



Development of REE mineralization in the giant Maoniuping deposit (Sichuan, China): insights from mineralogy, fluid inclusions, and trace-element geochemistry

Yan Liu^{1,2} · Anton R. Chakhmouradian³ · Zengqian Hou¹ · Wenlei Song⁴ · Jindřich Kynický⁵

Received: 20 February 2018 / Accepted: 19 August 2018 / Published online: 28 August 2018
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Abstract

Rare-earth deposits associated with intrusive carbonatite complexes are the world's most important source of these elements (REE). One of the largest deposits of this type is Maoniuping in the Mianning-Dechang metallogenic belt of eastern Tibet (Sichuan, China). In the currently mined central part of the deposit (Dagudao section), REE mineralization is hosted by a structurally and mineralogically complex Late Oligocene (26.4 ± 1.2 Ma, $^{40}\text{Ar}/^{39}\text{Ar}$ age of fluorophlogopite associated with bastnäsite) hydrothermal vein system developed in a coeval syenite intrusion. Low-grade stockworks of multiple veinlets and breccias in the lower part of the orebody grade upwards into progressively thicker veins (up to 12 m in width) that are typically zoned and comprise ferromagnesian micas (biotite to fluorophlogopite), sodium clinopyroxenes (aegirine to aegirine-augite), sodium amphiboles (magnesio-arfvedsonite to fluororichterite), K-feldspar, fluorite, barite, calcite, and bastnäsite. The latter four minerals are most common in the uppermost 80 m of the Dagudao section and represent the climax of hydrothermal activity. Systematic variations in the fluid inclusion data indicate a continuous hydrothermal evolution from about 230–400 °C (fluid inclusions in feldspar, clinopyroxene, and amphibole) to 140–240 °C (fluid inclusions in bastnäsite, fluorite, calcite). Hydrothermal REE transport was probably controlled by F^- , $(\text{SO}_4)^{2-}$, Cl^- , and $(\text{CO}_3)^{2-}$ as complexing ligands. We propose that at Dagudao, silicate magmas produced orthomagmatic fluids that explored and expanded a fissure system generated by strike-slip faulting. Initially, the fluids had appreciable capacity to transport REE and, consequently, no major mineralization developed. The earliest minerals to precipitate were alkali- and Fe-rich silicates containing low levels of F, which caused progressive enrichment of the fluid in Ca, Mg, F, Cl, REE, $(\text{SO}_4)^{2-}$, and $(\text{CO}_3)^{2-}$, leading to the crystallization of aegirine-augite, fluororichterite, fluorophlogopite, fluorite, barite, calcite, and bastnäsite gradually. Barite, fluorite, calcite, and bastnäsite are the most common minerals in typical ores, and bastnäsite generally postdates these gangue minerals. Thus, it is very probable that fluid cooling and formation of large amount of fluorite, barite, and calcite triggered bastnäsite precipitation in the waning stage of hydrothermal activity.

Keywords Maoniuping deposit · Mianning-Dechang metallogenic belt · REE mineralization · Carbonatite-syenite complex · Mineral compositions · Fluid inclusions · Ar-Ar age

Editorial handling: R. Hu

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s00126-018-0836-y>) contains supplementary material, which is available to authorized users.

✉ Yan Liu
ly@cags.ac.cn

✉ Anton R. Chakhmouradian
Anton.Chakhmouradian@umanitoba.ca

¹ Institute of Geology, Chinese Academy of Geological Sciences, Beijing 100037, People's Republic of China

² State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, People's Republic of China

³ Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

⁴ Mendel University, 361300 Brno, Czech Republic

⁵ Central European Institute of Technology, Brno University of Technology, 61600 Brno, Czech Republic

Introduction

Some 530 carbonatite localities have been documented worldwide (Woolley and Kjarsgaard 2008), but only a few of these host significant rare-earth deposits (≥ 100 -kt REO, where REO = total rare-earth oxide). For the purpose of this paper, the term “rare-earth elements” or REE, is understood to include the 14 naturally occurring lanthanides and Y, but not Sc. Giant deposits, containing reserves in excess of 1-Mt REO, are exceptionally rare. China is known for its wide spectrum of rare-earth deposits that have been producing since the 1980s and firmly established this country as a leader in the global REE market (Hou et al. 2009; Chakhmouradian and Wall 2012; Kynicky et al. 2012; Liu and Hou 2017). Among them are geologically complex deposits spatially associated with, and in some cases hosted by, intrusive carbonatites. This type of deposit is the most economically significant form of REE mineralization in China, accounting for about 65% of the nation’s reserves. The major carbonatite-associated REE deposits in China are Bayan Obo in Inner Mongolia (Yang et al. 2009, 2011a, b, 2016; Lai et al. 2012, 2015, 2016; Lai and Yang 2013; Ling et al. 2013) and those in the Mianning-Dechang (MD) belt of Sichuan (Hou et al. 2009; Liu et al. 2015a, c). The genesis of these deposits was not a simple one-stage process of ore deposition, but involved a sequence of juxtaposed tectonic, magmatic, and hydrothermal events, which produced a complex assemblage of rocks and mineralization styles. Because of this complexity, deciphering the evolution of these deposits is a challenging task that requires a meticulous study of both geochemical characteristics of the principal rock types (Hou et al. 2006, 2015) and variations in the distribution and composition of their constituent minerals. The giant Maoniuping deposit in the MD belt offers excellent opportunities for studying the genesis of this type of mineralization because it is young (21–23 Ma; Liu et al. 2015a, b, c), well-exposed due to mining and exploration activities, comprises both igneous and hydrothermal mineral assemblages, and shows a clear, traceable sequence of formation.

The Cenozoic MD belt (Fig. 1) is situated in eastern Tibet and western Sichuan (southwestern China) and measures about 270 km in length and 15 km in width (Fig. 2). The belt contains total reserves of > 3 -Mt REO, most of which are associated with the Maoniuping syenite-carbonatite complex (3.17-Mt of REO at an average grade of 2.95 wt%) (Hou et al. 2009). Maoniuping and other REE deposits in the MD belt formed under similar tectonic background, but are characterized by different ore grades and tonnages, and vary widely in mineralization style.

There is an impressive volume of literature on the Maoniuping deposit, but most of these previous studies focused on the petrogenesis of carbonatite (Hou et al. 2006, 2015; Xu et al. 2008, 2012, 2015), fluorite trace-element chemistry (Xu et al. 2012), fluid inclusions (Niu et al. 1996,

2003; Xie et al. 2009), and geochronology (Yang et al. 2014; Liu et al. 2015a, Ling et al. 2016, Liu and Hou 2017). Importantly, field relations reported in the literature are largely based on outdated geological survey reports, which provide a dearth of information on the vein systems, even though these systems host the bulk of REE mineralization. Some of the basic characteristics of mineralized rocks at this deposit, including paragenetic sequences and the relative timing of REE deposition and hydrothermal-metasomatic processes (e.g., fenitization) remain poorly constrained. In this paper, we present detailed field and petrographic features of the vein systems in the Maoniuping deposit. In addition, fluid inclusion and geochemical data were obtained for major minerals in the vein system, in order to place constraints on the nature, source, and evolution of the ore-forming fluids. The newly obtained data, in combination with previous laboratory experimental results, also allow us to discuss the transport and deposition mechanisms of REE. Finally, we put forward a comprehensive model for the formation of the vein system and REE ore in the Maoniuping deposit.

Geological background

The 65–50-Ma collision between India and Asia that produced the Himalayan Orogen (Yin and Harrison 2000; Zhong et al. 2001; Mo et al. 2003) also affected the western margin of the Yangtze Craton (Fig. 1; Yin and Harrison 2000; Hou et al. 2003, 2006; Hou and Cook 2009). This interaction gave rise to the N–S-striking Jinpingshan orogenic belt (Fig. 2; Luo et al. 1998). The MD metallogenic belt is adjacent to the Jinpingshan orogen to the east (Fig. 1; Hou et al. 2009). In this part of the Yangtze Craton, the basement is composed predominantly of Archean high-grade metamorphic rocks and Proterozoic metasedimentary rocks and overlain by Phanerozoic clastic and carbonate sequences (Cong 1988; Luo et al. 1998). This area was also affected by the Permian Emeishan mantle plume, which produced flood basalts and layered mafic intrusions. Geochronological data available for zircon from host rocks, bastnäsite (REECO_3F), and gangue minerals from REE deposits in the MD belt indicate that the mineralization developed during the Himalayan Orogeny (27–10 Ma; Yuan et al. 1995; Pu 2001; Tian et al. 2008; Ling et al. 2016; Liu and Hou 2017) in a collisional, rather than a continental rift, setting (Hou et al. 2009). Tectonically, the India-Asia collision gave rise to a series of Cenozoic strike-slip faults (Fig. 1), which served as conduits for mantle-derived melts, including lamprophyres at 40–24 Ma (Guo et al. 2005) and younger carbonatites (27–11 Ma; Liu and Hou 2017).

The MD carbonatites occur as dikes and stocks associated with silica-oversaturated syenites that intruded the Precambrian crystalline basement (Hou et al. 2006). Spatial distribution of carbonatite-syenite complex and related REE deposits was

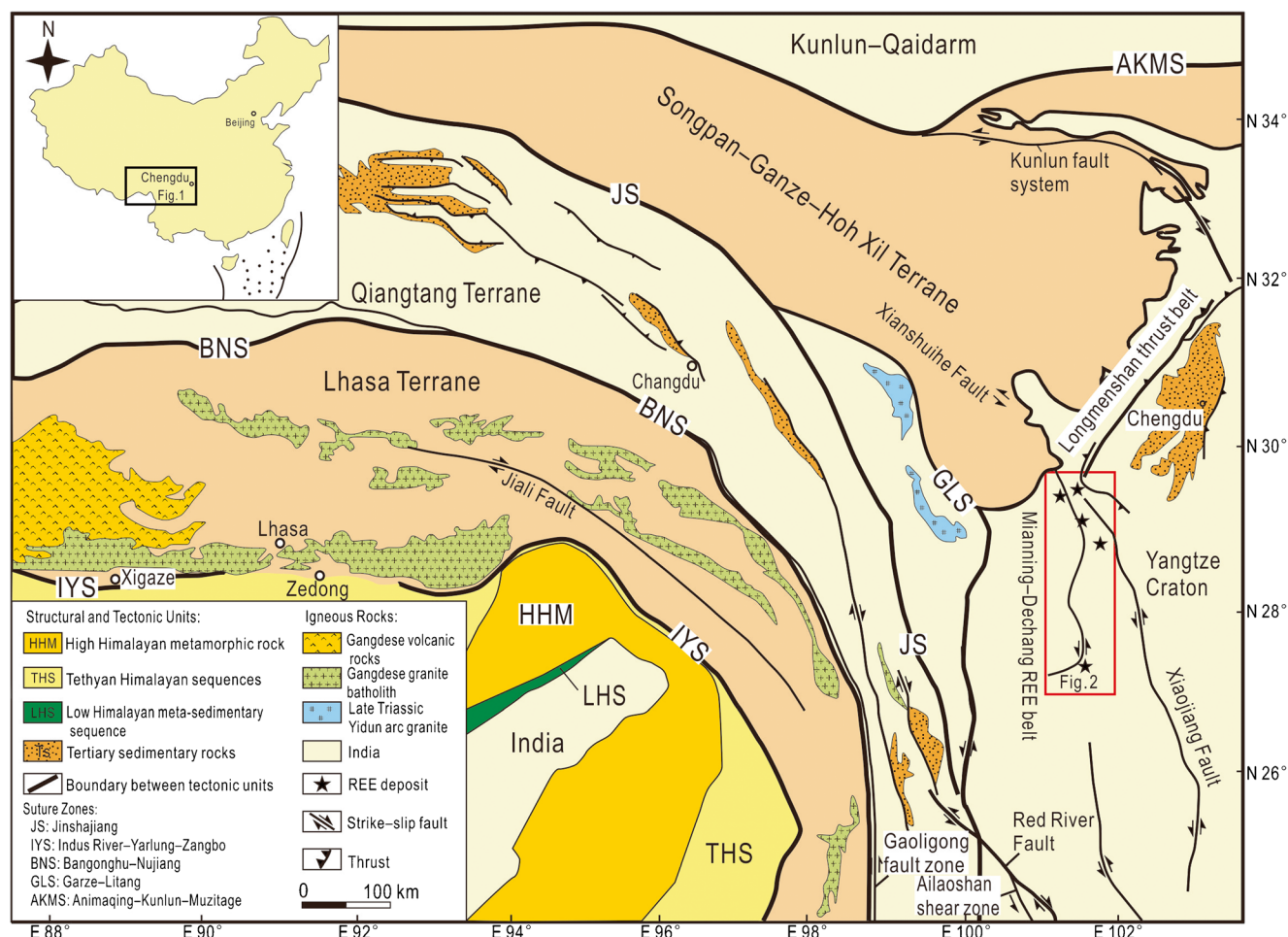


Fig. 1 Simplified tectonic map of the Himalayan–Tibetan Orogen (modified after Yin and Harrison 2000; Hou et al. 2003). The area outlined red is shown in Fig. 2

controlled by the longitudinal MD strike-slip fault (Fig. 2). Sensitive high-resolution ion microprobe U–Pb dating results for zircon from the MD syenites and SIMS (secondary ion mass spectrometry) data for bastnäsite from carbonatite yielded the first systematic and precise age determinations for these rocks. In the Maoniuping samples, both zircon and bastnäsite gave ages of ~25 Ma (Liu et al. 2015a; Ling et al. 2016; Liu and Hou 2017). Importantly, ^{40}Ar – ^{39}Ar dating of magnesioarfvedsonite from mineralized hydrothermal veins in the same complex gave the same age (27.6 ± 2.0 Ma; Liu and Hou 2017).

Geology of the Maoniuping deposit

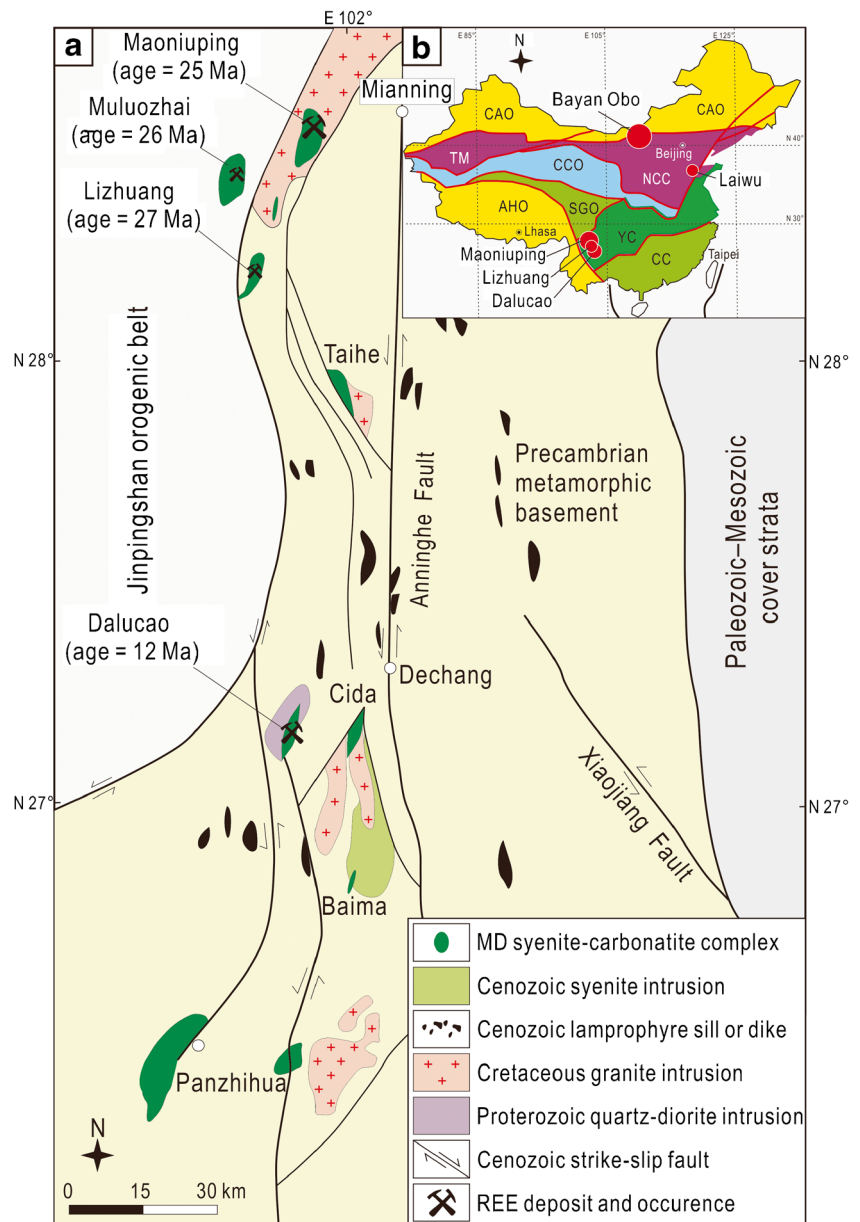
General geology

The MD metallogenic belt was discovered in the 1990s, and related REE deposits were subsequently identified by Geology Exploration Team No. 109 from the Sichuan Bureau of Geology and Mineral Resources. Most of these deposits have since been mined by Chinese companies. The

largest and economically most significant deposit in this group is Maoniuping, located some 15-km WSW of the town of Mianning, western Sichuan. The reported reserves of this deposit comprise 3.17-Mt REO at an average grade of 2.95 wt% (with a cutoff of 1.0-wt% REO), 0.6-Mt Pb (average grade = 0.44 wt%), 13.24-Mt fluorite (6.7-wt% CaF_2), 19.76-Mt barite (8.03-wt% BaO), and 0.83-Mt celestine (1.03-wt% SrO) (Geology Exploration Team No. 109 2010).

The bedrock geology in the Maoniuping area comprises five major lithological units (Fig. 3): (1) a series of N–S-trending granitic plutons (90 km long and 6–14 km wide) dated at 723.1 ± 8.8 Ma (Liu and Hou 2017); (2) a rhyolitic succession with ages of 600–750 Ma; (3) a 1100-m-thick sequence of metamorphosed Devonian–Permian clastic rocks, limestones, and flood basalts intruded by Mesozoic granite; (4) a 700-m-thick coal-bearing Triassic sedimentary sequence that overlies the metamorphic rocks; and (5) a complex of syenitic stocks and carbonatite sills, which extends for about 1400 m and has a width of 260–350 m. The location of the Maoniuping syenite-carbonatite pluton is controlled by the Haha strike-slip fault, which is a secondary structure with

Fig. 2 **a** Schematic tectonic map of China showing the locations of the major carbonatite-associated REE deposits (Hou et al. 2015). **b** Regional tectonic map showing the distribution of Cenozoic carbonatite-alkaline complexes controlled by strike-slip faulting in western Sichuan (modified from Yuan et al. 1995)



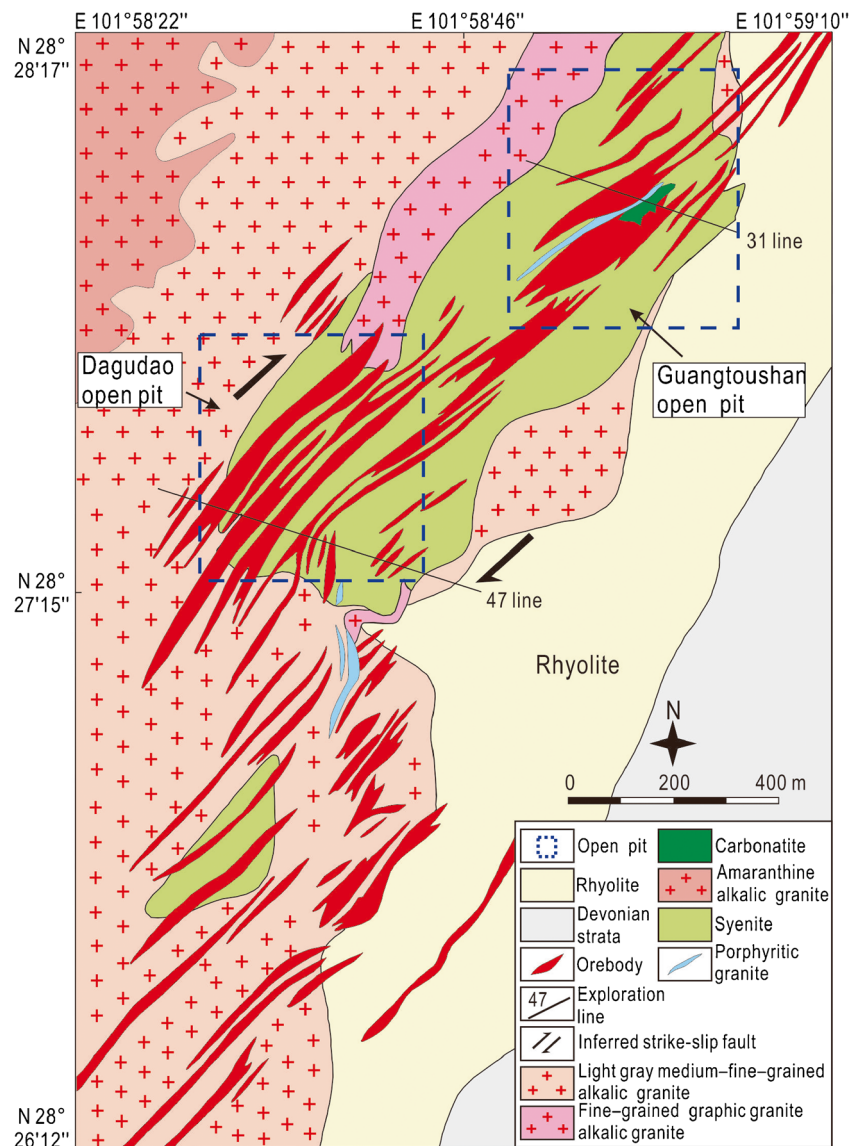
respect to the MD fault. The complex intruded a Mesozoic granitic complex and associated rhyolitic rocks (711.8 ± 9.4 Ma) (Fig. 3). In previous studies, it has been shown that syenite is the predominant lithology at Maoniuping and that it is the major host rock for REE mineralization (Yuan et al. 1995; Liu and Hou 2017). The majority of carbonatite bodies (referred to as “sills” in previous publications) are located in the northern part of the intrusion (Guangtoushan section). These rocks are dominated by medium- to coarse-grained calcite (50–90% by volume), with subordinate proportions of aegirine-augite, alkali amphibole, K-feldspar, barite, and fluorite. Although the currently mined part of the deposit (Dagudao section) contains some carbonatite bodies, their proportion is relatively small. This section consists predominantly of quartz syenite, which hosts a stockwork grading into

multiple branching veins of variable thickness. Fenitization, manifested by mica-, sodium clinopyroxene-, and amphibole-rich zones, is very prominent at Dagudao, where it is spatially associated with REE mineralization.

Maoniuping vein system

In contrast to the other deposits in the MD belt, the REE ores at Maoniuping are hosted by a structurally complex system of mineralized veins, veinlets, and stockwork zones, which has an “S”-like outline in plain view and extends roughly in a NNE-SSW direction (Fig. 3). This configuration suggests that the mineralization was controlled by strike-slip faulting. A total of 71 orebodies have been identified by drilling and assaying; their size ranges from 10 to 1168 m in length and

Fig. 3 Geological map of the Maoniuping REE deposit, showing the location of the Dagudao and Guangtoushan section (modified from Yuan et al. 1995)

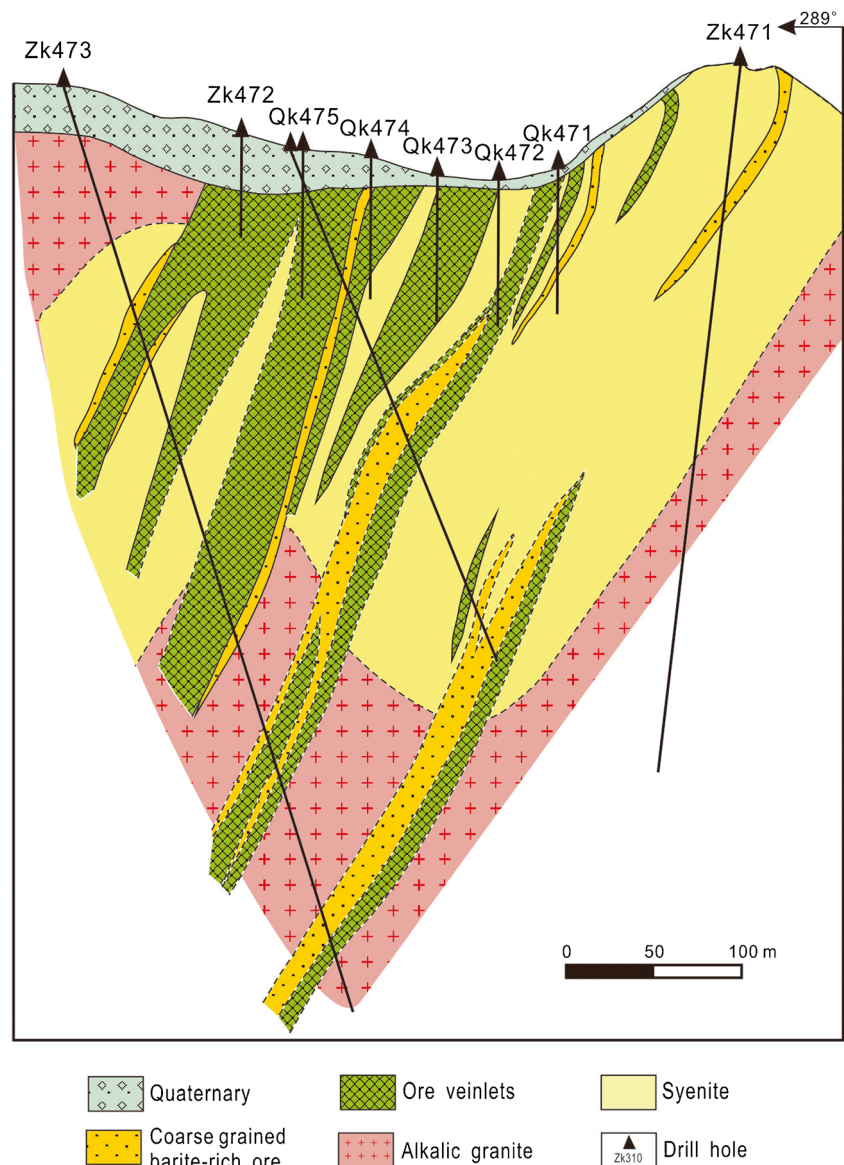


from 1.2 to 32 m in thickness (Yuan et al. 1995). The orebodies dip steeply towards the northwest at 65–80° and vary from massive to complexly zoned, to pod-, or pocket-like mineralized structures. Most veins in the Dagudao section are hosted in fine- to medium-grained quartz syenites (Fig. 4). Geological cross-sections along a series of exploration lines, constructed on the basis of drill-core data, suggest that the Dagudao section is the core area of the Maoniuping deposit (Yuan et al. 1995). The base of the mineralized section was delineated at 150 m below the surface by drilling.

In previous studies (e.g., Yuan et al. 1995), the mineralized veins were categorized into five different types based on their morphological and mineralogical characteristics. However, this classification relied on the limited field evidence that was available at the time, i.e., prior to the excavation of the Dagudao open pit. In recent years, bedrock exposure has much improved due to mining, which enables us to revise

the old classification and ideas regarding the structure of the vein system. In the present work, we identified three distinct units within the Dagudao section, each characterized by specific vein types, mineralogy, and ore potential (Fig. 5a). Transitions between these units are gradational. The top unit (~80-m thick) is the major source of high-grade REE ores and contains swarms of mineralized veins (Fig. 5b) concentrated within the core area of the complex. The veins can be classified into four visually distinct types on the basis of their predominant coarse-grained mineral(s) and structure (Fig. 5c–f): (1) calcite veins, also comprising sodium amphibole and clinopyroxene, barite, fluorite (colorless, purple, and green varieties), and minor sulfides (notably, galena); (2) sodium clinopyroxene type, also containing sodium amphibole, fluorite (colorless and purple), and barite; (3) K-feldspar veins, with subordinate sodium clinopyroxene, barite, and quartz; and (4) micaceous type; all four contain bastnäsite.

Fig. 4 Cross-section of the Dagudao orebody along exploration line 47 (modified from Yang et al. 2000)



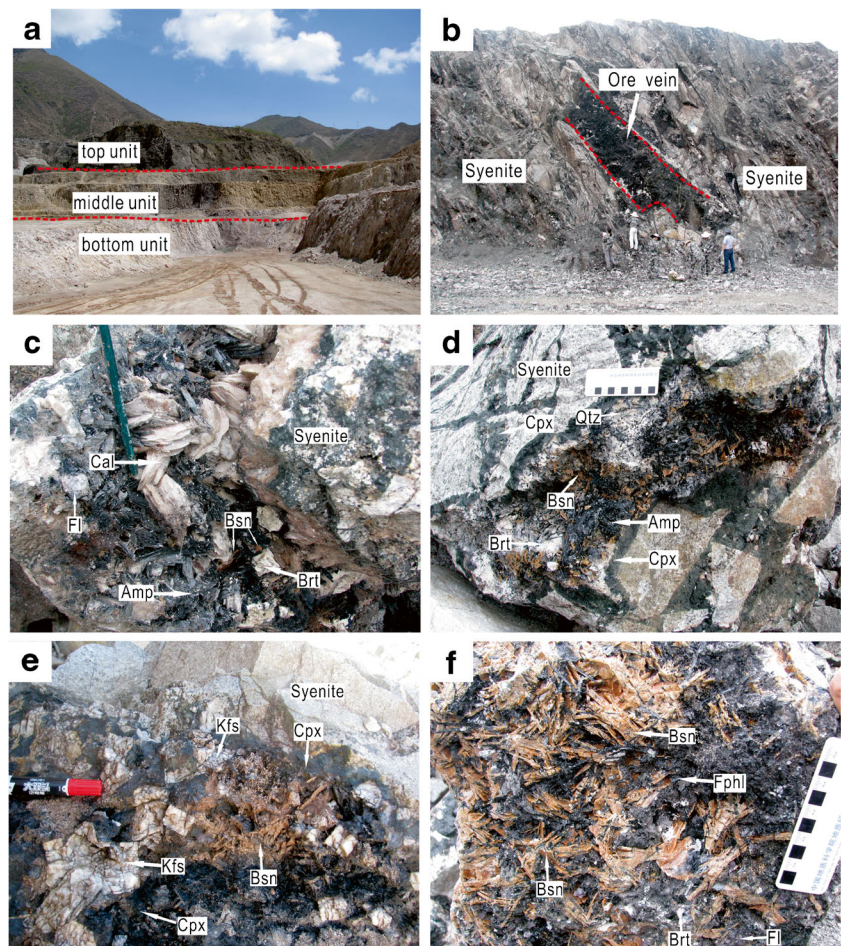
Most of the veins range from 15 to 30 cm, but locally reach 12 m, in width (Fig. 5b), and show a clear zoned structure. From the contact with the wall-rock syenite inwards, the following five zones can be recognized: (1) mica of generation 1 (biotite, usually thinner than 2 cm); (2) K-feldspar; (3) sodium clinopyroxene; (4) sodium amphibole (partially replacing clinopyroxene); and (5) axial zone comprising colorless to purple fluorite ($\pm$ mica of generation 2 (fluorophlogopite), quartz, calcite, and barite) with occasional clusters of bastnäsite crystals, galena, and other sulfides (Fig. 5e–f). All the veins are modally zoned, but not every one of the five zones may be present in a given vein.

Thick veins do not occur in isolation; instead, they are commonly accompanied by sets of subparallel and intersecting thinner veinlets and brecciation zones (Fig. 6a). These are particularly common in the southeastern part of the

Dagudao section, i.e., down-slip from the core area (Fig. 4). Breccias are composed of angular wall-rock syenite clasts set in a matrix of ferromagnesian silicates (predominantly, sodium clinopyroxene and amphibole; Fig. 6b). Locally, pervasively fenitized older metamorphic rocks are also present as clasts (Fig. 6c). Adjacent to the vein system, the wall-rock syenite exhibits conspicuous jointing crudely parallel to the major veins (Fig. 6d); some of the joints are filled with very fine-grained ferromagnesian silicates.

The bottom unit is essentially a dense stockwork of veinlets (Fig. 6e) whose width does not normally exceed 1 cm. They are composed predominantly of fine- to medium-grained aegirine-augite, biotite, K-feldspar, albite, and quartz. Here, fluorite, barite, and bastnäsite are not nearly as common as in the top unit, and modal variations do not follow any discernible pattern. The middle unit ($\sim$ 50 m in thickness) is

Fig. 5 Characteristic field and mineral relations in the Dagudao section. **a** Three units within the orebody. **b** Thick ore veins crosscutting syenites in the top unit. **c** Calcite-rich vein type. **d** Clinopyroxene-amphibole vein type. **e** K-feldspar-rich type. **f** Micaceous type. Abbreviations: Amp sodium amphibole, Brt barite, Bsn bastnäsite, Cal calcite, Cpx sodium clinopyroxene, Fl fluorite, Fphl fluorophlogopite, Kfs K-feldspar, Qtz quartz

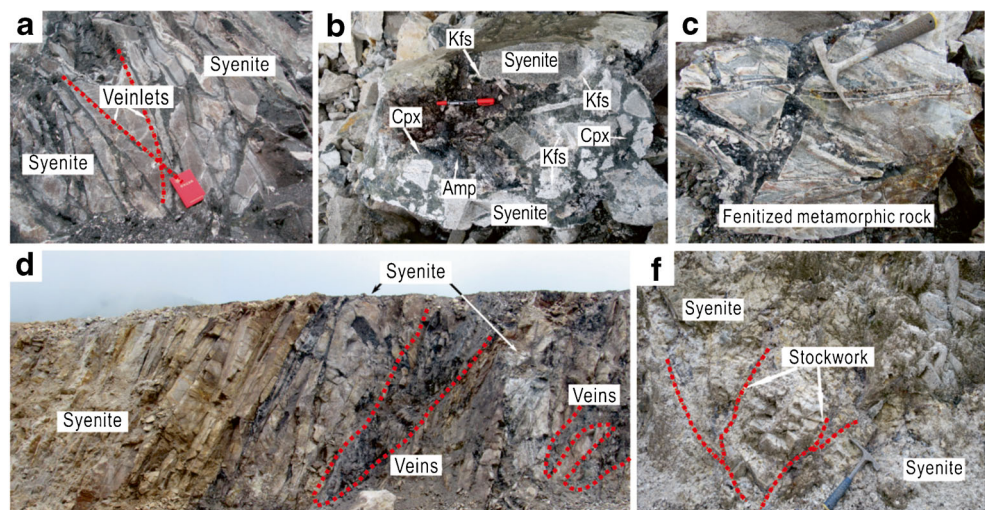


mineralogically and structurally transitional between the top and bottom units. Unlike the latter, it contains sodium amphibole developed after sodium clinopyroxene. Here, vein thickness increases upwards, but the majority of veins are < 3 cm in width.

Petrography

Both thick veins, veinlets, and stockworks are clearly recognizable in outcrop due to their dark color reflecting the proportions of biotite, phlogopite, sodium clinopyroxene, and

Fig. 6 Characteristic structures and rock relation in the Dagudao section. **a** Multiple mineralized veinlets crosscutting wall-rock syenite (top unit). **b** Breccia comprising syenite clasts in a clinopyroxene-amphibole-rich matrix. **c** Breccia comprising fenitized clasts of older metamorphic rocks. **d** Panoramic view of the open pit wall 10–11-m high (top unit) showing jointed syenites and part of the vein system. **e** Stockwork (bottom unit). Abbreviations as in Fig. 5



amphibole in their modal composition. Thicker veins and vein intersections typically contain honey- to greenish yellow tabular isolated crystals of bastnäsite, as well as their subparallel and radiating clusters measuring up to 10 cm in size. This mineral is intimately associated with coarse-grained white barite, white to pinkish calcite, colorless to purple fluorite, and fine- to medium-grained mica of generation 2. Notably, the middle and bottom units contain a smaller proportion of these minerals, and the majority of veins in stockworks are dark-colored owing to the predominance of ferromagnesian silicates in their modal composition. Magnetite can also be found associated with these gangue minerals, albeit in very small quantities. At the contact with the veins, syenite clasts contain fine-grained albite and muscovite developed at the expense of K-feldspar.

Sampling and analytical methodology

For this study, samples were selected from different vein types in the Dagudao section. Representative mineral samples were prepared using conventional methods (crushing, sieving, heavy liquid separation, etc.). Back-scattered electron (BSE) images and major-element analyses of minerals were acquired using a JXA-8230 electron microprobe at the Institute of Mineral Resources, Chinese Academy of Geological Sciences (CAGS), in Beijing, China. The microprobe was operated at an accelerating voltage of 15 kV, a beam current of 20 nA, and beam size of 5 μm . The following natural and synthetic standards, analytical line, and detector types were used for electron-microprobe analysis (EMPA): jadeite (NaK α and AlK α on TAP, SiK α on PET); forsterite (MgK α , TAP); topaz (FK α , TAP); K-feldspar (KK α , PET); wollastonite (CaK α), hematite (FeK α , LIF); rutile (TiK α , LIF); MnO (MnK α , LIF); and NaCl (ClK α , PET). For bastnäsite, synthetic orthophosphate standards (La, Ce, Pr, Nd, and Sm) and natural thorite were employed to measure the abundances of REE (La, Ce, Pr, Nd, Sm) and Th, respectively. Heavier lanthanides and Y were sought, but found not to be present at levels detectable by EMPA. Matrix corrections were carried out using the ZAF correction program supplied by the manufacturer.

Whole-rock geochemical analyses of syenite were performed at the National Research Center of Geoanalysis, CAGS. Pulverized whole-rock samples (0.7 g) were mixed with 5.3-g $\text{Li}_2\text{B}_4\text{O}_7$, 0.4-g LiF, and 0.3-g NH_4NO_3 in a porcelain crucible. The powder mixture was transferred to a platinum alloy crucible, and 1-mL LiBr solution was added to it. The fluxed sample was then dried and melted in an automatic flame-fusion furnace and quenched to glass. The glass was analyzed by X-ray fluorescence (XRF) for major elements; analytical errors were estimated to be <2% relative.

The following procedure was adopted for the analysis of REE and other trace elements in wall-rock syenite and

monomineralic samples (State Standard of the People's Republic of China 2010). Powder samples (50 mg) were dissolved in distilled 1-mL HF and 0.5-mL HNO_3 in 15-ml Savillex Teflon screw-cap capsules at 190 °C for 1 day, dried, digested with 0.5-mL HNO_3 , and then dried again. The capsule content was digested with 0.5-mL HNO_3 and dried again to ensure complete digestion. Then, the sample was digested with 5-mL HNO_3 and held at 130 °C in an oven for 3 h. After cooling, the solution was transferred to a plastic bottle and diluted to 50 ml before analysis. The sample solutions were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Standards GBW07120, GBW 07103, GBW 07105, and GBW 07187 were measured together with the samples; precision within 5% relative was achieved.

A monomineralic fluorophlogopite sample was separated from sample MNP13-3MUS1, representing a typical zoned, mineralized vein in the Dagudao section. Mica grains were hand-picked under a binocular microscope, crushed, and sieved to 60- and 80-mesh fractions and then washed with distilled water and acetone. The sample was wrapped in aluminum foil, irradiated together with muscovite standard Bern4M, and monitored for 31 h at the B4 position of the 49-2 reactor, Beijing, China. The total fusion and step-heating analyses of the sample were performed at the $^{40}\text{Ar}/^{39}\text{Ar}$ Geochronology Laboratory, Institute of Geology and Geophysics, Chinese Academy of Sciences, using an MM 5400 mass spectrometer operated in static mode. The sample was degassed at 600 °C for 10 min before being incrementally heated in a double-vacuum furnace. The gases released during each step were purified using two SAES Group getters (operated at 350 and 100 °C, consecutively) before their introduction into the mass spectrometer for Ar isotope determination. The ^{40}Ar , ^{39}Ar , ^{38}Ar , ^{37}Ar , and ^{36}Ar isotopic abundances were determined by linear extrapolation of the peak intensities to time zero. The data were corrected for system blanks, Ca interference, K-derived Ar isotopes, and the decay of ^{37}Ar from the time of irradiation. The decay constant used throughout the calculations was $\lambda = (5.543 \pm 0.010) \times 10^{-10} \text{ a}^{-1}$, as recommended by Steiger and Jäger (1977). Details of the analysis and data processing are given in He et al. (2006). The results of the $^{40}\text{Ar}/^{39}\text{Ar}$ experiments were plotted as age spectra and isotope correlation diagrams. Identification of a plateau in the age spectrum was based on a minimum number of concordant age steps and a minimum proportion of ^{39}Ar release; as different minimum values have been given, the selected steps should be contiguous. At a minimum, the ages may be viewed as concordant only if they do not differ at the 95% confidence level. The isotopic ratios that correspond to the heating steps used for the plateau age calculations were used to fit an inverse isochron age line. The Ca and K correction factors were calculated from the CaF_2 and K-glass monitors as follows: $(^{40}\text{Ar}/^{39}\text{Ar})_{\text{K}} = 3.3 \times 10^{-4}$, $(^{39}\text{Ar}/^{37}\text{Ar})_{\text{Ca}} = 8.52 \times 10^{-4}$, and $(^{36}\text{Ar}/^{37}\text{Ar})_{\text{Ca}} = 2.69 \times 10^{-4}$, respectively.

Results

Mineral compositions in mineralized veins

Because little data is available in the literature for major rock-forming constituents of the Maoniuping rocks/ores, we analyzed the composition of amphiboles, clinopyroxenes, micas, feldspars, calcite, fluorite, and bastnäsite from several representative vein samples from the bottom and top units (Tables 1 and 2). Amphibole-group minerals, which are indistinguishable in hand specimen or thin section, range in composition from fluororichterite to intermediate members of the ferriwinchite-magnesio-arfvedsonite series (for nomenclature, see Hawthorne et al. 2012). All measured compositions are enriched in K (1.3–1.5-wt% K_2O) and F (2.2–3.3 wt%), but poor in Al and Ti (0.5–1.0- and < 0.1-wt% respective oxides). Sodium-rich and Mn-bearing (0.2–0.7-wt% MnO) amphiboles approaching magnesio-arfvedsonite were identified only in the bottom unit.

Clinopyroxenes cover a large compositional range spanning from aegirine-augite to aegirine. Both aegirine-augite and aegirine were identified in the bottom unit, but only the former in the top one (Table 1). In common with the amphiboles, the Al and Ti contents are consistently low (0.2–1.0- and < 0.2-wt% respective oxides), and the proportions of Ca and Mg increase, whereas those of Na, Mn and Fe decrease upwards. If described in terms of the four end-member components (aegirine, Ae; diopside, Di; hedenbergite, Hd; johannsenite, Jh), the measured compositions range from $Ae_{27}Di_{46}Hd_{24}Jh_3$ to $Ae_{40}Di_{38}Hd_{19}Jh_3$ (aegirine-augite) and from $Ae_{69}Di_{26}Hd_3Jh_2$ to $Ae_{98}Di_2$ (aegirine). Further analyses are required to confirm the absence (or otherwise) of compositions intermediate between Ae_{40} and Ae_{69} .

Mica of generation 1 is biotite containing comparable proportions of phlogopite and annite (Table 1). It is characterized by high Al and Ti (16.2–16.6- and 1.5-wt% respective oxides) and relatively low F content (2.0 wt%). Mica of generation 2 (fluorophlogopite) is more volumetrically abundant; it is comparatively rich in Mg and F (17.6–20.8-wt% MgO , 4.4–7.9-wt% F), but poor in Na, Ti, and Mn (≤ 0.2 -, 0.8-, and 0.4-wt% respective oxides). Its Al content is also very low relative to biotite of generation 1 (5.0–7.5-wt% Al_2O_3), which translates into a lower-than-stoichiometric Al content in the tetrahedral sites (0.30–0.58 Al atoms per formula unit, apfu). This Al deficiency is coupled to low totals of medium-sized cations in the octahedral sites [2.61–2.75 apfu ($Mg + Fe + Mn + [^{VI}]Al + Ti$)]. These unusual characteristics may result from the presence Li in these sites, because this element may substitute for Mg (Tischendorf et al. 2007), but is not detectable by EMPA. Bulk analysis of mica-rich zones (authors' unpublished data) suggests the presence of significant Li content in the fluorophlogopite (up to 4000 ppm). Simple calculations show that this amount (i.e., 0.75-wt% Li_2O) is

sufficient to compensate the observed cation deficiency. Hence, the majority of the analyzed micas can be tentatively identified as fluorophlogopite transitional to annite (8–20 mol%) and the Li-Mg end-member tainiolite (for nomenclature, see Tischendorf et al. 2007). Laser-ablation studies of these samples are currently underway to confirm the distribution of Li and other trace elements between generations 1 and 2. Importantly, neither micas nor amphiboles contain Cl at levels detectable by EMPA (> 0.02 wt%).

Several grains of K-feldspar and albite were analyzed by EMPA and found not to deviate significantly from their stoichiometric compositions. The Na content of K-feldspar ranges from 0.8- to 1.7-wt% Na_2O , whereas the K content of albite is ~ 0.1 -wt% K_2O ; neither mineral contains detectable Ba. Muscovite replacing feldspar in syenite clasts invariably contains elevated Mg, Fe, and F levels (2.3–2.7-wt% MgO , 6.4–6.6-wt% Fe_2O_3 , 0.9–1.1-wt% F). The low analytical totals (88–93 wt%) and deficiency of large cations in interlayer sites (0.63–0.90 apfu K + Na) suggest that these micas are hydrated, i.e., transitional to illite.

Calcite from the axial zone of mineralized veins contains minor Mg, Mn, Fe, and relatively high Sr contents (on average, 0.2-, 0.5-, 0.4-, and 1.3-wt% respective oxides). Trace-element analysis also shows that this mineral is enriched in Ba, ΣREE , and Pb (550–950, 3290–3980, and 100–120 ppm, respectively). The Zn, Th, and U abundances are low (Table 2). The REE budget of calcite is dominated by light lanthanides ($Ce > La > Nd > Pr > Sm$). Its chondrite-normalized patterns (Fig. 7) exhibit a negative slope [$(La/Yb)_{cn} = 47$ relative to CI values of Anders and Grevesse 1989] and appear relatively smooth. However, the Eu/Eu^* [$Eu_{cn}/0.5 \times (Sm_{cn} + Gd_{cn})$] and Y/Ho ratios are consistently below the chondritic values (0.78 and 24, respectively).

Colorless fluorite grades into purple fluorite. The two fluorite varieties do not have clear textural relationships, and thus they are treated together in the following text. The mineral is characterized by appreciable Sr, Ba, and Pb contents (2380–3350, 120–350, and 15–39 ppm, respectively), moderately high levels of ΣREE (510–800 ppm), and very low Th and U abundances (≤ 0.5 ppm for both). Its chondrite-normalized pattern shows a gentle negative slope [$(La/Yb)_{cn} = 8$ –11] and a positive Y anomaly ($Y/Ho = 57$ –89; Fig. 7a). In common with the calcite, fluorite shows slight depletion in Eu relative to the extrapolated value ($Eu/Eu^* = 0.76$ –0.80; Table 2).

Bastnäsite is close to its ideal composition [$(Ce_{0.50}La_{0.36}Nd_{0.10}Pr_{0.04})(CO_3)(F_{0.92}OH_{0.07}Cl_{0.01})$] and contains only minor Ca, Th, and Cl (ca. 0.1-wt% CaO , 0.2-wt% ThO_2 , and 0.1-wt% Cl). Trace-element analysis gave low Sr, Ba, Pb, and U values, whereas Mn and Zn are near their detection limit (Table 2). Chondrite-normalized REE patterns show appreciable variation in slope, but no Y anomaly ($Y/Ho = 26$ –30). The Eu/Eu^* value is invariably low (0.50–0.58).

Table 1 Representative EMPA analyses of ferromagnesian silicate from the Dagudao ore vein system

Sample mineral	MNP15-40-3-01		MNP8-1-1		MNP8-1-3		MNP15-40-3-04		MNP15-40-3-07		MNP15-40-3-06		MNP15-40-3-10		MNP15-35-5-05		MNP15-40-3-16		MNP15-41-02		MNP15-35-5-12		MNP10-1-1		MNP10-1-2		
	Magnesio-arfvedsonite		Fluorrichterite		Aegirine-augite		Aegirine		Aegirine		Aegirine		Biotite		Fluorphlogopite		Fluorphlogopite		Fluorphlogopite		Fluorphlogopite		Fluorphlogopite		Fluorphlogopite		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Na ₂ O	7.30	5.85	5.40	5.90	4.12	5.69	9.17	10.70	13.10	14.60	0.15	0.09	0.07	0.09	0.09	0.09	0.09	0.15	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
MgO	13.30	15.80	15.50	15.10	8.03	6.61	4.51	2.51	0.13	0.36	10.60	18.40	17.60	17.60	17.60	17.60	17.60	10.60	20.30	20.30	20.30	20.30	20.30	20.30	20.30	20.30	20.30
Al ₂ O ₃	0.97	0.70	0.83	0.89	0.31	0.77	0.57	0.52	0.22	0.62	16.60	6.58	7.11	7.11	7.11	7.11	7.11	16.60	5.11	5.11	5.11	5.11	5.11	5.11	5.11	5.11	5.11
SiO ₂	53.90	54.50	54.20	54.40	53.10	52.80	52.90	52.20	52.60	53.20	35.20	46.50	44.70	44.70	44.70	44.70	44.70	35.20	49.00	49.00	49.00	49.00	49.00	49.00	49.00	49.00	49.00
K ₂ O	1.52	1.36	1.37	1.41	0.00	0.00	0.00	0.00	0.00	0.00	8.55	9.75	9.37	9.37	9.37	9.37	9.37	8.55	10.10	10.10	10.10	10.10	10.10	10.10	10.10	10.10	10.10
CaO	2.10	4.91	5.78	4.94	16.90	14.40	8.89	5.77	0.42	0.75	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TiO ₂	0.05	0.01	0.07	0.05	0.01	0.06	0.09	0.09	0.09	0.09	1.51	0.57	0.81	0.81	0.81	0.81	0.81	1.51	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
MnO	0.18	0.65	ND	ND	0.96	0.86	0.51	0.30	0.04	0.07	0.25	0.23	0.23	0.23	0.23	0.23	0.23	0.25	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
FeO	8.41	7.12	10.13	9.71	7.46	5.70	0.87	0.71	1.42	0.00	18.30	7.52	9.06	9.06	9.06	9.06	9.06	18.30	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27	4.27
Fe ₂ O ₃	8.33	5.09	1.30	3.10	9.27	13.78	23.82	27.33	31.54	32.89	ND	ND	ND	ND	ND	ND	ND	32.89	ND	ND	ND	ND	ND	ND	ND	ND	ND
F	2.24	3.30	2.73	2.88	ND	ND	ND	ND	ND	ND	1.96	5.84	4.91	4.91	4.91	4.91	4.91	1.96	7.91	7.91	7.91	7.91	7.91	7.91	7.91	7.91	7.91
-O=F2	0.94	1.39	1.15	1.21	NA	NA	NA	NA	NA	NA	0.83	2.46	2.07	2.07	2.07	2.07	2.07	0.83	3.33	3.33	3.33	3.33	3.33	3.33	3.33	3.33	3.33
Total	97.36	97.90	96.16	97.17	100.16	100.67	101.33	100.13	99.56	102.58	92.34	93.00	91.81	91.81	91.81	91.81	91.81	92.34	93.63	93.63	93.63	93.63	93.63	93.63	93.63	93.63	93.63

Table 2 Representative trace-element analyses of non-silicate minerals from the Dagudao ore vein system

Mineral	Fluorite 1	Fluorite 2	Fluorite 3	Fluorite 4	Calcite 1	Calcite 2	Calcite 3	Calcite 4	Bastnäsite 1	Bastnäsite 2
Mn	40.6	110	1781	345	4187	3865	4228	4104	1.13	0.13
Zn	13.7	25.0	10.8	31.7	8.20	15.3	11.6	9.91	1.00	0.06
Sr	2444	2503	3353	2513	10,520	11,040	11,600	10,920	292	244
Y	222	191	189	164	146	137	150	148	323	382
Ba	122	120	326	322	928	614	950	554	2.07	1.70
La	43.5	52.4	107	57.4	711	755	966	736	270,954	279,666
Ce	86.4	97.3	228	114	1388	1511	1682	1467	287,700	287,700
Pr	13.3	15.0	31.1	18.1	160	174	186	174	21,608	22,615
Nd	73.7	82.2	138	94.1	622	664	710	674	62,890	66,004
Sm	19.1	19.2	29.7	20.7	97.5	104	108	107	3690	4483
Eu	5.38	5.24	7.72	5.67	21.9	23.0	23.9	23.6	487	642
Gd	22.6	21.1	27.8	22.0	64.9	68.8	71.1	73.4	1577	1774
Tb	2.62	2.35	3.40	2.44	7.31	7.28	7.73	7.60	65.3	78.5
Dy	13.8	12.2	18.0	12.7	37.0	37.4	39.0	38.8	135	162
Ho	2.50	2.18	3.30	2.28	5.90	5.80	6.10	6.00	12.1	13.9
Er	6.25	5.25	8.68	5.87	13.9	13.90	14.60	14.9	19.5	21.1
Tm	0.75	0.64	1.18	0.72	2.00	2.00	2.00	2.10	0.78	0.86
Yb	3.89	3.39	6.91	4.03	12.0	11.7	12.1	12.5	2.07	2.36
Lu	0.46	0.41	0.93	0.53	1.60	1.60	1.70	1.70	0.18	0.18
Pb	30.8	14.7	29.8	28.6	100	105	107	118	3.45	9.46
Th	0.27	0.27	0.51	0.13	1.10	0.90	1.80	0.40	1444	2321
U	0.24	0.35	0.30	0.46	1.00	1.40	0.70	1.20	9.23	5.93
Sum REE	516	509	800	524	3291	3516	3980	3486	649,467	663,549
Eu/Eu*	0.78	0.79	0.80	0.80	0.79	0.78	0.78	0.77	0.53	0.58
Y/Ho	88.8	87.6	57.2	71.9	24.7	23.6	24.5	24.6	26.6	27.3
(La/Yb) _{cn}	7.74	10.7	10.7	9.86	41.0	44.6	55.2	40.7	90,575	81,911

Whole-rock data

Eight samples of syenite from the Dagudao section were analyzed for major and trace elements (ESM Table 1). Similar to syenites elsewhere in the MD belt (Hou et al. 2006), these rocks are silica-oversaturated (16–20-wt% normative quartz)

and mildly peralkaline (1–2-wt% normative aegirine). The examined samples exhibit enrichment in Ba, Pb, and light REE [2050–4270, 52–106, and 450–5370 ppm, respectively; (La/Yb)_{cn} = 82–635], but low levels of high-field-strength elements (≤ 0.1 -wt% P₂O₅, 72-ppm Nb, and 1-ppm Ta). Their trace-element budget is characterized by slight Eu deficiency

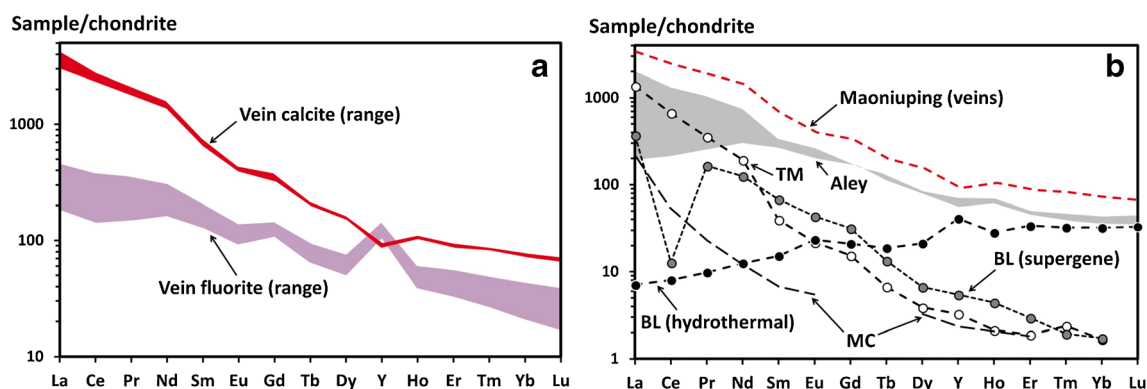


Fig. 7 **a** Chondrite-normalized REE distributions in calcite and fluorite from the inner zone of mineralized veins (CI values from Anders and Grevesse 1989). **b** Average chondrite-normalized REE profiles of Maoniuping calcite compared to igneous and non-igneous calcite from

selected carbonatites (Chakhmouradian et al. 2016). Aley = variation range for Aley (Canada), BL = Bear Lodge (Wyoming, USA), MC = Magnet Cove (AR, USA), TM = Turiy Mys (Russia)

(Eu/Eu* = 0.84 ± 0.04) and near-chondritic Y/Ho, Zr/Hf, and U/Th values (28.7 ± 1.5 , 35.2 ± 1.4 , and 5.0 ± 1.4).

Ar-Ar dating of fluorophlogopite

The monomineralic fluorophlogopite sample (generation 2) yielded a plateau spectrum shown in Fig. 8. The early and later heating steps show obvious excess ^{40}Ar , and the middle seven steps accounted for 70% of the total ^{39}Ar released and defined a plateau age of 26.4 ± 1.2 Ma (2σ) (Fig. 8a; ESM Table 2). This value is in good agreement with an inverse isochron age of 26.2 ± 2.3 Ma (2σ , MSWD = 1.11; Fig. 8b). The $^{40}\text{Ar}/^{36}\text{Ar}$ intercept of 297 ± 14 (2σ) is not distinguishable from the ratio of these isotopes in air, indicating that the middle seven steps were not significantly affected by ^{40}Ar contamination (Fig. 8a). Therefore, we consider 26.4 ± 1.2 Ma (2σ) as the best age estimate for the development of REE mineralization at Dagudao.

Fluid inclusions: microthermometric results

Fluid inclusions in different minerals from the Maoniuping deposit have been examined in a number of previous studies (Niu et al. 1996; Hou et al. 2009; Xie et al. 2009, 2015). However, these publications have not addressed the inclusion-hosting mineral associations in much detail nor examined silicate minerals other than quartz. In the present work, fluid inclusions in K-feldspar, sodium clinopyroxene, sodium amphibole, fluorite, bastnäsite, and calcite from zoned veins were investigated. Below, we provide a brief description of these inclusions and present the results of microthermometric analysis. All minerals investigated here host variably shaped aqueous inclusions of V-L type at room temperature. These aqueous inclusions are typically 5–15 μm in their longest dimension, although some minerals (notably, clinopyroxene) contain elongate inclusions up to 25 μm in length (Fig. 9). The proportion of the vapor phase usually ranges from 10 to 15 vol%, but larger bubbles (up to 20 vol%) were observed in K-feldspar (Fig. 9a). Upon heating,

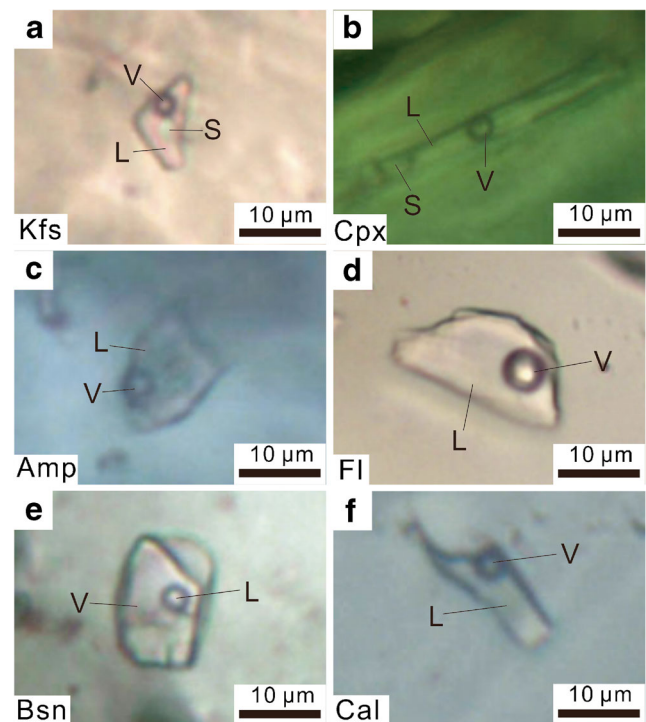


Fig. 9 Selected examples of fluid inclusions in minerals from the ore vein system (photomicrographs in transmitted light). **a** K-feldspar. **b** Sodium clinopyroxene. **c** Sodium amphibole. **d** Fluorite. **e** Bastnäsite. **f** Calcite. L = liquid, S = solid, V = vapor

V-L inclusions in K-feldspar, clinopyroxene, and amphibole yield the widest range of homogenization temperatures (T), i.e., 150–390, 150–390, and 190–410 $^{\circ}\text{C}$, respectively (Fig. 10a–c). Those in fluorite and bastnäsite gave a much more restricted range of values (110–230 and 140–240 $^{\circ}\text{C}$), whereas the majority of V-L inclusions in the fluorite and bastnäsite homogenizes between about 150 and 200 $^{\circ}\text{C}$ (Fig. 10d, e). Calcite shows the narrowest range of values (130–190 $^{\circ}\text{C}$; Fig. 10f). Most of the studied samples also contain solid-bearing fluid inclusions (V-L + S), sometimes with more than one daughter phase (e.g., Fig. 10a–d). One notable exception is bastnäsite (Fig. 10e). Most of fluorite-hosted inclusions of V-

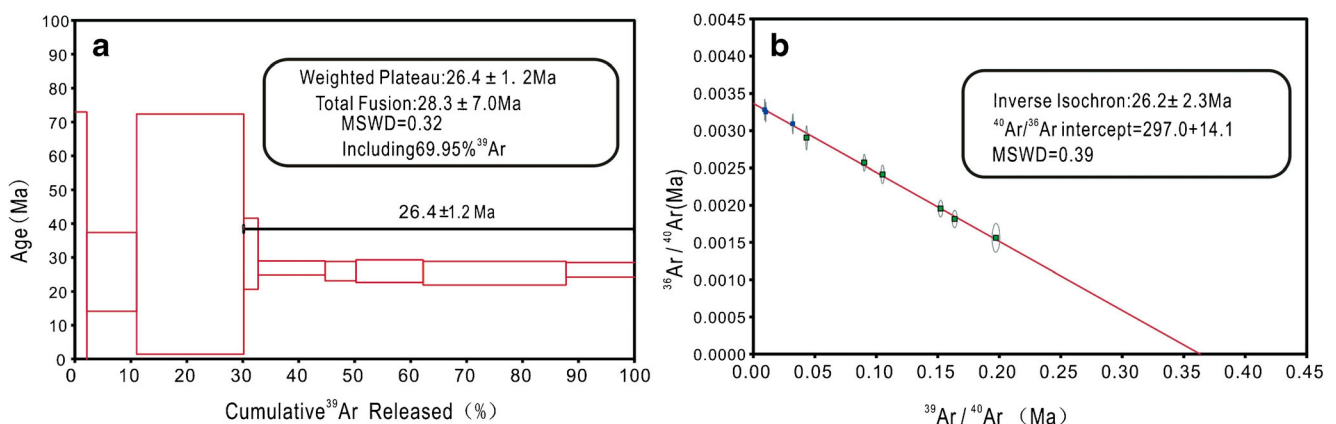
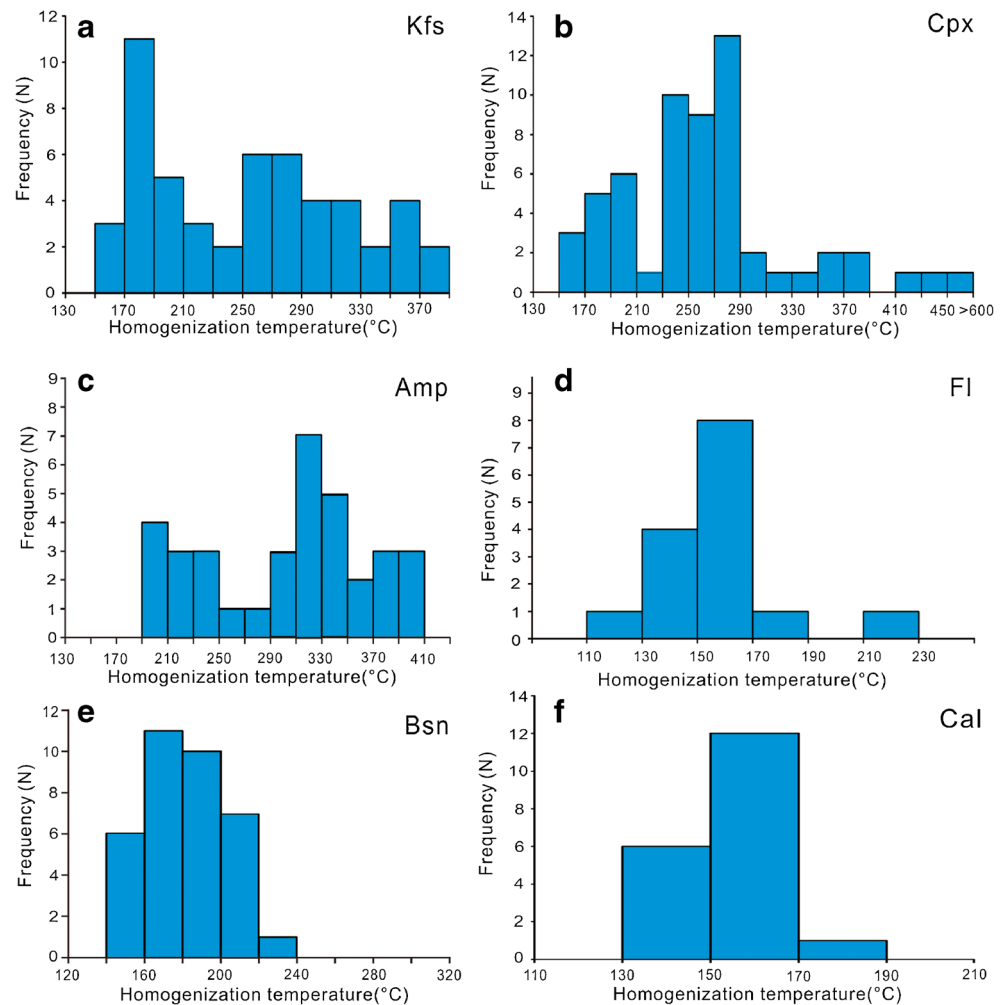


Fig. 8 $^{40}\text{Ar}/^{39}\text{Ar}$ dating results for fluorophlogopite (MNP13-3MUS1). **a** Plateau spectrum. **b** Inverse isochron diagram

Fig. 10 Histograms of homogenization temperatures of aqueous fluid inclusions in minerals from the ore vein system (photomicrographs in transmitted light). **a** K-feldspar. **b** Sodium clinopyroxene. **c** Sodium amphibole. **d** Fluorite. **e** Bastnäsite. **f** Calcite



L + S type yield daughter phase homogenization T in the range 300–400 °C. Because most of these daughter minerals are sulfate phases with very low solubilities, their precipitation took place immediately after trapping under decreasing T and P. V-L inclusions in fluorite have much lower salinities (0.9–1.4-wt% NaCl equivalent, determined for nine samples) in comparison to those in bastnäsite (8.8–16.2-wt% NaCl equivalent; 28 samples).

Discussion

Above, we presented new data on the field relations, mineralogy, geochemistry, and age of REE-mineralized assemblages in the Dagudao section of the Maoniuping deposit. We identified several previously unrecognized mineralogical and trace-element characteristics of these rocks that warrant a detailed discussion in the context of the current understanding of the MD belt, as well as our own ideas about the development of REE mineralization in carbonatite-related REE deposits.

Provenance and evolution of mineralizing fluids

The new field and mineralogical (EMPA and fluid-inclusion) evidence presented above clearly indicates the continuity of hydrothermal processes in the currently mined Dagudao section of the Maoniuping deposit. The three types of ferromagnesian silicates making up the bulk of the mineralized vein system (mica, clinopyroxene, and amphibole) all cover a wide compositional range. In particular, the Fe-rich mica of generation 1 (biotite) gives way to a more Mg-F-rich variety (fluorophlogopite) towards the final stages of ore deposition (generation 2 associated with bastnäsite). Aegirine ($\text{Ae}_{69-98}\text{Di}_{2-26}\text{Hd}_{0-3}\text{Jh}_{0-2}$) is a common clinopyroxene in the bottom unit, but was not observed at higher levels, where clinopyroxenes show more Ca-Mg-rich compositions (aegirine-augite, $\text{Ae}_{27-40}\text{Di}_{38-46}\text{Hd}_{19-24}\text{Jh}_3$). Thus, clinopyroxenes exhibit an evolutionary trend of Ca-Mg enrichment (with a concomitant decrease in the proportion of Na, Fe, and Mn) upwards. Magnesio-arfvedsonite (transitional to ferriwinchite) is common in the bottom unit of the Dagudao section, whereas in the top unit, the predominant amphibole is fluorrichterite.

Again, the general trend of compositional evolution is from Na-Fe-Mn-rich amphibole to Ca-Mg-F-rich species. Thus, our preliminary data suggest that from the bottom unit upwards, the composition of major ferromagnesian silicates changes systematically by becoming enriched in Ca, Mg, and F at decreasing Na, Fe, and Mn contents. However, further sampling and analyses are desirable to confirm this observation.

Phlogopite, sodium clinopyroxenes, and amphiboles contain very low levels of REE (< 150 ppm; Reguir et al. 2009, 2012) and, hence, cannot be used to track the behavior of these elements in the studied vein system. Calcite, fluorite, and bastnäsite, on the other hand, account for the bulk of REE in these veins and, thus, can provide further useful insights regarding the provenance and evolution of mineralizing fluids. All three minerals are enriched in light lanthanides relative to heavy lanthanides and Y, but bastnäsite is much more remarkable [$(\text{La}/\text{Yb})_{\text{cn}} \approx 100,000$] than either calcite or fluorite [$(\text{La}/\text{Yb})_{\text{cn}} \approx 47$ and 10, respectively]. These minerals also exhibit moderate depletion in Eu, but bastnäsite has an appreciably lower Eu/Eu^* value (0.54 ± 0.03) than the other two minerals ($\text{Eu}/\text{Eu}^* \approx 0.8$ for both). Importantly, the bulk-rock data for the wall-rock syenites in the Dagudao section are also characterized by light REE enrichment and Eu depletion [$(\text{La}/\text{Yb})_{\text{cn}} = 245 \pm 145$, $\text{Eu}/\text{Eu}^* = 0.84 \pm 0.04$; Fig. 11]. The chondrite-normalized REE profiles of the examined vein calcite are visually similar to those of igneous calcite from carbonatites (Fig. 7b), but the latter generally lacks Eu anomalies (Chakhmouradian et al. 2016). The strong positive Y anomaly in the Dagudao fluorite is complemented by a negative anomaly in the calcite (Fig. 11), whereas no anomaly is observed in the syenites or bastnäsite, which show chondritic Y/Ho ratios (28.7 ± 1.5 , and 27.8 ± 1.3 , respectively). The observed variations clearly arise from decoupling between Y and Ho on the one hand and between Eu and the rest of the lanthanides on the other, in the course of fluid evolution. These processes could be best explained by different speciation

behavior of Y and Eu relative to other REE in aqueous systems (Bau and Dulski 1995; Bach et al. 2003; Loges et al. 2013). Burbankite (Na-Ca-Sr-REE carbonate) with a negative Eu anomaly was reported in inclusions representing trapped carbonatite-derived fluids at Kalkfeld, Namibia, by Bühn and Rankin (1999). The composition of its parental fluid, reported by Bühn and Rankin (1999), is characterized by extreme enrichment in light REE [up to $(\text{La}/\text{Yb})_{\text{cn}} = 116$], moderate depletion in Eu and chondritic (or higher) Y/Ho ratios. Bastnäsite is one of the latest phases to crystallize in the Dagudao veins, but relative Eu depletion in this mineral is not accompanied by decoupling of Y from Ho (Table 2), whereas the other two REE carriers (fluorite and calcite) show mutually complementary Y-Ho patterns (Fig. 11). It is thus plausible that simultaneous precipitation of calcite and fluorite (in a proportion of ~ 10:1) maintained the initially chondritic Y/Ho value in their parental fluid. Because the Eu/Eu^* values of these two minerals are similar and consistently below the chondritic value (~ 0.8), their crystallization would have produced progressive enrichment in Eu in the evolving fluid, which is difficult to reconcile with the much lower Eu/Eu^* ratios in bastnäsite (~ 0.5). There are no other REE phases present in the veins that would conceivably compensate for the observed Eu deficiency. Hence, we conclude that the mineralizing fluid was inherently depleted in Eu, with a Eu/Eu^* value somewhere between 0.53 and 0.58. Recent experimental data show that there are no significant differences between heavy and light REE in partitioning behavior between carbonatitic melts and halogen-bearing fluids (Song et al. 2016). In contrast to the Dagudao syenites, carbonatites from Maoniuping (Wang et al. 2001; Xu et al. 2003; Hou et al. 2006) show much less lanthanide fractionation, i.e., lower $(\text{La}/\text{Yb})_{\text{cn}}$ values (< 100 and on average, 65; Fig. 11). Hence, it seems unlikely that the light REE-enriched, but relatively Eu-depleted mineralizing fluid that produced the Dagudao vein system could derive from a carbonatitic source. Silica-oversaturated melts, on the other hand, are capable of producing fluids characterized by extreme enrichment in light REE and negative Eu anomaly (Lukanin and Dernov-Pegarev 2010).

Our fluid-inclusion data show that silicate assemblages in the selvages of mineralized veins crystallized over a much wider range of T (220–260 °C) in comparison to the non-silicate phases in their axial zones (120 °C for fluorite and 60 °C for calcite). Also, the fluorite, calcite, and bastnäsite crystallized at lower T (≤ 240 °C) than the early generations of K-feldspar, clinopyroxene, and amphibole, in which the majority of inclusions homogenize at $T > 230$ °C (Fig. 10). Our results for fluorite and bastnäsite are in agreement with the data presented for the Guangtoushan section by Xie et al. (2015), who also reported a similar range of homogenization T (140–250 °C) for barite. The continuity of thermometric data for the silicate minerals is

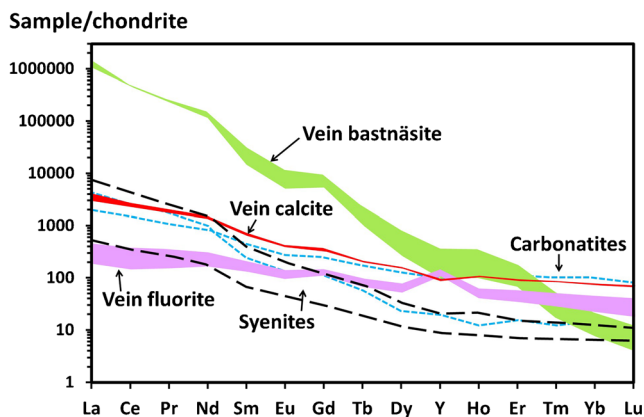


Fig. 11 Comparison of REE distributions (normalized to CI values of Anders and Grevesse 1989) in calcite (red), fluorite (purple), bastnäsite (green), and syenite (black dashed line) from the Dagudao section. The compositional range of carbonatite from Maoniuping (Wang et al. 2001; Xu et al. 2003; Hou et al. 2006) is shown for comparison (blue dotted line)

consistent with the wide compositional ranges exhibited by sodium clinopyroxene and amphibole.

To summarize, the cumulative petrographic, fluid-inclusion and chemical evidence shows that mineralizing fluids at Dagudao evolved from initially high-Na-Fe compositions capable of precipitating K-feldspar, aegirine and magnesioarfvedsonite at 230–400 °C to progressively more Ca-Mg-F-rich derivatives at lower temperatures, eventually producing F-sulfate-carbonate residua that deposited barite, fluorite, and calcite. Because none of the early-crystallizing minerals have much structural capacity for REE, these elements were concentrated in the late-stage fluid, as manifested by their high levels in calcite and fluorite (Fig. 11). Extreme REE enrichment in continuously active fracture systems facilitated the deposition of large quantities of bastnäsite at higher levels in the Dagudao section (Fig. 5). These data seem in disagreement with the very low solubility of bastnäsite in F-carbonate-rich fluids (Gysi and Williams-Jones 2015). Chlorine was not detected in any of the ferromagnesian silicates analyzed in the present work. This element is expected to partition into ferromagnesian micas in equilibrium with K-feldspar, muscovite, albite and a high-T Cl-bearing fluid (Zhu and Sverjensky 1991). In previous experimental work and empirical modeling studies, chloride is important for the transport of REE in the ore-forming fluids (Lehmann et al. 1994; Migdisov et al. 2009, 2014; Williams-Jones et al. 2012). In this study, available salinity measurements for V-L inclusions also indicate that Cl^- activity remained not low (9–16-wt% NaCl) until the deposition of bastnäsite. That's much more than any possible F^- concentration in a Ca-bearing environment. These data suggest the prevalent role of Cl^- complexes in REE transport, which is also consistent with the case studies for REE-bearing metallic deposits and their models, such as Sin Quyen Deposit in Northwestern Vietnam (Li and Zhou 2018) and Bastnäs-type deposits in Sweden (Holtstam et al. 2014). Based on the mineralogical evidence, barite, fluorite, calcite, and bastnäsite often form stable mineral assemblages and bastnäsite commonly formed later than these gangue minerals and others. Then, we conclude that fluorine, sulfate, chloride, and CO_3^{2-} complexes were the principal REE carriers in the Dagudao ore system. Naturally, a gradual increase in Ca and Ba concentration in the fluid with decreasing T led to the deposition of fluorite, barite and calcite, probably breakdown of REE complexes and development of bastnäsite mineralization.

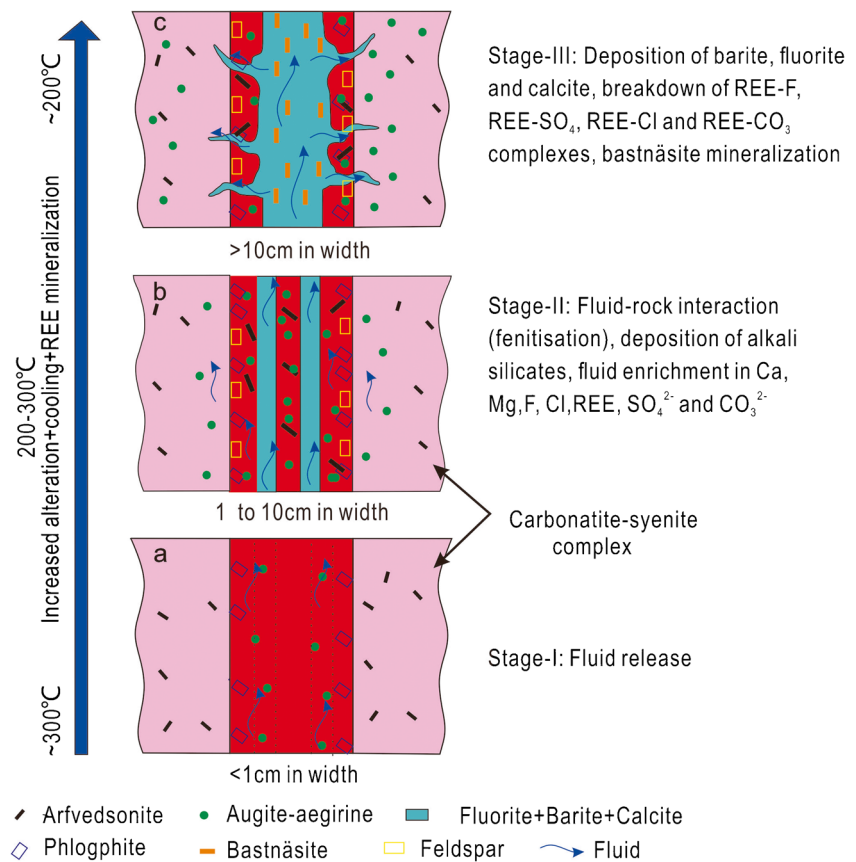
Preliminary model for the development of the Dagudao orebody

Although a number of models have been proposed for the MD REE deposits on the basis of fluid-inclusion data (Xie et al. 2015), field, and geochemical evidence (Hou et al. 2015; Liu and Hou 2017), the development of complex REE-bearing vein systems in these deposits received little attention. Here, we synthesize the previously published and new findings to

propose a new model for the high-grade Dagudao section of the Maoniuping deposit (Fig. 12). The development of the Anninghe River structure and associated strike-slip faulting within the study area controlled the emplacement of carbonatite-syenite complexes beginning in the Late Oligocene. Along the MD belt, tectonic activity and associated mantle-derived magmatism spanned some 15 Ma, culminating with the formation of the Dagudao orebody in the Maoniuping deposit ca. 26 Ma (Fig. 2; Liu and Hou 2017; Liu et al. 2015a, b, c). In this work, we analyzed fluorophlogopite that is intimately associated with bastnäsite (see above) to further constrain the timing of REE deposition. The ^{40}Ar - ^{39}Ar age of 26.4 ± 1.2 Ma is in excellent agreement with recently published data, indicating that the development of REE mineralization was essentially coeval with the emplacement of the syenite. In the Maoniuping area, this activity provided passageways for magmas and, at shallower crustal levels, for fluids derived from these magmas.

In the Dagudao area, fluids were channeled along an extensive (~1 km along strike) NNE-SSW system of fissures, which now hosts the mineralized vein system (Figs. 3 and 4). The veins developed in the coeval syenites and have no obvious connection to carbonatite bodies, at least at the current level of exposure. We identify three major stages in the formation of REE mineralization. At stage I, ascending silicate magmas experienced volatile overpressure (probably due to both decompression and retrograde boiling caused by the crystallization of quartz, feldspar, and aegirine-augite), generating orthomagmatic fluids that explored and expanded the existing fissure system (Fig. 12a). A drop in volatile content of the parental magma (crystal mush?) would raise its solidus T, facilitating further solidification. Along fluid passageways, wall-rock syenites were fenitized to an assemblage of albite, muscovite, phlogopite, and aegirine. At this stage, the fluids still had appreciable capacity to transport REE and, consequently, no major mineralization developed. The earliest minerals to precipitate in the veins were K-Na silicates either devoid, or containing relatively low levels, of F. This caused depletion of the fluid in alkalis and Fe and progressive enrichments in Ca, Mg, F, Cl, REE, sulfate, and carbonate at stage II (Fig. 12b). As the ascending fluids cooled, they reached the limits of solubility for CaF_2 , BaSO_4 , and CaCO_3 , triggering the deposition of fluorite, barite, and calcite in fractures that had not yet been “choked” with earlier-crystallized material. None of the minerals in the vein infill show evidence of deformation, which suggests that faulting ceased prior to this stage, i.e., no new fracture networks developed. If the fluids were derived from silica-oversaturated magma, we can expect that their $(\text{La/Yb})_{\text{cn}}$ ratio was initially higher than in the source and in the consanguineous syenites (Lukanin and Dernov-Pegarev 2010). Voluminous deposition of fluorite and calcite, which both have lower $(\text{La/Yb})_{\text{cn}}$ values, and also of barite, further raised the concentration of light lanthanides, while simultaneously stripping the fluid of complexing ligands [F^- , $(\text{SO}_4)^{2-}$, Cl^- , and $(\text{CO}_3)^{2-}$]. The loss

Fig. 12 Three-stage conceptual model for the development of the mineralized vein system at Dagudao (see text for details)



of these anions and decreasing temperature for the ore-forming fluids severely diminished the transporting capacity of the fluid, triggering bastnäsite precipitation. The absence of daughter phases in aqueous inclusions hosted by this mineral indicates that the residual liquid was no longer saturated with respect to sulfates (Xie et al. 2009; Liu and Hou 2017), lending further support to its crystallization in the waning stage of fluid activity (stage III, Fig. 12c).

Obviously, the schematic diagram shown in Fig. 12 does not reflect either the three-dimensional character or the apparent continuity of vein development and associated processes. The wide range of compositions observed in the micas, clinopyroxenes, amphiboles, and fluorite (in terms of REE abundances) and their long crystallization span (recorded by inclusion homogenization T) indicate that some fissures remained open throughout the entire period of fluid activity. It remains to be determined whether the processes that gave rise to the Dagudao orebody represented a single pulse of hydrothermal activity or perhaps several pulses and, if the latter, their sources also need to be constrained. Could the mineralogical complexity, such as observed in the present work, originate from a discrete, evolving magma body, or did it require contributions from external sources? A careful study of stable-isotope distributions ($\delta^7\text{Li}$ in amphiboles and micas, $\delta^{34}\text{S}$ in barite and sulfides, $\delta^{44}\text{Ca}$ in fluorite and calcite) and mineral zoning (particularly, trace-element variations) will be required to answer these questions.

Conclusions

- (1) Three units can be recognized in the Dagudao REE orebody at Maoniuping; from the bottom unit upwards, stockworks of veinlets grade into thick (up to 12 m in width) veins that host the bulk of bastnäsite mineralization. The mineralized veins are invariably zoned; from the contact inwards, biotite- and K-feldspar-rich selvages are followed by zones dominated by sodium clinopyroxene, sodium amphibole, and a “core” composed predominantly of barite, fluorite, calcite, and bastnäsite.
- (2) The ferromagnesian silicates in the veins show a wide compositional variation; their earlier generations are enriched in Na and Fe (magnesio-arfvedsonite transitional to ferriwinchite, aegirine, biotite), whereas later-crystallized varieties in Ca, Mg, and F (fluorrichterite, aegirine-augite, fluorphlogopite). Although bastnäsite is the principal REE carrier in the mineralized veins, significant quantities of these elements are hosted by fluorite and calcite; all three minerals are enriched in light REE relative to heavy lanthanides and show moderate depletion in Eu.
- (3) Mineralizing fluids likely derived from the syenites and were channeled along a system of fissures produced by NNE-SSW strike-slip faulting. Aqueous fluid inclusions hosted by major constituent minerals in the veins

homogenize over a wide T range; K-feldspar, clinopyroxenes, and amphiboles give a wider range of homogenization T extending to higher values (~ 400 °C) in comparison to fluorite, calcite, and bastnäsite (typically 150–200 °C). REE transporting capability of the fluid (s) was due to the presence of F^- , $(SO_4)^{2-}$, $(CO_3)^{2-}$, and Cl^- complexing ligands. Fluid cooling and precipitation of fluorite, barite, and calcite triggered widespread deposition of bastnäsite in the final stage of fluid evolution.

- (4) $^{40}Ar/^{39}Ar$ dating of fluorophlogopite associated with bastnäsite gave an age of 26.4 ± 1.2 Ma; this value is in agreement with the previously published data for other minerals, providing further support to the temporal association between the emplacement of syenites and the development of mineralized vein system at Dagudao.

Acknowledgments We are grateful to Editor Bernd Lehmann for his encouragement, patience, and helpful suggestions and to Associate Editor Ruizhong Hu and anonymous referees for their constructive criticisms on the earlier versions of this manuscript.

Funding information The present study was funded by the Natural Sciences Foundation of China (grant no. 41772044), Chinese State Key Research and Development Program (2016YFE0203000), Fundamental Research Funds for the Chinese Academy of Geological Sciences (YYWF201705), China Geological Survey (1212011020000150011-03), and Canada-China Scholars' Exchange Fund.

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