Cassiterite and Sn mineralization in the giant Bayan Obo Fe-Nb-REE deposit, North China

Ya-Ting Xu¹, Ru-Cheng Wang¹,*, Mei-Fu Zhou², Fu-Yuan Wu³

¹ State Key Laboratory for Mineral Deposits Research, FSC for Critical Earth Material Cycling, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China

² State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

³ State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

* Corresponding author: E-mail, rcwang@nju.edu.cn
Critical rare metal deposits are strategic resources as these metals are significant for high-tech industries. Among the critical rare metals, stannum (Sn) in nature is mostly found in Sn-oxide mineral, cassiterite (SnO$_2$), and closely associated with granite or pegmatite. Carbonatite and alkaline rocks are more likely to contain huge amounts of critical rare metals, especially REEs and niobium (Nb). We reported abundant cassiterite (SnO$_2$) and evaluated potential Sn mineralization in the Bayan Obo Fe-Nb-REE deposit in northern China, the largest REE deposit worldwide. In this paper, evidence for the Sn enrichment in a carbonatite-hosted REE deposit is given for the first time.

REE-Fe ores are dominantly mined in the Bayan Obo deposit. Disseminated, banded and massive ores contain tens to hundreds ppm Sn and vein-type ores are notably rich in Sn (up to 1500 ppm). Through in situ micro-zonation mineralogical analyses, two occurrences of cassiterite and several Sn-rich minerals are identified in these REE-Fe ores. Abundant early-stage nanoscale cassiterite inclusions are present within magnetite grains in banded and massive REE-Fe ores, and ubiquitous late-stage granular cassiterite, Sn-rich rutile, titanite, and bafertisite are present in vein-type REE-Fe ores. Multiple U-Th-Pb dating of monazite and columbite-Mn in association with cassiterite yields peak ages of 425 Ma and 419±18 Ma, respectively, revealing coeval Sn and Nb mineralization. We concluded that Sn was derived from carbonatitic magmas, and the dense distribution of cassiterite inclusions in magnetite
marked the pre-enrichment of Sn in the Bayan Obo deposit. Subsequent Early Paleozoic hydrothermal events led to the reactivation and further Sn mineralization. Similar to Nb, Sn was mineralized in the Bayan Obo deposit probably to form economically important resources. Our study highlights the potential of Sn mineralization associated with carbonatite-hosted REE deposits.

**Keywords:** critical rare metals; cassiterite; Sn mineralization; Bayan Obo deposit; TEM; geochemical characteristics; U-Th-Pb Dating; SIMS

**INTRODUCTION**

Stannum (Sn), a versatile and economically significant metal, is vital in modern times. Its applications include traditional uses in soldering and plating and high-tech industries such as electronics and renewable energy. Cassiterite (SnO₂) is the most common Sn oxide mineral and the primary ore mineral for Sn extraction. In nature, Sn mineralization is associated mainly with granites, pegmatites, and related metasomatic and hydrothermal systems (e.g., greisens and quartz veins) (Lehmann, 2021) but rare in other rocks.

The mantle-derived carbonatites and carbonatite-related deposits are well known to be the primary sources of the world’s rare earth elements (REEs), and alkaline-carbonatite complex-related deposits are rich in niobium (Nb), as well as phosphate (P), iron (Fe), and fluorine (F) (Smith et al. 2015; Simandl and Paradis 2018; Beland and Williams-Jones 2021; Verplanck et al. 2022). However, other critical metals in
carbonatites or in carbonatite-hosted deposits are still poorly understood. Whereas REEs and Nb are well studied as enriched in specific carbonatite-hosted deposits, adequate data on the occurrences and mineralization potentials of other critical metals in such deposits are lacking.

The Bayan Obo REE-Fe deposit in Inner Mongolia, China, is hosted in carbonatites, where intense magmatic differentiation of carbonatite is deemed to facilitate the great REE accumulation (Yang et al. 2019). Multi-stage superposition of magmatism, hydrothermal alteration, and metamorphism has influenced the distribution and characteristics of minerals within the deposit (Song et al. 2018; Yang et al. 2019; Liu et al. 2020; She et al. 2021). Major mineralization events in the deposit, i.e., Nb mineralization, proceed from magmatic to hydrothermal crystallization (Campbell et al. 2014; Smith et al. 2015; Fan et al. 2016; Liu et al. 2020). The immense REE mineralization initially took place at around 1.3 Ga in association with carbonatite magmatism (Yang et al. 2011a; Fan et al. 2014; Yang et al. 2017; Li et al. 2021). In addition, at least two younger magmatic-hydrothermal events at around 430 Ma and 270 Ma subsequently contributed to the mineralization through leaching and reactivation of primary minerals (Yang et al. 2011a, 2017; Campbell et al. 2014; Fan et al. 2014; Ling et al. 2014; Li et al. 2021). Although REEs, especially light rare earth elements (LREEs), niobium, and iron have long been recognized as the prime mining resources in the Bayan Obo deposit, we find another valuable hidden resource within this world-class deposit, Sn mineralization, mainly in
the form of cassiterite.

This study describes the distribution of cassiterite and other Sn-rich minerals among REE-Fe ores, and reveal the genesis of Sn mineralization in the Bayan Obo deposit. We also report precise ages of monazite and parisite associated with cassiterite. Combining all the dating results, we confirm a link between Sn mineralization and other major mineralization events in the Bayan Obo deposit, indicating a potential for Sn resources. By elucidating the nature of Sn mineralization within the Bayan Obo deposit, this study could enhance the understanding of processes that govern Sn enrichment in similar geological settings, and has practical implications for resource assessment, mining strategies, and the sustainable exploitation of Sn resources in carbonatite-hosted REE deposits.

MATERIALS AND ANALYTICAL METHODS

Sample collection

Several typical REE-Fe ores from the Bayan Obo deposit have been investigated in detail in this work. All the samples were collected from the Main, East, and West Open Pits (see below). Samples DK19-, DK20-, XK19-, XK20-, 17BY-, ZK1917, ZK1918 and ZK1919 were collected at the bottom of the open pits, and ZK1932 from a drill hole in the Main Open Pit. The hand specimens are representative ore blocks, comprising the disseminated ores, the banded ores, the massive ores and the vein-type ores. Detailed features of hand specimens are shown in Figure 2.
Whole rock trace element analysis

Whole-rock trace element compositions of different types of ore from the Bayan Obo deposit were determined using inductively coupled plasma mass spectrometry (ICPMS) at FocuMS Technology, Nanjing, China and the ALS Laboratory Group, Guangzhou, China. About 40 mg powder was mixed with 0.5 ml 60 wt.% HNO₃ and 1.0 ml 40% HF in high-pressure PTFE bombs. These bombs were steel-jacketed and placed in the oven at 195°C for 3 days to ensure complete digestion. After cooling, the bombs were opened, dried down on a hotplate, re-dissolved with 5 ml 15 wt.% HNO₃ and 1ml Rh internal standard, then sealed and placed in the oven at 150°C overnight. Aliquot of the digestions (dilution factor 2000) were nebulized into Agilent Technologies 7700x quadrupole ICP-MS (Tokyo, Japan) to determine trace elements.

Geochemical reference materials of USGS: basalt (BCR-2, BHVO-2), andesite (AVG-2), rhyolite (RGM-2), granodiorite (GSP-2) were treated as quality control. Measured values of these reference materials were compared with preferred values in GeoReM database (Jochum and Nohl, 2008). Deviation were better than 20% for trace elements between 0.5 ~ 5 ppm, better than 10% for these between 5 ~ 50 ppm, and better than 5% for these exceeded 50 ppm.

EDS-equipped scanning electron microscope investigation of minerals

Textural and petrographic features of samples were investigated by scanning electron microscope (SEM), using the Zeiss Supra55 field emission scanning electron
microscope (SEM) equipped with an Oxford energy dispersive spectrometer (EDS) and a Gatan Mono CL$^{3+}$ detector. The mineralogical mapping was acquired using Advanced Mineral Identification and Characterization System (AMICS), using the Zeiss Sigma 300 field emission scanning electron microscope (SEM) with a Bruker XFlash detector at Nanjing University, China. Backscattered electron (BSE) and energy dispersive (EDS) data are collected on an irregular grid below 5 μm point spacing in the vacuum mode. Acceleration voltage of 20 kV and a beam current of 10 nA were used during the data acquisition. The individual spectra from points were grouped based on a similarity search algorithm, and areas of coherent BSE and EDS data were merged to produce segments (i.e., mineral grains). Data from each segment were then compared against a classification scheme to identify the mineral and assign its density. The results were plotted as a map showing the distribution of minerals within the sample.

Electron microprobe analyses of minerals

Chemical compositions of minerals were analyzed using the JEOL 8530 field-emission electron microprobe in Nanjing University. Optimized operation conditions were applied: accelerating voltage of 15 kV, beam current of 20 nA, and beam diameter of 2 μm, counting times of 20 seconds on each peak and half time for backgrounds. All data were updated using standard ZAF correction procedures. The ZAF correction compares the sample-to-sample differences in atomic number effects (Z) on incident electrons (including backscattering and blocking principal) as well as
absorption (A) and fluorescence (F) effects on X-rays to find the corresponding correction factor, and then converts the X-ray intensity ratio to elemental content.

**Transition electron microscope identification of minerals**

Magnetite microstructure investigation was carried out with transition electron microscope (TEM), using a FEI Tecnai G2 F30 instrument equipped with a Lorentz lens, a Bruker XFlash detector and a Fischione high-angle annular dark-field (HAADF) detector at Electron Microscopy Center of Lanzhou University (LZU) of China.

**Laser Ablation – Inductively Coupled Plasma – Mass Spectrometer (LA-ICP-MS) analyses**

Trace element composition of magnetite, U-Th-Pb ages of monazite and columbite-Mn were determined *in situ* by laser ablation inductively coupled plasma–mass spectrometry (LA-ICP-MS), using a system consisting of ASI RESOlution S-193 nm ArF Excimer laser coupled to Thermo Scientific iCAP Qc quadrupole ICP-MS at the State Key Laboratory for Mineral Deposits Research at Nanjing University of China. The trace element analyses were obtained using a laser beam diameter of 43 μm, maximum energy density of 100 mJ and ablation rate of 4 Hz. The dating analyses were obtained from polished sections using a laser beam diameter of 19 μm, maximum energy density of 75 mJ and ablation rate of 3 Hz.

**Secondary ion mass spectrometry (SIMS) analyses of U-Th-Pb dating**
In situ monazite and parisite U-Th-Pb dating was conducted by secondary ion mass spectrometry (SIMS), using a Cameca IMS-1280 instrument at Nanjing University, China. The sample mounts were coated with about 30 nm of high-purity gold to reach < 20 Ω resistance. Positive secondary ions were extracted with a 10 kV potential. Sample charging effects were minimized by optimizing the energy offset to maximum transmission in a 60 eV energy window at the start of each analysis, using the Th\(^{+}\) and Y\(_2\)O\(^{++}\) as reference peaks for monazite and parisite, respectively. The size of the ellipsoid analyzed spot was 15 μm × 10 μm. The monazite U-Th-Pb analyses calibrated against RW-1 standard (\(^{207}\)Pb/\(^{235}\)U age = 904.15 ± 0.26 Ma [2σ], Th = 11.8 ± 1.0 wt.% [2σ], and Th/U = 42.5 ± 3.0 [2σ]). Monazite MAD and M6 were employed as secondary standards. Parisite grains were mounted together with standard Nist-610 and K-9 for accuracy monitoring. A repeatability of 1.5% (1σ RSD) was derived from the measurement of standards. Detailed analytical procedures are the same as those described in (Li et al. 2013) and (Li et al. 2020).

DEPOSIT GEOLOGY

The Bayan Obo REE-Nb-Fe deposit is located at the northern margin of the North China Craton, south of the Central Asian Orogenic Belt (Yang et al. 2011b), about 150 km north of Baotou City in northern China. The deposit is hosted by rocks of Paleo- to Mesoproterozoic Bayan Obo Group, which is unconformably underlain by a basement complex of the North China Craton (Zhu et al. 2015; Fan et al. 2016a).
Proterozoic carbonatite dikes, Permian gabbroic, and granitic plutons are widespread (LeBas et al. 1992; Yang et al. 2011a, 2011b; Ling et al. 2014; Zhang et al. 2017). The H8 dolomite unit confined to the south of the Kuangou anticline hosts the majority of orebodies. A narrow ore belt, with an area of ~ 48 km$^2$, lies in the east–west direction (about 18 km long and 2 ~ 3 km wide). Several REE-Fe orebodies varying in size have been recognized throughout this area, among which are the three largest orebodies, i.e., the Main, East and West Orebodies, being located in the central part of the ore-bearing belt (Fig. 1). Iron ores are the primary commodities from orebodies, followed by REE-Fe ores, REE ores and dolomites.

**RESULTS**

**REE-Fe ore types and mineral assemblages**

The giant Bayan Obo deposit was formed through multi-stage mineralization. Consequently, REE-Fe ores have complex textures and mineral assemblages (Table 1). REE-Fe ores can be classified into four main types, namely disseminated, banded, massive, and vein-type ores (Fig. 2). Generally, disseminated ores formed slightly earlier than other types. The disseminated ores occur in the orebodies diffusely, and are mainly composed of dolomite, with minor presences of evenly distributed magnetite, fluorite, bastnaesite and monazite (Fig. 2a, e). Banded ores are composed of alternating bands of deep purple fluorite, magnetite, greenish aegirine, and yellow bastnaesite (Fig. 2b). These bands are thin and narrow in hand specimens, usually less
than one centimeter in width (Fig. 2b, f). Massive ores are dominantly composed of magnetite, minor fluorite and aegirine, and a few variably distributed REE minerals (Fig. 2c, g). The vein-type ores are usually formed later than other types, sometimes penetrate or crosscut other types of ores, and are more complex in mineral assemblages of fluorite, calcite, apatite, aegirine and so on (Fig. 2d, h).

**Sn concentrations of REE-Fe ores**

Whole-rock chemical analyses of REE-Fe ore samples from the Bayan Obo deposit were carried out by ICP-MS, and the full dataset is available in the Appendix. Table A1. Sn contents of the ores are positively correlated with the Nb contents (Fig. 3a), but are not strongly correlated with REE contents, such as La (Fig. 3c). Stannum is particularly enriched in late-formed vein-type ores (Fig. 3b, d). Disseminated ores contain the lowest Sn (9 ~ 27 ppm, average of 15 ppm), and banded ores have overall higher Sn contents ranging from 13 to 151 ppm, with an average of 62 ppm. Sn contents in massive ores are variable from 17 to 200 ppm, with an average of 62 ppm. One massive ore (ZK1918) composed of magnetite, aegirine, fluorite and calcite has 200.21 ppm Sn. Notably, the aegirine veins contain over 200 ppm Sn and those with numerous bafertisite grains (DK2003) contain the highest Sn up to 1515 ppm among all the analyzed samples in this study (Table 1).

**Mineralogy**

*Magnetite associated with cassiterite*
Magnetite is the main ore mineral in REE-Fe ores, particularly in massive ores. Although cassiterite is rarely reported in carbonatites in literature, magnetite with the appearance of nano to micron-sized cassiterite inclusions is commonly observed in the Bayan Obo REE-Fe ores (Fig. 4a), which is an exotic feature that is worth further studying. Through high-resolution backscattered electronic observation, we recognized some porous domains of magnetite grains in massive ores. Moreover, cassiterite grains included in these porous domains tends to be more than 10 µm in size, distinctly larger than that occurring in relatively intact domains of the same magnetite grains (Fig. 6c). This feature suggests that these magnetite grains underwent hydrothermal alteration and the hydrothermal activities promoted Sn enrichment. As a different occurrence, magnetite may also be observed as small discrete euhedral crystals with well-developed {111} faces in association with clustered cassiterite (Fig. 4c) in vein-type ores of late stage.

EPMA results indicate slight variations in chemical compositions between granular magnetite aggregates (massive magnetite) and discrete magnetite grains (Fig. 5). LA ICP-MS analyses show that massive magnetite grains with no mineral inclusions have Sn contents of only tens ppm (below 30 ppm), confirming the Sn depletion in this type of magnetite (Table A2). Small discrete magnetite grains exhibit slightly higher Sn (0.07 ~ 0.23 wt.%), Ti (0.40 ~ 1.29 wt.%), and Ca (0.24 ~ 1.37 wt.%) and lower Mn than the dominant massive magnetite grains (0.06 ~ 0.16 wt.% Mn) (Table A3). Changes in trace element contents of the two magnetites also reflect
further Sn enrichment in the later mineralization process.

Cassiterite

Cassiterite (SnO$_2$) is the most common and economically important Sn-bearing ore mineral in nature. In this study, cassiterite, usually in two forms, is widely present in massive and vein-type REE-Fe ores from the Bayan Obo deposit. One is micron-sized cassiterite inclusions dispersed within magnetite grains, and the other is tens of micron-sized clusters associated with hydrothermal minerals veins consisting of fluorite, apatite, calcite, or aegirine (Fig. 6).

Across all REE-Fe ore types, cassiterite inclusions in magnetite are anhedral and less than one micrometer; they occur sporadically in some magnetite grains from disseminated ores but are abundant within magnetite grains from massive and banded ores (Fig. 6a-c). Nb-bearing ilmenite or Sn-bearing rutile are also occasionally identified near cassiterite inclusions (Fig. 4a). At least 75 micro-grains of cassiterite (smaller than 1µm) without clear orientation are counted in a small area of about 0.05 mm$^2$ within the massive magnetite from the sample ZK1918 (Fig. 6b). Further TEM study was conducted on ion milling system-assisted foils of magnetite with cassiterite inclusions and, from the perspective of crystal structure, confirmed the existence of tiny cassiterite. HRTEM imaging identified local crystal orientations notably with $d$-spacings of 2.654 Å (101), 2.366 Å (200), 1.672 Å (220) and 2.308 Å (111) for cassiterite, and $d$-spacing of 2.709 Å (104) for ilmenite, respectively (Fig. 4b). In addition, the fast Fourier transform (FFT) image indicated the crystalline cassiterite.
Lattice fringe images in the contact area of cassiterite and magnetite show a gradual transition, indicating simultaneous formation rather than later mechanical mixing (Fig. 4d). Dense cassiterite inclusions formed at the same time as massive magnetite mark the pre-enrichment stage of Sn mineralization.

Granular cassiterite in banded, massive, and vein-type ores typically occurs as clusters from tens to hundreds of microns in size (Fig. 6a, d, e). These clustered cassiterite grains are closely associated with aegirine, amphibole, fluorite, or calcite, and together form veinlets with variable mineral assemblages that crosscut the magnetite grains. In this case, the individual cassiterite grains are subhedral, tens of microns in size, and closely coexisting with other REE-Nb minerals (commonly bastnaesite, monazite, columbite, and pyrochlore). Clustered cassiterite grains may also densely accumulate in association with Fe-Ti oxides (ilmenite and rutile) (Fig. 7a, b). The zoned internal texture of cassiterite grains is revealed by cathodoluminescence (CL) imaging (Fig. 8). As shown in Table 2 (compiled in Table A4), clustered cassiterite grains usually contain trace amounts of Ti, Nb, Fe and Mn. In the Nb + Ta vs Fe + Mn diagram (Fig. 8), all these cassiterite grains are vertically scattered on the left side with higher Fe + Mn than Nb + Ta, plotting within the field of hydrothermal origin. The genesis of clustered cassiterite indicates the promotion of Sn enrichment by hydrothermal activities in the Bayan Obo deposit.

**Sn-rich rutile**

 Nb-rich variety of rutile (TiO$_2$), or sometimes ilmenorutile [(Ti,Nb,Fe)O$_2$], has a
widespread occurrence in REE-Fe ores from the Bayan Obo deposit. In massive ores, rutile may occur as subhedral crystal aggregates of about 100 µm, coexisting with tiny cassiterite grains (Fig. 7a, b). In vein-type ores, several veinlets of rutile, tens of microns wide and several millimeters long, can be observed in penetrating aegirine grains (Fig. 7c). Sn may substitute for Ti, Fe or Nb in the mineral composition.

Chemically, rutile may contain up to 3.36 wt.% SnO₂ (0.30 ~ 3.36 wt.% SnO₂, Table A5-1) and ilmenorutile contains SnO₂ as high as 6.58 wt.% (2.65 ~ 6.58 wt.%, Table A5-2).

**Sn-rich titanite**

Titanite, CaTi(SiO₄)O, usually appears around Sn-bearing ilmenite in vein-type ores and sometimes shows a zoning texture characterized by alternating brighter and darker strings. Single titanites are variable in SnO₂, and the brightness corresponds well with SnO₂ concentrations: the brighter zones have 9.70 ~ 10.69 wt.% SnO₂, much higher than that of the darker area (0.69 ~ 2.93 wt.%) (Fig. 7d, Table A6). The ion radius of Sn²⁺ ion is close to that of Ca²⁺, so substitution of homomorphism is obvious among titanite.

**Sn-rich bafertisite**

Bafertisite, ideally Ba₂Fe²⁺₂Ti₂(Si₂O₇)₂O₆(OH)₂F₂, is an important Sn-rich mineral phase typifying the vein-type ores. It may occur as narrow veinlets only below 300 microns wide but extending to tens of centimeters long (Fig. 7e) and typically coexists with other Ba-bearing minerals such as baryte, baotite, and
cordylite. Bafertisite also appears as fibrous aggregates (Fig. 7f). Sn$^{2+}$ will substitute for divalent iron (Fe$^{2+}$) in the mineral composition. This mineral generally contains moderate Sn exceeding 2 wt.% (2.70 ~ 4.40 wt.% SnO$_2$), and fiber bafertisite is much richer in Sn with up to 16.68 wt.% SnO$_2$ (9.80 ~ 16.68 wt.%), approaching a Sn-analogue of bafertisite (Table A7).

Constraints on the timing of Sn mineralization

Cassiterite grains observed in Bayan Obo are too small to be in situ dated with LA-ICP-MS or SIMS techniques. Instead, their coexisting and cogenetic REE minerals (monazite and parasite) from vein-type ores (Fig 9), and Nb mineral (columbite-Mn) from massive ores were subjected to geochronological work on Sn mineralization in the Bayan Obo deposit (Fig. 10).

Th-Pb ages tested on thirty monazite grains by LA-ICP-MS range from 375 to 663 Ma (Fig. 10a, Table A8). This mineral, co-existing with cassiterite, was also targeted for SIMS dating, yielding an age spectrum of 281 ~ 932 Ma (Fig. 10c, Table A9). Modeled by frequency distribution plot, the monazite ages obtained by the two methods gave the same peak age of 425 Ma (Fig. 10b, d). In situ LA-ICP-MS dating for thirteen large grains of columbite-Mn associated with cassiterite, directly analyzed on thin sections, yielded a similar lower-intercept age of 419 ± 18 Ma (Fig. 10e, Table A10) and a weighted average age of 426 ± 26 Ma (Fig. 10f). Besides, another younger peak age of 275 Ma was also obtained by SIMS dating on fifty parasite grains (Fig. 10g, h, Table A11). The dating results denote the connection between Sn enrichment
and Early Paleozoic hydrothermal activities in the Bayan Obo deposit.

The generation or formation of both the ore-hosting dolomite and local carbonatite dykes shared similar ages ranging from 1.4 to 1.2 Ga, indicating a Mesoproterozoic REE mineralization event related to carbonatite intrusion (Yang et al. 2011a; Fan et al. 2014; Li et al. 2021). The subsequent Paleozoic hydrothermal events had caused two significant geological processes including the subduction at approximate 430 Ma or the granite intrusion at approximate 270 Ma, both of which would lead to the local remobilization (Yang et al. 2011a, 2017; Campbell et al. 2014; Fan et al. 2016; Ling et al. 2014; Liu et al. 2020). Hence, hydrothermal activity leads to the reactivation of Sn and the formation of diverse Sn-rich minerals.

**DISCUSSION**

**Two different generations of cassiterite in the Bayan Obo deposit**

Cassiterite (SnO₂) is an essential ore mineral in Sn deposits but has not been previously noted in Bayan Obo. For the first time, we report abundant cassiterite in this carbonatite-hosted Fe-REE-Nb deposit and demonstrate the presence of Sn mineralization. The occurrence modes of cassiterite argue for two distinctive environments of crystallization.

In the Bayan Obo deposit, micron-sized inclusions of cassiterite are restricted within massive magnetite. These two oxide minerals, cassiterite and magnetite, appear to have different crystallographic affinity (tetragonal versus cubic). However,
their co-existence has been reported in at least two type of Sn deposits, granite-related and skarn-type deposits, where the occurrence of cassiterite in magnetite has been normally interpreted as an exsolution product (Wang et al. 2012, 2013). However, in our present study, TEM microstructural observations provide strong evidence for the simultaneous crystallization of cassiterite inclusions within the host magnetites. Furthermore, magnetite forms under high-$fO_2$ conditions and is a sensible indicator of the oxidized environment as simply known (Slack et al. 2020). On the other hand, experiments demonstrated that dominates Sn in melts relative to Sn$^{2+}$: therefore, the enrichment of Sn as cassiterite from melt also needs higher $fO_2$ (Bhalla et al. 2005; Slack et al. 2020). This coincidence of oxidized conditions in melts may interpret the intergrowth of cassiterite and magnetite in Sn deposits. As discussed above, our observation could prove the co-crystallization of cassiterite with the host magnetite. Columbite, Sn-bearing rutile, and monazite were also trapped in magnetite, which supports a similar formation environment for magnetite and other Nb-Sn-REE minerals. Yang et al. (2019) noted a similar cogenetic assemblage of magnetite with hematite inclusions and suggested that the strong carbonate magmatic differentiation has caused the formation of dolomite, magnetite, and significant REE accumulation in the Bayan Obo deposit. Thus, it is reasonable to infer that mineral inclusions share the same formation genesis with the massive magnetite that micron-, even nano-sized cassiterite primarily crystallized in an early stage of carbonatite-related mineralization.
Clustered grains of cassiterite are typically distributed in the frame of ore-hosting veins. Mostly, they are observed outside of massive magnetite, indicating a later formation than that of disseminated cassiterite inclusions. The Fe-rich features of clustered cassiterite indicate a hydrothermal origin with relatively low forming temperatures between 250 and 500 °C (Tindle and Breaks 1998a). This nature of the hydrothermal environment is also supported by the intergrowth with fluorite, apatite, calcite, bastnaesite, and monazite, which are considered hydrothermal minerals in the Bayan Obo deposit (Liu et al. 2020; She et al. 2021).

Sn mineralization in the Bayan Obo deposit

In the Bayan Obo deposit, Sn enrichment is first marked by abundant cassiterite inclusions in magnetite. Based on the evidence of crystallography and oxygen fugacity, this study could establish a link between the early-stage Sn mineralization and synchronous extensive iron mineralization during carbonatite magma evolution in Bayan Obo. Interestingly, porous domains are common in massive magnetite (Fig. 6c). In such areas, cassiterite grains are clearly larger: this phenomenon may be linked to the hydrothermal attack by fluids on magnetite, a process leading to the dissolution of micron-sized cassiterite inclusions in magnetite and subsequent remobilization of Sn. Successive crystallization of larger cassiterite certainly took place in this process. If extensive fluid-induced fracturing occurs in magnetite during deformation, large cassiterite may crystallize, even accumulate, commonly as clusters, in association with fluorite, calcite, aegirine or hydrothermal amphibole, etc (Fig. 6a, d, e). Other
Sn-bearing minerals such as Sn-rich rutile, titanite or bafertisite, textually of hydrothermal origin, have also supported the activity of Sn in hydrothermal environments. The remobilization of ore-forming elements and the carbonatite-related hydrothermal reaction with the country rocks have been suggested to be the driving forces of REE and Nb hydrothermal mineralization in the Bayan Obo deposit, as evidenced by large amounts of REE fluorocarbonates, monazite, aeschynite, and pyrochlore occurring within complex mineral assemblages with fluorite, aegirine, or amphibole (Liu et al. 2020; She et al. 2023). Thus, a substantial hydrothermal overprinting process of Sn mineralization may be constrained.

The geochronological framework of the Bayan Obo deposit has been established previously. As a whole, three stages can be mostly recognized, corresponding to multiple magmatic and hydrothermal activities during the formation of the Bayan Obo REE-Nb-Fe deposit. The original mineralization began at around 1.3 Ga, and the reworking mineralization took place at 450 ~ 420 Ma as a consequence of the Paleozoic magmatism (Yang et al. 2011a, 2017; Campbell et al. 2014; Fan et al. 2014). Younger granite of about 269 Ma (a narrow time from 263 to 281 Ma) has a similar superimposed reactivation effect on the Bayan Obo district (Ling et al. 2014). Indeed, the stocked Sn in magnetite can be conceived as an original Sn mineralization (or enrichment), which is a part of the polymetallic mineralization during the Neoproterozoic period. Our dating results of ore minerals genetically coexisting with cassiterite in vein-type ores notably gave an age of 425 Ma, thus constraining an
Paleozoic-stage Sn mineralization, which probably has originated from the reactivation of cassiterite in magnetite by the Paleozoic magmatism.

**Sn resources in the Bayan Obo deposit**

Most Sn ore deposits are associated with granite (Lehmann, 2021); by contrast, carbonatites are the main source of niobium and rare earth elements (Verplanck et al. 2016; Simandl and Paradis 2018). Although Sn may be considered an element geochemically similar to niobium, its enrichment in carbonatites is uncommon, as evidenced by the low Sn contents in carbonatitic rocks (several ppm, GEOROCK, Appendix. Table A12) with the rare occurrence of carbonatitic cassiterite worldwide. Even so, significant Sn contents may be searched out in some carbonatites. For instance, the Elk Creek carbonatite in southeast Nebraska hosts the largest Nb resource in the United States of America (Karl et al. 2021), which contains Sn higher than 50 ppm (up to 125 ppm) in a dozen of samples (Verplanck et al. 2022). Mitchell and Smith (2017) noted the “uncommon but relatively abundant” cassiterite in the Ashram Zone carbonatite of the Eldor Complex (Canada); in fact, this carbonatite also contains a certain amount of Sn with a weighted median of 22 ppm (Beland and Williams-Jones 2021). Thus, as reported in this study, Sn enrichment and mineralization in the carbonatite-related Bayan Obo deposit is not accidental but merits attention on the potential importance of Sn resource in carbonatites. Based on the evidence of whole-rock chemical compositions, the Bayan Obo carbonatite-related deposit effectively hosts a strong Sn mineralization. The averages of bulk Sn contents
in banded and massive REE-Fe ores are 60 ppm, even higher than that in Sn granites (usually 18 ~ 26 ppm, Lehmann, 2021). Particularly, the vein-type REE-Fe ores contain 735 ppm on average, comparable with the classic threshold of Sn-mineralized granites (~800 ppm, at FMQ + 3.12) (Linnen and Cuney 2005). Thus, if we earnestly consider the truth of such Sn enrichment, the vein-type ores of the Bayan Obo deposit and their genetic formation are worthy of continued study.

The Bayan Obo carbonatite-hosted deposit has immense resources of rare earth elements (48 million metric tons of REEs grading 6 wt.% RE_2O_3), iron (1500 million metric tons of Fe grading 35 wt.% Fe_2O_3) and niobium (2.2 million metric tons of Nb grading 0.13 wt.% Nb_2O_5) (Smith et al. 2015; Fan et al. 2016). Carbonatites in Bayan Obo, generally containing iron, are orebodies of rare earth elements (Fan et al. 2016).

As discussed above, Sn mineralization in REE-Fe ores has a close relationship with Nb mineralization, thus we generally assume that the amount of Sn-bearing ores corresponds to the amount of Nb-bearing ores. Therefore, we can estimate the resource volume of Sn in Bayan Obo based on the Sn/Nb ratios of REE-Fe ores and the known Nb resource volume of 2.2 Mt (Smith et al. 2015; Fan et al. 2016). The average Sn/Nb ratios of analysed Fe-REE ores is 0.19 while the Sn/Nb ratios of vein-type ores range from 0.06 to 1.09, with an average value of 0.66 according to the whole-rock geochemical data. Given that the vein-type ores have the highest Sn concentration, they could be the economically important ores for Sn exploration in Bayan Obo. The resource volume is equal to the quantity of ores times the grade,
hence we can give an rough estimation of Sn resource of 0.42 to 1.45 Mt in the Bayan Obo deposit.

**IMPLICATIONS**

We have identified abundant cassiterite grains and several associated Sn-rich minerals in the Bayan Obo deposit, and conclude the genetic framework of Sn mineralization in this carbonatite-hosted deposit: Sn is derived from carbonatitic magma, pre-enriched at around 1.3 Ga, as evidenced by the formation of dense micron-sized cassiterite inclusions in massive magnetite. The subsequently Early Paleozoic hydrothermal events led to the remobilization of Sn, forming larger clustered cassiterite grains and Sn-rich minerals at around 425 Ma. Vein-type ores are important ore-bearing rocks from Bayan Obo. Similar to Nb mineralization, Sn mineralization in Bayan Obo probably forms a huge resource, thereby designating this deposit as a prospective target for Sn mining. The potential Sn resource volume is estimated to be 0.42 ~ 1.45 Mt. By studying and summarising the Sn mineralization process in Bayan Obo, we can propose a possible Sn mineralization model in carbonatite or carbonatite-alkaline systems. Genetically, Sn originates from deep carbonate magmas and the pre-enrichment of Sn may have been the co-generation between cassiterite and other dominant ore minerals of the carbonatite deposit in an oxidizing environment. Subsequently hydrothermal events facilitate the reactivation and precipitation of Sn, which may result in a large-scale Sn mineralization, as
represented by cassiterite and other Sn-bearing minerals. Our work is prospective and instructive for further studies of Sn enrichment in carbonatite systems.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (grant 42230809, 92262001), and the Fundamental Research Funds for the Central Universities. The authors acknowledge the Innovation Academy for Earth Science, CAS for an initial Key Research Program (IGGCAS-201901). Yating XU was supported by the China Scholarship Council (grant no. CXXM2110080163). We thank Wenlan Zhang and Huan Hu for their kindly help on EMP and LA-ICP MS testing. Many thanks to Prof. Xiaolei Wang, Yue Guan and Junyong Li for their support in SIMS laboratory work. We thank Yiqun Zhao and Xuan Meng from Electron Microscopy Centre of Lanzhou University for their help in TEM laboratory work. We are grateful to the two anonymous reviewers for their detailed and constructive comments. Thanks also go to Associate Editor Dr. Julie Roberge for handling our manuscript.

REFERENCES CITED


<table>
<thead>
<tr>
<th>Ore type</th>
<th>Main mineral assemblages</th>
<th>Sn contents (ppm)</th>
<th>Nb contents (ppm)</th>
<th>Sc contents (ppm)</th>
<th>La contents (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disseminated</td>
<td>Dolomite+fluorite (DK2006)</td>
<td>9.04</td>
<td>356.07</td>
<td>56.26</td>
<td>5259.68</td>
</tr>
<tr>
<td></td>
<td>Dolomite (DK2012)</td>
<td>10.00 (15.03)</td>
<td>80.60 (677.80)</td>
<td>26.60 (43.92)</td>
<td>9220.00 (4594.30)</td>
</tr>
<tr>
<td></td>
<td>Dolomite+fluorite (DK1904)</td>
<td>11.67</td>
<td>170.63</td>
<td>19.70</td>
<td>2434.09</td>
</tr>
<tr>
<td></td>
<td>Dolomite (XK1922)</td>
<td>17.45</td>
<td>2279.68</td>
<td>41.92</td>
<td>4557.72</td>
</tr>
<tr>
<td></td>
<td>Dolomite+fluorite (XK2035)</td>
<td>27.00</td>
<td>502.00</td>
<td>75.10</td>
<td>1500.00</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>(15.03)</td>
<td>(677.80)</td>
<td>(43.92)</td>
<td>(4594.30)</td>
</tr>
<tr>
<td>Banded</td>
<td>Magnetite+fluorite+REE minerals (ZK1917)</td>
<td>44.52</td>
<td>1922.62</td>
<td>113.95</td>
<td>3233.93</td>
</tr>
<tr>
<td></td>
<td>Phlogopite+magnetite+REE minerals (17BY39)</td>
<td>151.00 (61.92)</td>
<td>1845.00 (945.62)</td>
<td>80.80 (73.29)</td>
<td>1165.00 (&gt;5758.15)</td>
</tr>
<tr>
<td></td>
<td>Fluorite+aegirine+magnetite (DK1901)</td>
<td>15.00</td>
<td>57.10</td>
<td>13.60</td>
<td>&gt;10000</td>
</tr>
<tr>
<td></td>
<td>Fluorite+aegirine+magnetite (DK1903)</td>
<td>29.00</td>
<td>546.00</td>
<td>72.50</td>
<td>7170.00</td>
</tr>
<tr>
<td></td>
<td>Fluorite+magnetite+aegirine (DK2004)</td>
<td>119.00</td>
<td>758.00</td>
<td>91.60</td>
<td>&gt;10000</td>
</tr>
<tr>
<td></td>
<td>Fluorite+dolomite (XK2037)</td>
<td>13.00</td>
<td>545.00</td>
<td>67.30</td>
<td>2980.00</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>(61.92)</td>
<td>(945.62)</td>
<td>(73.29)</td>
<td>(&gt;5758.15)</td>
</tr>
<tr>
<td>Massive</td>
<td>Magnetite+dolomite (17BY16)</td>
<td>23.16</td>
<td>972.35</td>
<td>28.16</td>
<td>1475.52</td>
</tr>
<tr>
<td></td>
<td>Magnetite+Fluorite (17BY158)</td>
<td>34.56 (62.42)</td>
<td>645.25 (717.64)</td>
<td>116.15 (53.95)</td>
<td>277.28 (&gt;3801.15)</td>
</tr>
<tr>
<td></td>
<td>Aegirine+magnetite (17BY62)</td>
<td>42.00</td>
<td>267.00</td>
<td>42.50</td>
<td>&gt;10000</td>
</tr>
<tr>
<td></td>
<td>Magnetite+aegirine (ZK1932)</td>
<td>36.00</td>
<td>297.00</td>
<td>31.50</td>
<td>518.00</td>
</tr>
<tr>
<td></td>
<td>Fluorite+magnetite (DK1909)</td>
<td>17.00</td>
<td>340.00</td>
<td>17.80</td>
<td>&gt;10000</td>
</tr>
<tr>
<td></td>
<td>Magnetite+fluorite/calcite/aegirine/Na-amphibole (ZK1918)</td>
<td>200.21</td>
<td>871.90</td>
<td>51.12</td>
<td>3167.26</td>
</tr>
<tr>
<td></td>
<td>Magnetite+fluorite/calcite/aegirine/Na-amphibole (ZK1919)</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>Fluorite+magnetite+calcite (XK2028)</td>
<td>84.00</td>
<td>1630.00</td>
<td>90.40</td>
<td>1170.00</td>
</tr>
<tr>
<td>Vein-type</td>
<td>Aegirine+magnetite (DK1906)</td>
<td>256.91 (735.23)</td>
<td>4407.34 (1857.84)</td>
<td>164.46 (93.77)</td>
<td>2370.91 (&gt;5820.23)</td>
</tr>
<tr>
<td></td>
<td>Aegirine+fluorite+bafertisite (DK2003)</td>
<td>1515.00 (735.23)</td>
<td>1650.00 (1857.84)</td>
<td>108.50 (93.77)</td>
<td>7090.00 (&gt;5820.23)</td>
</tr>
<tr>
<td></td>
<td>Aegirine+Na-amphibole+bafertisite (DK2007)</td>
<td>794.00</td>
<td>759.00</td>
<td>49.40</td>
<td>3820.00</td>
</tr>
<tr>
<td></td>
<td>Aegirine (DK2022)</td>
<td>375.00</td>
<td>615.00</td>
<td>52.70</td>
<td>&gt;10000</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>(173.84)</td>
<td>(978.07)</td>
<td>(64.18)</td>
<td>(&gt;4882.25)</td>
</tr>
<tr>
<td>All samples</td>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 2. Representative electron-microprobe results of clustered cassiterite in from vein-type ores

<table>
<thead>
<tr>
<th>No.</th>
<th>Cassiterite associated with fluorite (n=17)</th>
<th>Cassiterite associated with aegirine (n=11)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.57</td>
<td>0.27</td>
</tr>
<tr>
<td>CaO</td>
<td>0.59</td>
<td>1.07</td>
</tr>
<tr>
<td>SnO₂</td>
<td>97.42</td>
<td>97.30</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.16</td>
<td>0.24</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>FeO</td>
<td>0.89</td>
<td>0.17</td>
</tr>
<tr>
<td>MnO</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Nb₂O₅</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>MgO</td>
<td>0.12</td>
<td>0.22</td>
</tr>
<tr>
<td>Total</td>
<td>99.88</td>
<td>99.36</td>
</tr>
</tbody>
</table>

a.p.f.u based on O=2

| Si | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Ca | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Sn | 0.96 | 0.97 | 0.97 | 0.98 | 0.97 | 0.90 |
| Ti | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Fe | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| Mn | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Nb | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Mg | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| Total | 1.02 | 1.02 | 1.01 | 1.02 | 1.02 | 1.03 |
FIGURE 1. Geological map of the Bayan Obo region modified after Fan et al. (2016). Inset tectonic map showing the location of the Bayan Obo deposit at the northern margin of the North China Craton, adapted from Ling et al. (2013).
FIGURE 2. Single polarized microscope images and AMICS (Advanced Mineral Identification and Characterization System) images illustrating ore textures and mineral assemblages of REE-Fe ores in the Bayan Obo deposit. (a, e) disseminated ore; (c, g) banded ore; (b, f) massive ore; (d, h) vein-type ore.
FIGURE 3. Binary plots (logarithmic scales) of Nb content vs. Sn content (a, b) and La content vs. Sn content (c, d) in bulk from Bayan Obo deposit and other carbonatites.
FIGURE 4. BSE (a, c) and TEM images (b, c) of magnetite grains associated with cassiterite.
FIGURE 5. Binary plots of Fe vs. Sn (a), Fe vs. Ti (b), Fe vs. Ca (c) and Fe vs. Mn (d) to distinguish massive magnetite and discrete magnetite in the Bayan Obo deposit.
FIGURE 6. Scanning electron microscope investigation of cassiterite in the Bayan Obo deposit. (a) Disseminated cassiterite inclusions in massive magnetite. The inset enlargement shows the micron-sized grains of cassiterite (arrowed). Note that larger cassiterite grains tens of microns across occurs in the calcite vein outside of magnetite. (b) Abundance of micro-inclusions of disseminated cassiterite grains within massive magnetite (numbers alongside 75 grains of cassiterite identified with Sn X-ray scanning); Sn-bearing rutile is also arrowed. (c) Porous domain with one larger cassiterite grain (upper left) in magnetite. Micron-sized cassiterite inclusions are also indicated by arrow for comparison. (d, e) Clustered cassiterite in fluorite surrounding or cutting magnetite. Abbreviation: Cst = cassiterite; Mgt = magnetite; Cal = calcite; Rt = rutile; Flr =
fluorite.
FIGURE 7. Scanning electron microscope investigation of other Sn-bearing minerals in the Bayan Obo deposit. (a) BSE and Sn X-ray scanning mapping of cassiterite accumulating with aggregates of subhedral Sn-rich rutile. (b) Same area in (a) showing occurrence of cassiterite with rutile (Sn scanning image). (c) Veinlets of rutile crosscutting the aegirine (BSE image). (d) BSE image of Sc-rich titanite in vein-type ore (e) Veinlet of Sn-bearing bafertisite (BSE image). (f) Aggregates of fiber Sn-rich bafertisite (BSE image). Aeg = aegirine; Amp = amphibole; Bao = baotite; Bft = bafertisite; Brt = baryte; Bsn = bastnaesite; Cst = cassiterite; Irt = ilmenorutile; Phl = phlogopite; Qtz = quartz; Rt = rutile; Ttn = titanite.
FIGURE 8. (Nb+Ta) vs (Fe+Mn) diagram for clustered cassiterite (EPMA data). Shaded areas indicate cassiterite of magmatic or hydrothermal origin (modified after Tindle & Breaks, 1998). Inset CL images show zonation of representative analyzed cassiterite grains. Cst = cassiterite; Ap = apatite; Cal = calcite.
FIGURE 9. The backscattered electron (BSE) images of monazite and parisite co-existing with cassiterite in the vein-type ore from the Bayan Obo deposit.
FIGURE 10. *In-situ* U-Th-Pb dating of ore minerals coexisting with cassiterite.

(a, b) Frequency distribution histogram and relative probability plots of monazite LA-ICP-MS ages; (c, d) Frequency distribution histogram and relative probability plots of monazite SIMS ages; (e, f) Columbite LA ICPMS ages; (f, g)
Frequency distribution histogram and relative probability plots of parasite SIMS ages.