the mineral in sample TS-16 and TS-23 contains some scandium. But scandium is not detected in coexisting niobian rutile to ilmenorutile in those samples in the present study. The distribution of scandium is sporadic throughout the deposit.

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