



Geochemical and mineralogical characteristics of weathered ore in the Dalucao REE deposit, Mianning–Dechang REE Belt, western Sichuan Province, southwestern China



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ABSTRACT

The Dalucao deposit in western Sichuan Province, southwest China, is one of the largest and most extensive rare earth element (REE) deposits in the Himalayan Mianning–Dechang REE Belt. Moreover, this is the only deposit identified in the southern part of the belt. The deposit contains the No. 1, 2, and 3 orebodies. The No. 1 and 3 orebodies are hosted in two breccia pipes within syenite–carbonatite rocks that intrude a Proterozoic quartz–diorite pluton. Both breccia pipes have elliptical horizontal cross-sections at the surface, being 200–400 m long, 180–200 m wide, and extending to >450 m depth. The No. 1 and No. 3 orebodies have total thicknesses of 55–175 m and 14–58 m, respectively. REE mineralization is associated with four brecciation events that are recorded in both pipes. The ore grades in the No. 1 and 3 orebodies are similar, with the rocks containing 1.0–4.5% rare earth oxides (REOs). The No. 1 orebody is characterized by a mineral assemblage comprising fluorite + barite + celestite + bastnäsite (i.e., Type I), whereas the No. 3 orebody is characterized by an assemblage comprising fluorite + celestite + pyrite + muscovite + bastnäsite + strontianite (i.e., Type II). Significant amounts of weathered high-grade REE ore (up to 60 wt.% of the rock mass) is mainly present in the No. 1 orebody. This is the main ore-type targeted for exploration within the Dalucao deposit, but is rarely present in other deposits in the Mianning–Dechang REE Belt.

Faulting and cryptoexplosive breccia events, possibly linked to movement on the Panxi Fault, were more common in the No. 1 orebody than in the No. 3 orebody. This facilitated the introduction of ore-forming hydrothermal fluids and provided space for the precipitation of REE minerals. Based on the present results, we infer that the Dalucao deposit was the product of multiple stages of ore formation. REE minerals formed in envelopes around, or fractures within, quartz, fluorite, calcite, barite, and celestite in the brecciated ores. The main REE minerals were deposited from hydrothermal fluids within cryptoexplosive breccia, followed by weathering that increased the ore grade. Petrographic studies and X-ray powder diffraction (XRD) analyses indicate that the weathered ore contains 5–60% REE minerals (including bastnäsite, parisite, and monazite), together with gangue (quartz, barite, celestite, and fluorite), large amount of clay minerals (smectite, illite, kaolinite, and sepiolite), and relict igneous minerals (quartz, albite, and K-feldspar). The weathered samples are strongly enriched in La (up to 92,390 ppm), Ce (up to 103,500 ppm), Pr (up to 8006 ppm), and Nd (up to 16,690 ppm) compared with the unweathered brecciated ores. Conversely, Sr concentrations are significantly more enriched in the brecciated ores (up to 256,500 ppm) than in the weathered ores (generally less than 2671 ppm with one exception of 37,850 ppm) due to less celestite. Calcite is largely absent from the weathered ores (except one sample with up to 30% mode), which contrasts with the brecciated ores that contain up to 75% calcite. The effects of weathering, oxidation, loss of ions, and hydration on the brecciated ores led to the refertilization of the REEs and an increase in the grade of the ore deposit.

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1. Introduction

The Mianning–Dechang REE Belt in western Sichuan Province, southwestern China, hosts several REE deposits, including the Dalucao deposit (0.76 Mt rare earth oxides (REO); Shi and Li, 1996), the

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Maoniuping deposit (1.2 Mt REO; Yuan et al., 1995), and the Muluoizhai (0.45 Mt REO; Tian, 2005) and Lizhuang deposits.

Different types of REE have been reported in the world, such as Zr–REE–Nb mineralization associated with highly evolved alkaline granite in Baerzhe (Yang et al., 2014) and a IOCG deposit (Fe–Cu–(REE)) in Yinachang in southwest China (Li et al., 2015). An association between carbonatites and syenites in the formation of hydrothermal REE deposits has long been recognized (e.g., Eby, 1975; Bai and Yuan, 1985; Williams-Jones et al., 2000; Hou et al., 2009; Xie et al., 2009; Xie et al., 2015; Liu et al., 2015a,b). Much less studies have proposed carbonatite-hosted REE ore deposit models, although some mineral systems associated with carbonatites have been reported (Pirajno, 2015). However, few studies have examined and identified the processes involved in the formation of brecciated and/or hydrothermal REE deposits, such as those found in the Gallinas Mountains of New Mexico and the Dalucao deposit in Sichuan Province (Williams-Jones et al., 2000).

Furthermore, almost no studies have been published on the genesis of high-grade weathered ores associated with hydrothermal REE deposits. This type of REE mineralization is developed extensively in the Dalucao REE deposits, which are located in a syenite–carbonatite complex in the Himalayan Mianning–Dechang REE Belt, western Sichuan Province, southwestern China.

Globally, weathered REE ores are an important ore type found in all high-grade deposits, such as the Tomtor REE deposits in northern Siberia with an REO grade of 8–31% (Kravchenko and Pokrovsky, 1995) and at Araxa and Catalao in Brazil with REO grades of 10–11% and 12%, respectively (Orris and Grauch, 2002). Recently, a REE deposit was found in a paleo-weathered succession in western Guizhou, China (Zhou et al., 2013). These weathered REE ores were hosted by carbonatite, sedimentary rock, and granite (Kynicky et al., 2012).

These are different to the weathered ores in the Dalucao deposit, where the high-grade ores are associated with large-scale weathering of brecciated ores within a syenite–carbonatite complex. Despite the occurrence of high-grade REE ores in the Dalucao deposit, no comprehensive studies have been published on the genesis of this particular type of REE mineralization. This has limited our understanding with respect to the relationships between the host rocks, brecciation events, and subsequent weathering in the formation of high-grade REE deposits.

In this study, we present petrographic, geochemical, and mineralogical data for the weathered ores and propose a model for its formation.

2. Geological setting of the Mianning–Dechang REE Belt

The geology of the Himalayan Mianning–Dechang (MD) REE Belt, and of the Dalucao deposit, have been described by Hou et al. (2009). The MD REE Belt is located in western Sichuan Province, southwestern China, on the western margin of the Yangtze Craton (Fig. 1; Hou et al., 2009). Basement rocks comprise Archean high-grade metamorphic and Proterozoic metasedimentary rocks, which are overlain by Phanerozoic clastic and carbonatite sequences (Cong, 1988; Luo et al., 1998). The Emeishan mantle plume led to the formation of the Panxi Rift (Fig. 2), which consists of a series of faults, a Permian paleo-rift zone that hosts the Mianning–Dechang REE Belt (Cong, 1988; Zhang et al., 1988), bauxite deposits in western Guangxi (Deng et al., 2010a), and the Beiya orefield (Deng et al., 2010b).

In eastern Tibet, late-collisional metallogenesis (ca. 40–26 Ma) developed in structures dominated by Cinozoic strike-slip faulting, shearing, and thrusting, which produced one of the most economically significant metallogenic provinces in China (Fig. 1). The REE mineralization is associated with carbonatite–syenite complexes in the MD Belt and constitutes one of the four significant metallogenic events in the

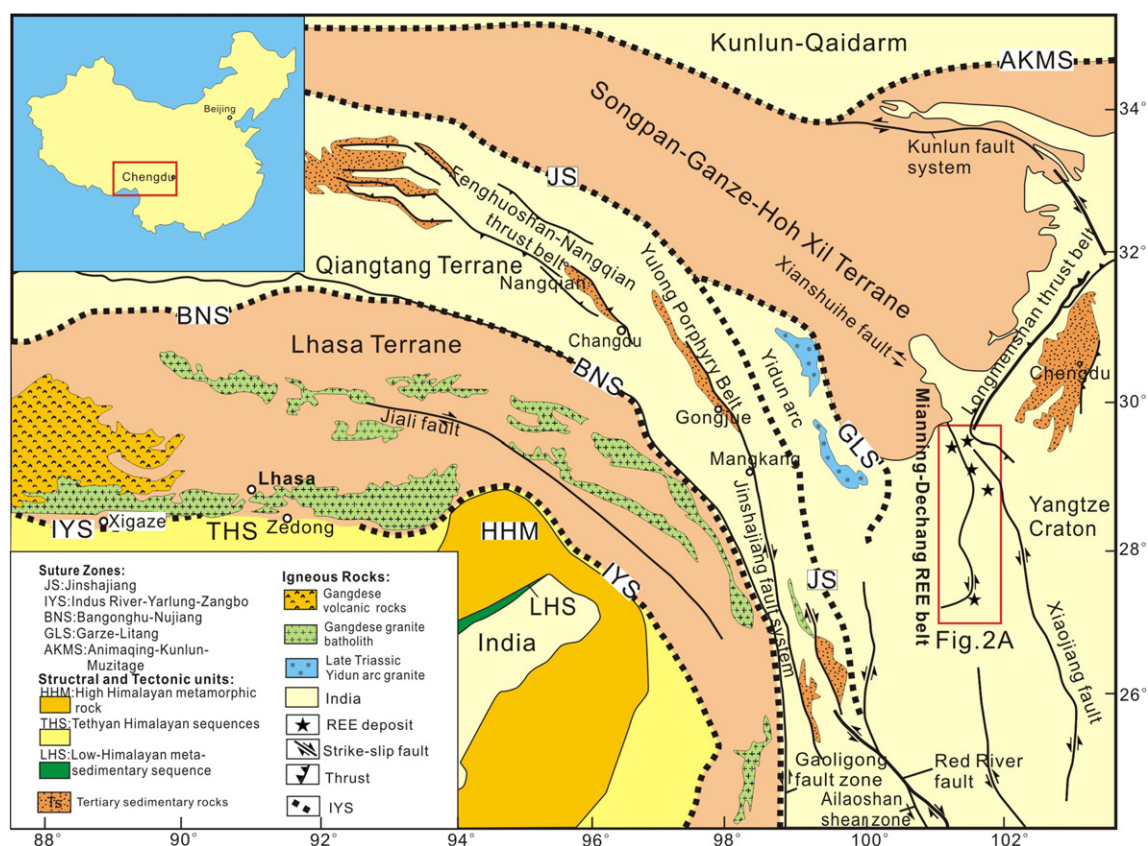


Fig. 1. Simplified tectonic map of the Himalayan–Tibetan orogen. Modified after Yin and Harrison (2000) and Hou et al. (2003).

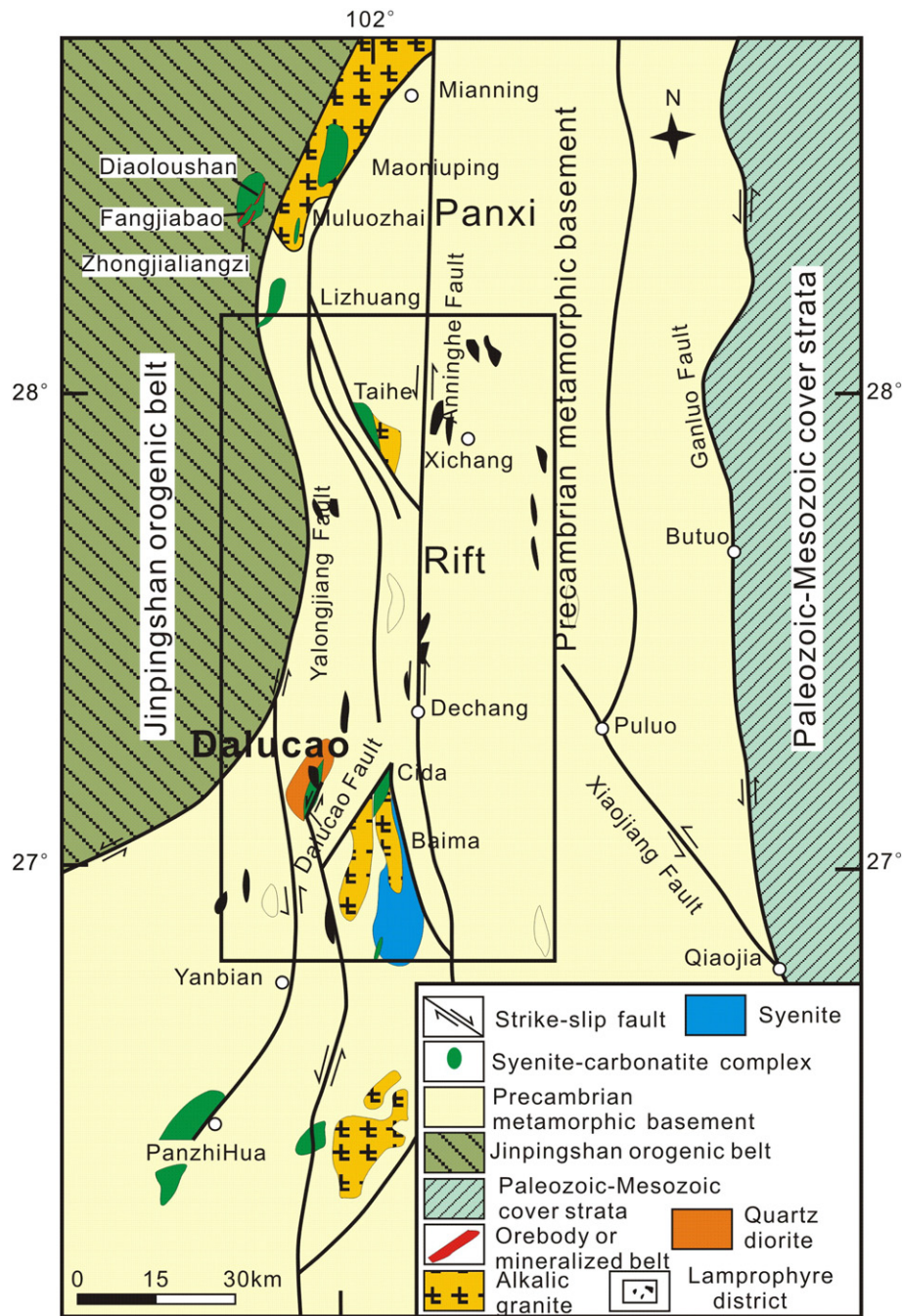


Fig. 2. Sketch tectonic map showing distribution of the Himalayan carbonatite-alkalic complexes controlled by reactivated faults in western Sichuan. Modified from Yuan et al. (1995).

study area; the other three include (1) porphyry-type Cu–Mo–Au systems controlled by Cainozoic strike-slip faults, (2) orogenic-type Au systems related to sinistral ductile shearing (Deng et al., 2015) and (3) Pb–Zn–Ag–Cu systems controlled by Cainozoic thrusting and subsequent strike-slip faulting (Hou and Cook, 2009; Deng et al., 2014a, 2014b).

The Mianning–Dechang REE Belt, which is up to 270 km long and 15 km wide, is one of the most economically significant mining areas in China. The belt hosts a single giant deposit (Maoniuping), one large deposit (Dalucao), two medium-sized deposits (Muluozhai and Lizhuang), and numerous smaller mineralized carbonatite–syenite complexes (Fig. 2). The Dalucao deposit is located in the southern part of the belt, whereas the Lizhuang, Muluozhai, and Maoniuping deposits

are located in the northern part (Fig. 2). The geochemical features of the host rocks and the types of REE mineralization in the MD REE Belt are similar to other REE deposits associated with rift zones. Rift zone environments are, therefore, key tectonic settings for carbonatite–syenite hosted REE mineralization.

The ages of the REE deposits in the MD REE Belt have been determined from isotope and mineralogical studies. In the Lizhuang deposit, for example, Ar–Ar dating of biotite and Re–Os dating of molybdenite yield mineralization ages of 30.55 ± 0.5 Ma and 28.5 Ma (model age), respectively (Tian et al., 2008a,b). For the Muluozhai deposit, Ar–Ar dating of phlogopite yielded a REE mineralization age of 35.5 ± 0.5 Ma (Tian et al., 2006). For the Maoniuping deposit, Re–Os dating of biotite from bastnäsite–aegirine–augite–fluorite–barite and bastnäsite–

barite–calcite veins yielded ages of 40.3 and 27.8 Ma, respectively (Yuan et al., 1995). Precise ages of the syenites in the Dalucao, Lizhuang Maoniuping, and Diaoloushan regions of the MD REE Belt have been determined by U–Pb zircon dating (Liu et al., 2015a). For the Dalucao deposit, these yielded concordant ages of 12.13 ± 0.19 and 11.32 ± 0.23 Ma, for the Lizhuang deposit 27.41 ± 0.35 Ma, for the Muluozechai deposit 26.77 ± 0.32 Ma, and for the Maoniuping deposit 22.81 ± 0.31 and 21.3 ± 0.4 Ma. The slight difference between the two ages for each deposit is believed to be related to hydrothermal alteration of the host syenite (Liu et al., 2015a). REE mineralization ages along the entire MD REE Belt were also acquired by LA–ICP–MS analyses of bastnäsite, which produced similar ages to the U–Pb ages for zircons from the syenite intrusions in the region (Yang et al., 2014). Argon ($^{40}\text{Ar}/^{39}\text{Ar}$) dating of hydrothermal muscovite intergrown with REE minerals in typical ores from the No. 1 and 3 orebodies in the Dalucao deposit yielded similar ages of 12.69 ± 0.13 and 12.23 ± 0.21 Ma, respectively, indicating that the mineralization in both orebodies formed coevally (Liu et al., 2015b). Furthermore, these ages are similar to the crystallization ages of the Dalucao syenite and carbonatite (Tian et al., 2008a; Liu et al., 2015a,b).

Both the No. 1 and No. 3 orebodies of the Dalucao deposit are hosted by breccia pipes in the same syenite–carbonatite complex, and both contain fine-grained REE minerals (0.2–2.0 mm in diameter). Petrographic studies suggest that the REE minerals occur mainly within fractures in or around quartz, fluorite, calcite, barite, and celestite (Liu et al., 2015a). Based on the geological characteristics of the ore–vein systems and the types of mineralization in the Mianning–Dechang REE Belt, it is assumed that the Dalucao deposit, located in the uppermost levels of the belt, and the Maoniuping and Lizhuang deposits, located in the middle and lowermost levels of the belt, represent different levels of similar ore deposits (Fig. 18 in Hou et al., 2009).

Previous research on the syenites and carbonatites in the Dalucao, Maoniuping, and Lizhuang deposits revealed that they contain high concentrations of total REEs (syenites = 63–3656 ppm; carbonatites = 2910–9741 ppm; Hou et al., 2006). Overlapping emplacement ages of the spatially associated syenites and carbonatites, together with similar Sr–Nd isotope compositions and mantle-normalized trace element patterns, suggest that liquid immiscibility played a role in their differentiation and origin (Hou et al., 2006; Hu et al., 2012).

In a previous study, the REE mineralization in the Dalucao deposit was thought to be related to the carbonatites (Xu et al., 2008). However, while the REE deposits in the MD REE Belt are hosted within syenite–carbonatite complexes, the potential for syenite involvement in the formation of these deposits has not been considered. Consequently, the relative contributions of syenite and carbonatite to the REE mineralization are unclear. In addition, although the presence of weathered ores has been mentioned in a previous study (Hou et al., 2009), the genesis of the weathered high-grade ore has not been studied in detail.

Worldwide, weathered ore is a distinct type of ore found in all high-grade REE deposits, such as the Tomtor REE deposits in northern Siberia with an REO grade of 8%–31% (Kravchenko and Pokrovsky, 1995), and Araxa and Catalao I in Brazil with REO grades of 10%–11% and 12%, respectively (Orris and Grauch, 2002). Recently, a REE deposit was found in paleo-weathering sedimentary crust in western Guizhou, China (Zhou et al., 2013). These weathered REE ores are hosted in carbonatite, sedimentary rock, and even in weathered granite (Kynicky et al., 2012), and they are different to the weathered ore in the Dalucao deposit, which is closely related to brecciated ores and a syenite–carbonatite complex.

The carbonatites and syenites across the Mianning–Dechang REE Belt are believed to have been generated by partial melting of subcontinental lithospheric mantle, which was metasomatized by Li-rich fluids derived from subducted oceanic crust and marine sediments (Tian et al., 2015). Furthermore, the ascent of asthenospheric mantle diapirs (types EM-I and EM-II) in the Cainozoic may have provided a thermal mechanism for the generation of the magmas that formed the

carbonatite–syenite complexes in the study area (Hou et al., 2006). Alternatively, the magmas may have been generated by decompression melting associated with a change from transpression to transtension at 27–11 Ma (Hou et al., 2006; Liu et al., 2015a).

The Dalucao deposit is hosted by a syenite–carbonatite complex that intrudes a Proterozoic quartz–diorite pluton that was exhumed by regional uplift and is now exposed over an area of 70 km² (Fig. 3). Jurassic sandstones are also exposed in the eastern part of this section of the MD REE Belt. The No. 1, No. 2, and No. 3 orebodies are hosted in two breccia pipes within the syenite–carbonatite complex and the No. 2 orebody is cut by post-mineralization strike–slip faulting (Fig. 3). Exposures of the No. 1 and No. 3 orebodies are elliptical in horizontal cross-sections with long-axis lengths of 200–400 m and short-axis lengths of 180–200 m. The breccia pipe in the No. 1 orebody is mineralized down to a depth of at least 450 m (the limit of drilling) with a total thickness that varies between 55 and 175 m (Fig. 4A). In the No. 3 orebody, mineralization extends downward for 180 m with a total thickness of 14 to 58 m (Fig. 4B; Yang et al., 1998).

The orebodies overprint a system of joints and fluorite–quartz veins in the quartz–diorite (Fig. 5). The veins and the orebodies are elongate and strike roughly perpendicular to the strike of the Dalucao strike–slip fault, which controlled the location of the Dalucao deposit (Fig. 2; Yang et al., 1998).

Four different breccia facies can be mapped (Fig. 6) based on the matrix and clasts of the breccias and crosscutting relationships among the various types of breccias. These facies indicate that the Dalucao Fault and its secondary faults, as well as the brecciation events, controlled REE mineralization by facilitating the circulation of ore-forming fluids and providing space for REE precipitation.

Some unaltered syenite and carbonatite is present around the Dalucao deposit although these rock types are generally strongly altered in the three orebodies (Figs. 3 and 7A). In the syenite, feldspars (albite and minor plagioclase) account for approximately 70% (mode) of the rock, with quartz accounting for 5–15% and muscovite 15%–25% (Fig. 7B–D). Mafic minerals include aegirine–augite, biotite, and amphibole, which collectively constitute less than 5% of the rock. Accessory minerals include apatite, zircon, allanite, and bastnäsite. In the syenite–carbonatite complex, fresh white carbonatite is composed mainly of calcite (80–90%) with small amounts of apatite, aegirine, aegirine–augite, biotite, quartz, arfvedsonite, and microcline (Fig. 7E). In the Dalucao deposit, altered pink or brown carbonatite is overprinted by bastnäsite, which has caused the surfaces and boundaries of the calcite grains to become indistinct (Fig. 7F).

Hydrothermal alteration halos occur around the veins in the syenite–carbonatite complex. Systematic sampling along a transect across the top part of the complex (within the top 6 m of the No. 1 orebody) (Fig. 8A) was undertaken to characterize the petrology of the zone of hydrothermal alteration. Optical microscopy observations of the samples reveal the gradual alteration of fresh feldspathic syenite (DL11-1 to DL11-8) to a biotite–sericite rock (DL11-8 to DL11-18). The K in the sericite and biotite was most probably derived from syenite- or carbonatite-related fluids. Thus, the high-temperature magmatic fluids are likely to have been K-rich, thereby promoting the formation of biotite (Liu et al., 2015b).

A close examination of the cross-section reveals that REE mineralization overprints the biotite–sericite alteration and the coarse-grained fluorite–quartz veins (Liu et al., 2015b). The REE mineralization along this cross-section is seen to as small veinlets within the syenite (Fig. 8A); the veinlets become wider with increasing depth. Large areas of the brecciated and altered syenite–carbonatite contain hydrothermal carbonate veins that host REE minerals (Fig. 8B and C).

Breccia ore is another main ore type in the Dalucao deposit, and it occurs in breccia pipes composed of syenite clasts, carbonate minerals, and accessory phases that include pyrite, fluorite, barite, celestite, muscovite, quartz, and REE minerals (Liu et al., 2015b). Based on the mineral assemblage, two types of breccia ores can be distinguished:

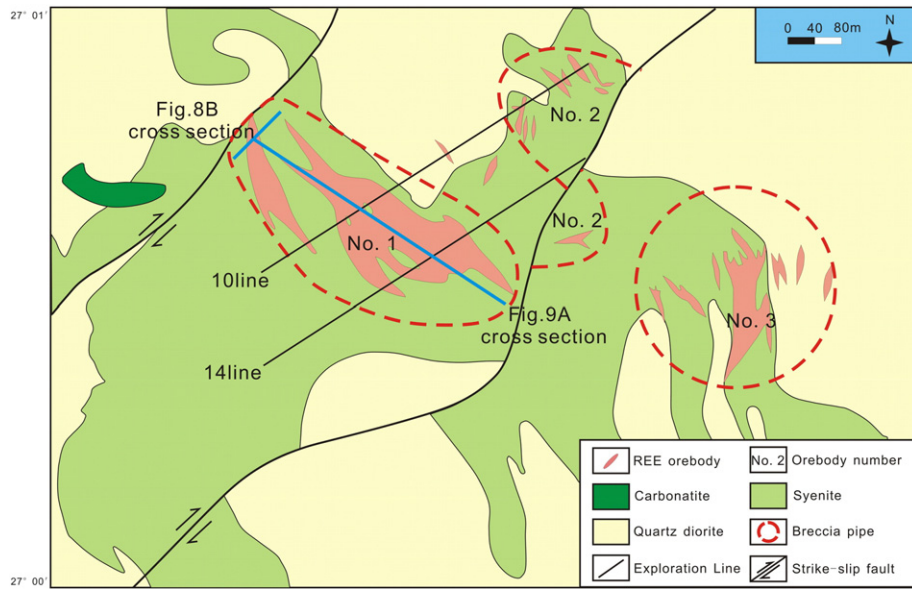


Fig. 3. Sketch geological map showing the features of the carbonatite-syenite complex and associated REE orebodies at Dalucao. Modified from Yang et al. (1998).

Type I ores occur primarily in the No. 1 orebody and are composed of barite + celestite + fluorite + bastnäsite, whereas Type 2 ores occur primarily in the No. 3 orebody and are composed of celestite + pyrite + muscovite + fluorite + bastnäsite + strontianite. The No. 1 and No. 3 orebodies are located in different breccia pipes. In the No. 3 orebody, hydrothermal carbonate veins containing REE minerals cross-cut pre-existing breccia assemblages, and therefore represent a further paragenetic stage of mineralization (Liu et al., 2015b). Shi and Li (1996) reported that ore in the No. 1 orebody contains 1.0–4.0% REO (based on

667 analyzed samples) and in the No. 3 orebody contains 1.0–4.5% REO (based on 194 analyzed samples).

3. Sampling and analytical methods

Fifteen weathered ore samples were selected from the No. 1 orebody for geochemical investigation. Weathered samples from DL11-3 to DL11-16 were selected along the cross section roughly perpendicular to the first platform in the No.1 orebody. Other weathered samples,

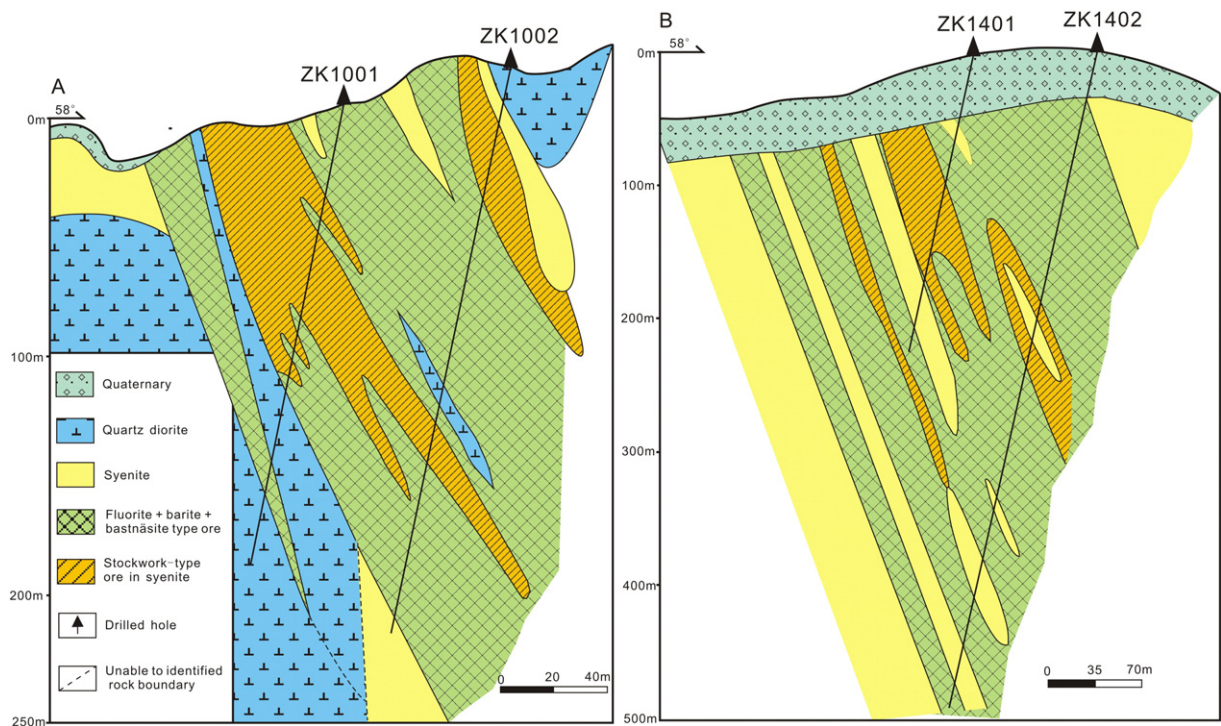


Fig. 4. Geological cross-sections along exploration lines 10 (A) and 14 (B) in the Dalucao REE deposit. Modified from Yang et al. (1998).

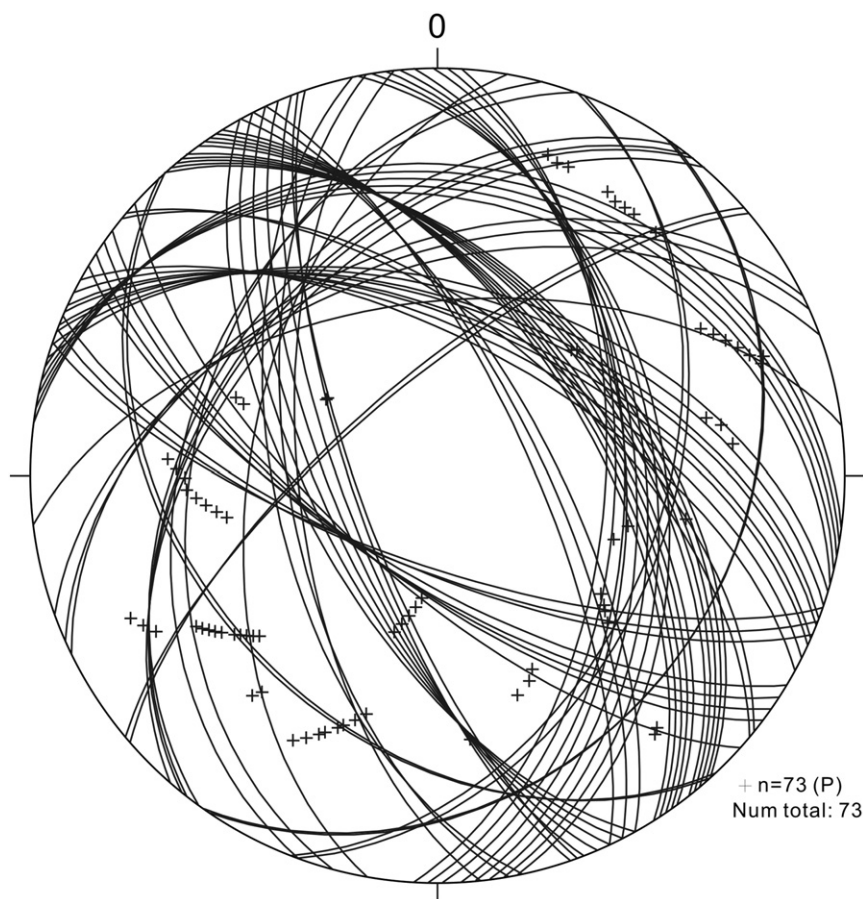


Fig. 5. Orientations of veins in the No. 1 and No. 3 orebodies in the Dalucao deposit. Modified from Yang et al. (1998).

including DL11-34, DL11-36, DL11-45, DL11-48, DL11-60, and DL11-70, were selected from the lower part of the orebody. In the orebody, the weathered samples are all very loose, and the weathered syenite, ores

and contact zone cannot be recognized. Major element compositions of minerals were analyzed using a JXA-8230 electron microprobe at the Institute of Mineral Resources, Chinese Academy of Geological

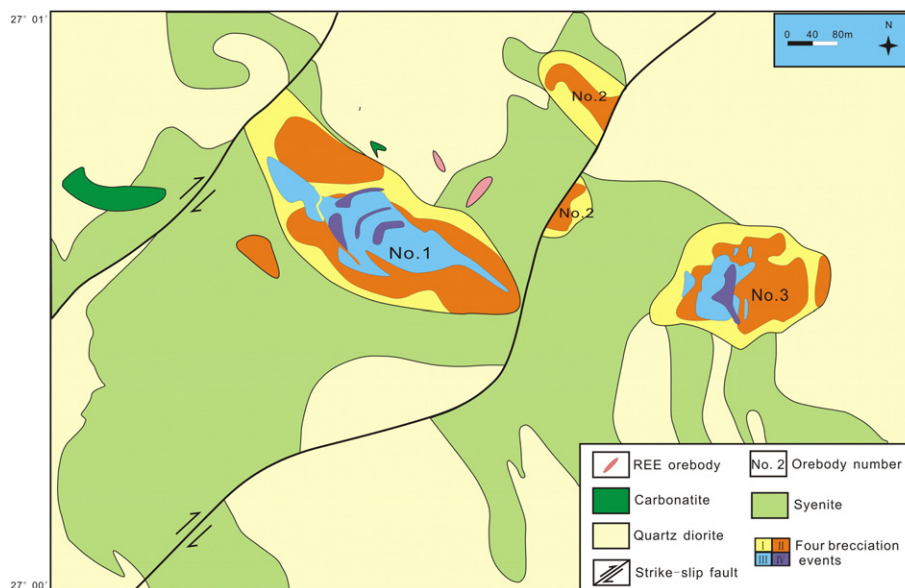


Fig. 6. Four different breccia facies mapped in the No. 1 and No. 3 orebodies in the Dalucao REE deposit. Modified from Yang et al. (1998).

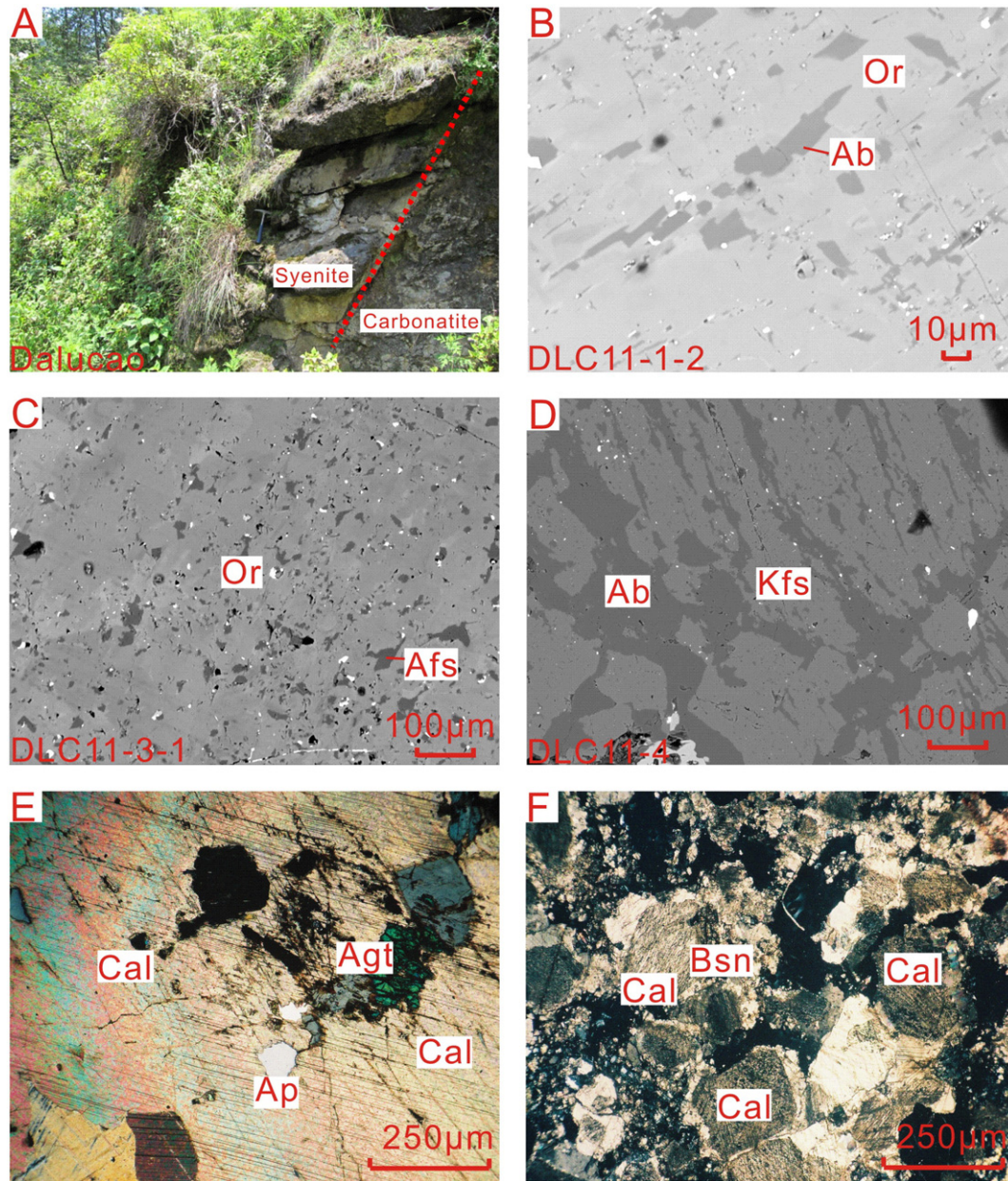


Fig. 7. A. Unaltered syenite and carbonatite with a close spatial relationship around No. 1 orebody in the Dalucao deposit. B. Unaltered anorthite with small grains of albite in fresh syenite. C. Unaltered anorthite with small grains of alkali feldspar in fresh syenite. D. Closely associated albite and K-feldspar in unaltered syenite. E. Photomicrograph showing fresh calcite, apatite, and pyroxene in unaltered carbonatite. F. Photomicrograph showing bastnäsite crystals replacing altered calcite in pink/brown altered carbonatite.

Sciences. Mineralized and barren syenite and carbonatite, and typical ore samples, were selected from both the No. 1 and No. 3 orebodies. A total of 43 samples were selected for systematic chemical analyses. Backscattered electron (BSE) images and mineral compositions were acquired at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), Beijing, China. The operating conditions were accelerating voltage of 15 kV for silicate and oxide, and 20 kV for sulfide, beam current of 20 nA and beam size of 5 µm. Natural minerals and synthetic oxides were used as standards. Matrix corrections were carried out using the ZAF correction program supplied by the manufacturer (Liu et al., 2015b). For the elements considered when minerals measured on EMP, the following standards and crystals were used: jadeite, NaKα, TAP; forsterite, MgKα, TAP; jadeite, AlKα, TAP; topaz, FKα, TAP; K-feldspar, K Kα, PETG; wollastonite, Ca Kα, jadeite, SiK, PETJ; hematite,

FeKα, LIF; rutile, TiKα, LIF; Apatite, PKα, PETJ; Cr₂O₃, CrKα, LIFH; MnO, MnKα, LIFH; NiO, NiKα, LIF; V₂O₅, VKα, LIFH; NaCl; ClKα, PETH. For other REE minerals, oxide minerals, synthetic five lanthanum phosphate, five cerium phosphate, five phosphoric acid praseodymium, five neodymium phosphate, five phosphoric acid samarium, five phosphate europium, five phosphoric acid gadolinium, five phosphoric acid gadolinium, five dysprosium phosphate, five phosphate holmium, five phosphate erbium, five phosphate thulium, five ytterbium phosphate, five phosphoric acid lutetium, five yttrium phosphate, barium titanate were used as standards. The XRD analyses of ore samples were performed at the China University of Geosciences, Beijing, using Rigaku D/Mac-RC and CuKα1 radiation with a graphite monochromator and continuous scanning under the following operating conditions: voltage of 40 kV, beam current of 80 mA, scanning speed of 8°/min, slit of DS = SS = 1°, ambient temperature of 18 °C, and

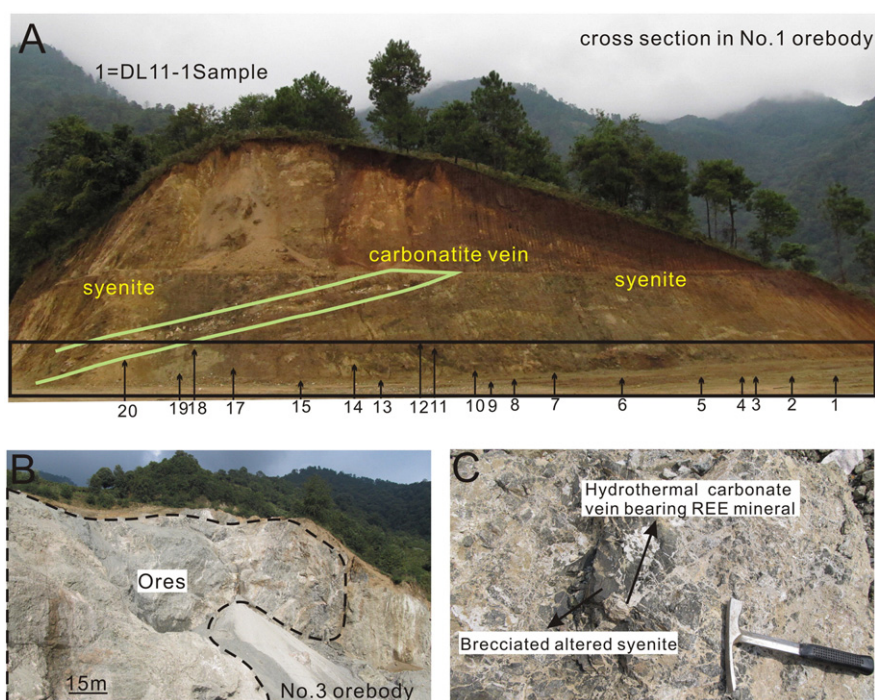


Fig. 8. A. The transect selected for analyzing the alteration, showing the locations of weathered samples, the relative locations of samples from the transect, and observations of the spatial relationship between syenite and carbonatite. B. Overall view of the No. 3 orebody in the Dalucao deposit. C. Typical brecciated ore in the No. 3 orebody at the Dalucao deposit (from Liu et al., 2015b).

humidity of 30%. The contents (mass%) of the primary mineral phases identified by the XRD were quantified using an internal standard, with corundum chosen as the reference material. The basic principles and procedures of quantitative analysis using the internal-standard method have been described in detail by Snyder and Bish (1989) and Liu et al (2013). Whole-rock geochemical analyses were performed at the National Research Center of Geoanalysis, Chinese Academy of Geological Sciences (CAGS), Beijing, China. Whole-rock powder 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 25-ml porcelain crucible. The powder mixture was transferred to a platinum alloy crucible, 1 mL LiBr solution was added to the crucible, and the sample was then dried. The sample was then melted in an automatic flame fusion machine and the resulting cooled glass was used for the X-ray fluorescence (XRF) major elements analyses. Major elements were analysed by inductively coupled plasma–atomic emission spectrometry (XRF). Analytical errors were <2%. For the complete digestion of refractory minerals such as zircons in the whole-rock analyses, Li-tetraborate fusion is also regarded as the best method. But solution of Li-tetraborate solution does not have a high purity in Chinese lab and some kinds of new salts will be introduced during digestion of carbonatite samples. Also, more dilution will affect the certainty of the detection line of elements and then the precision of the result during the measurement. The following procedure was adopted for analyses of trace elements and REEs in carbonatite, altered or mineralized carbonatite and REE ores. For analyses of trace elements and REEs, whole-rock powder samples (50 mg) were dissolved in distilled 1 mL HF and 0.5 mL HNO_3 in 15-ml Saville 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 sealed at 130 °C in the 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 analysed for trace elements by inductively coupled plasma–mass spectrometry (ICP–MS). The analytical precision for most elements was better than 5% according to the lab work procedure,

repeatability and reproducibility of standard samples measurement results.

4. Results

4.1. XRD analyses

The results of XRD and EPMA analyses of typical weathered ores from the No. 1 ore body reveal that the primary REE minerals in the deposit are bastnäsite and parisite (Figs. 9 and 10; Table 1). The gangue minerals in both orebodies are mainly fluorite, quartz, barite, and celestite. In addition, large amounts of clay minerals occur in the weathered ores, including illite, smectite, kaolinite, and minor illite, and in some cases the clay minerals make up 40% of the rock mass (Table 1; Fig. 10i). The brecciated ores contain large amounts of calcite, feldspar, and celestite, whereas the weathered ores contain much lower concentrations of these minerals. Compared with brecciated ore in the No. 1 and No. 3 orebodies (Fig. 9 and Table 1 in Liu et al., 2015b), the weathered ores contain large amounts of clay minerals such as illite, smectite, kaolinite, and sepiolite (Table 1).

4.2. Chemical compositions of typical weathered ores, brecciated ores, and fresh carbonatite and syenite

Chondrite-normalized REE patterns and primitive-mantle-normalized trace element patterns for the carbonatite and associated syenite samples from the Dalucao deposit are shown in Fig. 11. Enrichment in LILE is shown in samples of weathered and brecciated ores, and the altered syenite and carbonatite (Table 2). The REE patterns of the weathered ore samples are similar to those of the carbonatite (Fig. 11). The light REE (La, Ce, Pr, Nd, Sm, and Eu) contents of the weathered ores ($\Sigma = 17,701\text{--}220,886$ ppm) are 147 to 8495 times higher than the heavy REE contents ($\Sigma = 26\text{--}120$ ppm) (Gd, Tb, Dy, Ho, Er, Tm, Yb, Y, and Lu) (Table 2).

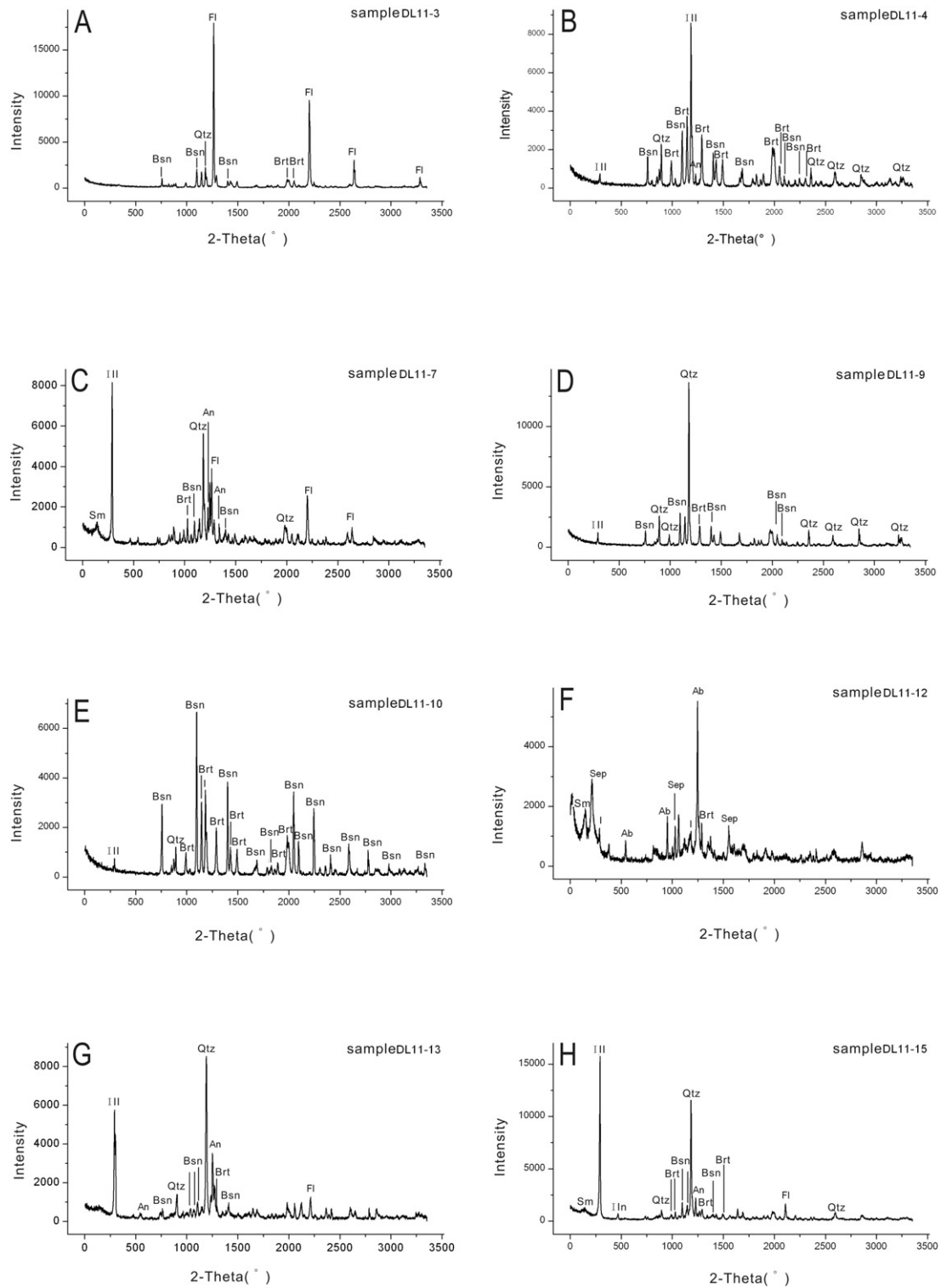


Fig. 9. XRD patterns of weathered ore, syenite, and the contact zone between syenite and ore veins. Ab: albite; An: anorthite; Brt: barite; Bsn: bastnaesite; Cal: calcite; Fl: fluorite; Ill: illite; Kln: kaolinite; Mnz: monazite; Par: parisite; Po: pyrrhotite; Qtz: quartz; Rt: rutile; Sm: smectite; Sep: sepiolite.

There are strong similarities in the chemical characteristics of the syenites and carbonatites in the Dalucao, Maoniuping, and Lizhuang deposits along with the other deposits in the MD REE Belt (Niu et al., 2003; Hou et al., 2006; Xu et al., 2008). The Sr, Ba, and REE contents reflect lithological differences between syenite and carbonatite. For example, the carbonatite in the Dalucao deposit contains extremely

high concentrations of LILE (Sr: 16,500–20,700 ppm; Ba: 3600–8400 ppm) and REE (2910–4423 ppm). The weathered ores are enriched in La (up to 92,390 ppm), Ce (up to 103,500 ppm), and Nd (up to 73,338 ppm), and have low contents of Sr (3660 ppm except 37,850 ppm) (Table 3). In comparison, the brecciated ores have lower concentrations of La (up to 27,400 ppm), Ce (up to

23,730 ppm), and Nd (up to 9780 ppm), and higher Sr (up to 256,500 ppm) (Table 2). The two ore types have similar Ba contents. Conversely, the syenite in Dalucao deposit contains

much lower concentrations of LILE and REE than the carbonatite (Sr: 155–277 ppm; Ba: 440–705 ppm; REE = 62.7–77.1 ppm) (Table 2).

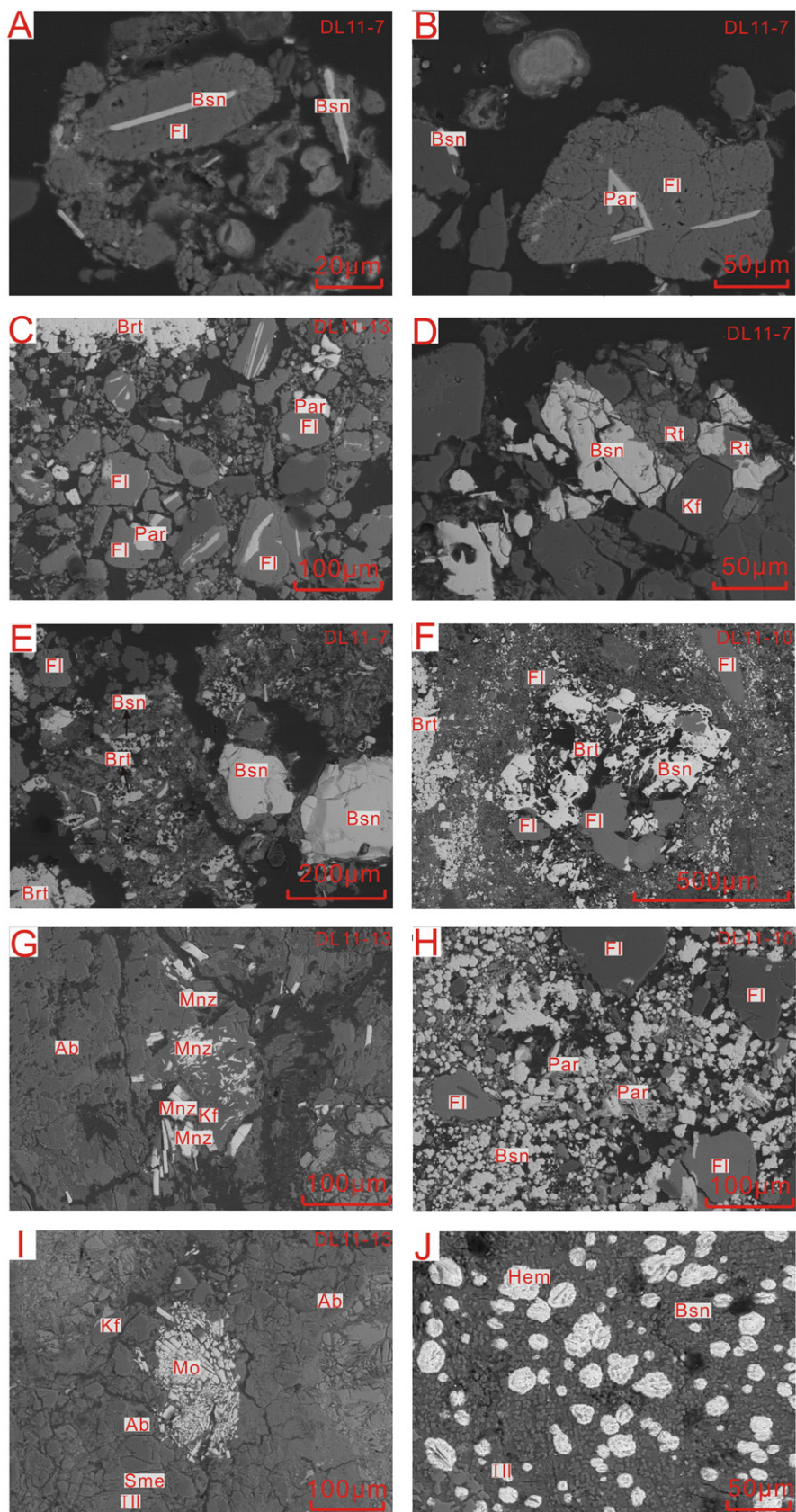


Table 1

Quantitative or semi-quantitative XRD analyses. Data shown are the percentages of REE and gangue minerals in the brecciated and weathered samples, together with possible precursor rocks to the weathered samples, the ores, syenite, hydrothermal gangue veins, and the contact zone between the syenite and ore veins.

Samples	Possible original rock	Amount of REE in samples	Gangue minerals	REE minerals
DL11-3	Ore	5%	Fluorite (70%), barite (10%), quartz (10%)	Bastnäsite
DL11-4	Ore	15%	Barite (20%), quartz (15%), illite (5%)	Bastnäsite
DL11-9	Ore	30%	Quartz (35%), barite (20%), illite (10%), some feldspar	Bastnäsite
DL11-10	Ore	60%	Barite (20%), quartz (15%), illite (5%)	Bastnäsite
DL11-45	Ore	10%	Fluorite (45%), calcite (30%), barite (10%), quartz (5%)	Monazite, bastnäsite
DL11-13	Contact zone	5%	Muscovite (55%), feldspar (15%), fluorite (10%), smectite (5%), kaolinite (5%), barite (5%)	Bastnäsite
DL11-15	Contact zone	5%	Illite (50%), quartz (15%), feldspar (10%), smectite (5%), kaolinite (5%), fluorite (5%), barite (5%)	Bastnäsite
DL11-7	Contact zone	10%	Illite (20%), smectite (10%), (plagioclase + alkali feldspar) (15%), quartz (15%), fluorite (15%), barite (10%), kaolinite (5%)	Bastnäsite, parisite
DL11-36	Ore	10%	Fluorite (50%), quartz (15%), illite (10%), barite (5%)	Bastnäsite
DL11-48	Ore	5%	Fluorite (65%), quartz (15%), barite (5%)	Bastnäsite
DL11-16	Syenite		Feldspar (30%), quartz (20%), illite (20%), smectite (10%), sepiolite (10%), amphibole (5%)	Non-ore
DL11-12	Syenite		Plagioclase (30%), sepiolite (25%), smectite (10%), fluorite (5%), illite (5%), barite (5%)	Non-ore
DL11-34	Hydrothermal gangue vein		Fluorite (60%), barite (30%)	Non-ore
DLC-60	Syenite		Illite (40%), feldspar (30%), quartz (15%)	Non-ore
DLC-70	Hydrothermal gangue vein		Quartz, fluorite, barite	Non-ore
<i>The following results from Liu et al. (2015b).</i>				
DL11-10	No. 1	10%	Calcite (30%), feldspar (20%), fluorite (15%), muscovite (10%), quartz (5%), barite (5%), celestite (5%)	Bastnäsite
DL11-11	No. 1	<15%	Calcite (30%), fluorite (15%), quartz (10%), feldspar (10%), muscovite (5%), iron mineral (5%), barite (5%), celestite (5%)	Bastnäsite, parisite
DL11-14	No. 1	<15%	Calcite (35%), fluorite (25%), muscovite (20%), quartz (10%), feldspar (5%), barite (5%), celestite (5%)	Bastnäsite, parisite
DL11-16	No. 1	0	Plagioclase (35%), muscovite (30%), quartz (20%), celestite (10%), iron mineral (5%), barite (<5%), unknown (5%)	
DL11-17	No. 1	7%	Calcite (60%), fluorite (25%), quartz (3%), celestite (3%), dolomitic marble (2%)	Bastnäsite, parisite
DL11-19	No. 1	<5%	Calcite (83%), aragonite (5%), barite (5%), fluorite (2%)	Bastnäsite
DL11-21	No. 1	0	Calcite (75%), feldspar (10%), barite (10%), celestite (5%)	
DL11-72	No. 3	15%	Muscovite (20%), feldspar (<5%), calcite (5%), fluorite (35%), celestite (15%)	Bastnäsite
DL11-70	No. 3	20%, 5%	Quartz (10%), fluorite (50%), barite (15%)	Bastnäsite, parisite
DL11-67	No. 3	10%	Muscovite (20%), feldspar (10%), quartz (10%), celestite (15%), fluorite (20%), calcite (10%), pyrite (5%)	Bastnäsite
DL11-63	No. 3	5%	Muscovite (15%), feldspar (10%), celestite (10%), fluorite (10%), calcite (45%), pyrite (5%)	Bastnäsite
DL11-62	No. 3	5%	Muscovite (5%), feldspar (15%), celestite (10%), fluorite (10%), calcite (25%)	Bastnäsite
DL11-57	No. 3	10%	Strontianite (25%), celestite (25%), fluorite (40%)	Bastnäsite
DL11-61-1	No. 3	10%	Muscovite (30%), fluorite (40%), celestite (20%)	Bastnäsite
DL11-61-2	No. 3	5%, 5%	Muscovite (10%), feldspar (15%), fluorite (55%), celestite (20%), calcite (5%)	Bastnäsite
DL11-61-3	No. 3	15%	Muscovite (40%), fluorite (20%), celestite (15%), strontianite (10%)	Bastnäsite
DL11-61-4	No. 3	10%, 5%	Muscovite (20%), feldspar (15%), fluorite (35%), celestite (20%), quartz (5%)	Bastnäsite, parisite
DL11-61-5	No. 3	5%, 10%	Muscovite (25%), fluorite (25%), celestite (25%), pyrite (10%)	Parisite, Bastnäsite

4.3. Petrographic studies of weathered ores

Previous studies have reported that bastnäsite is the primary REE mineral in the Dalucao, Maoniuping, Lizhuang, and Muluozechai deposits (Yang et al., 1998; Hou et al., 2009). Here, petrographic studies indicate the presence of REE minerals other than bastnäsite in these ores, which include parisite and monazite in weathered ores, together with the gangue minerals fluorite, barite, quartz, and celestite (Table 1). The majority of the REE minerals in the Dalucao deposit ores are fine grained (<200 µm).

The most prominent characteristic feature of the weathered ores is that they occur as unconsolidated material containing large pore-spaces between individual minerals and clasts (Fig. 10). The ore samples commonly contain bastnäsite, and both bastnäsite and other REE minerals occur in fractures within fluorite, barite, and other gangue minerals in the brecciated ores (Fig. 10). In addition, apatite, fluorite, and carbonate minerals are overprinted by long crystals of bastnäsite and other REE minerals (Fig. 10). Monazite is present as columnar crystals within fractures in albite and K-feldspar (Fig. 10G), and as aggregates replacing them (Fig. 10I). Elsewhere, K-feldspar and albite are altered

Fig. 10. BSE images of REE minerals in the Dalucao deposit. A. Needle-like bastnäsite overprinting brecciated fluorite fragments with a fluffy texture. B. Needle-like bastnäsite and parisite overprinting fluorite fragments and with a fluffy texture. C. Parisite with long columns either overprinting fluorite fragments, or precipitated in fractures or spaces between barite and fluorite fragments. D. Brecciated bastnäsite, rutile, and feldspar fragments they were brecciated during the same stage. E. Brecciated bastnäsite fragments with aggregates of fine-grained bastnäsite associated with fine-grained fluorite occurring with massive bastnäsite crystals, indicating several generations of REE mineralization. F. Evidence for cryptoexplosive brecciation shown by fine-grained barite and fluorite contrasting with coarse-grained bastnäsite and fluorite. G. Needle-like monazite crystals overprinting albite. Syenite is also the main wall-rock hosting the REE mineralization. H. Fibrous parisite and bastnäsite grains in spaces between brecciated fluorite fragments, indicating that REE mineralization continued after the brecciation events. I. Monazite crystals overprinting albite, feldspar, illite, and smectite. This shows that REE crystals were brecciated and that the REE mineralization occurred during later hydrothermal stages. Syenite is the main wall-rock for the REE mineralization and has been weathered. J. Hematite associated with bastnäsite and illite, indicating that the ores have undergone weathering. Bsn = bastnäsite, Bar = barite, Cal = calcite, Fl = fluorite, Kf = K-feldspar, Mnz = monazite, Qtz = quartz, Rt = rutile, Par = parisite, Ill = illite, Sme = smectite.

Table 2

Whole-rock major and trace element (including REE) compositions of representative carbonatite and associated syenite samples from the Dalucao deposit.

Sample	DL-12	DL-14	DL-17	DL-20	DL-22	MO-48	MOMO-52	MO-62	MN-24
	Syenite	Syenite	Carbonatite	Carbonatite	Carbonatite	Syenite	Syenite	Syenite	Syenite
References	Hou et al. (2006)					Hou et al. (2006)			Hou et al. (2006)
REE deposit	Dalucao deposit					Maoniuping deposit			
SiO ₂	63.41	66.08	2.87	10.22	7.56	67.52	69.15	68.94	70.92
TiO ₂	0.12	0.09	0.04	0.04	0.04	0.22	0.21	0.24	0.22
Al ₂ O ₃	19.61	19.07	0.46	0.28	0.56	14.71	14.74	14.8	15.97
TFe ₂ O ₃	1.68	1.4	0.86	1.43	1.43	–	–	–	1.41
Fe ₂ O ₃	1.46	0.58	0.36	0.1	0.77	1.61	1.51	1.32	0.93
FeO	0.2	0.74	0.45	1.2	0.59	–	–	–	0.43
MnO	0.02	0.02	0.34	0.3	0.35	0.04	0.04	0.03	0.05
MgO	0.13	0.36	0.41	0.43	0.44	0.39	0.45	0.3	0.35
CaO	1.42	0.48	49.21	45.79	46.67	1.86	1.47	1.17	0.15
Na ₂ O	7.5	8.83	0.19	0.08	0.25	5.69	5.73	5.08	3.97
K ₂ O	5.05	3.64	0.04	0.05	0.03	5.18	4.71	5.94	5.78
P ₂ O ₅	0.01	0.02	0.2	0.26	0.14	0.12	0.08	0.11	0.05
H ₂ O +	0.62	0.46	0.58	0.72	0.48	–	–	–	–
CO ₂	0.32	0.05	38.76	35.2	37.38	1.89	1.91	1.24	0.05
SiO ₃	–	–	5.8	4.18	3.18	–	–	–	–
LOI	–	–	–	–	–	–	–	–	–
Total	99.87	100.42	99.62	98.87	98.94	99.23	100	99.17	100.21
La	23.8	17.4	946	884	1400	381	158	625	554
Ce	30.3	22.4	1600	1400	2000	651	285	1125	870
Pr	3.37	2.42	141	124	203	66	32	113	102
Nd	10.7	8.15	451	384	636	183	94	300	322
Sm	1.65	1.35	52.9	44.1	72.1	23	14	35	33.4
Eu	0.67	0.4	13.9	11.6	18	3.3	3.8	2.1	7.08
Gd	1.63	1.41	35.3	29.6	48.5	14	9.3	21	20.5
Tb	0.24	0.24	3.87	3.21	4.87	1.1	1.1	1.9	1.85
Dy	1.63	1.72	16.8	13.9	19.7	4.4	4.2	5.7	7.1
Ho	0.38	0.45	2.98	2.42	3.29	0.7	0.6	0.8	1.18
Er	1.17	1.78	8.52	7.13	9.59	1.7	1.8	2	3.76
Tm	0.18	0.37	0.99	0.82	1.02	0.2	0.3	0.3	0.4
Yb	1.2	3.64	5.4	4.7	5.82	1.6	1.4	1.7	2.54
Lu	0.2	0.95	0.65	0.61	0.74	0.2	0.2	0.2	0.38
Y	10.8	14.9	91.6	77.1	92	22	22	24	36.7
Sc	0.33	1.04	1.01	1.94	3.04	–	–	–	1.36
Rb	67	58.6	0.85	1.35	1.18	194	197	214	163
Ba	440	705	8400	5200	3600	2418	2145	3044	1384
Th	6.3	49.5	5.38	5.87	18.8	57	53	50	60
U	1.02	7.16	2.72	2.99	8.27	20	9.9	18	5
Nb	3	5.59	2.94	4.98	6.2	31	21	48	14.8
Sr	277	155	20,700	16,500	17,000	1885	728	2004	225
Ta	0.34	0.98	0.15	0.1	0.06	1	0.9	1.3	0.72
Zr	210	279	20.1	11.7	18.3	192	194	201	201
Pb	9.21	19.5	1806	2245	416	135	96	91	930
Hf	10.1	23.7	0.6	0.47	0.7	4.8	4.1	5.1	6.21
REE	77.12	62.68	3279.31	2910.09	4422.63	1331.2	605.7	2233.7	1926.19
LREE	70.49	52.12	3204.8	2847.7	4329.1	1307.3	586.8	2200.1	1888.48
HREE	6.63	10.56	74.51	62.39	93.53	23.9	18.9	33.6	37.71
LREE/HREE	10.63	4.94	43.01	45.64	46.29	54.7	31.05	65.48	50.08

Sample	MO-52	MO-46	MN-2-6	MO-54	MO-59	MNP-11	MNP-10	MNP-16	LZ-07	LZ-01	LZ-03
	Syenite	Syenite	Carbonatite	Syenite	Syenite	Carbonatite	Carbonatite	Carbonatite	Syenite	Carbonatite	Carbonatite
References	Hou et al. (2006)	Wang et al. (2001)		Wang et al. (2001)		Xu et al. (2002)			Hou et al. (2006)		
REE deposit	Maoniuping deposit								Lizhuang deposit		
SiO ₂	69.15	67.81	1.44	68.18	75.34	1.67	3.65	2.88	74.75	2.61	<0.01
TiO ₂	0.21	0.23	<0.001	0.15	0.04	0	0	0	0.08	0.1	0.03
Al ₂ O ₃	14.74	14.78	0.1	14.2	13.34	0.09	0.14	0.09	13.29	1.2	0.98
TFe ₂ O ₃	–	1.68	0.32	1.25	0.84	0.47	0.29	0.38	1.12	2.08	0.5
Fe ₂ O ₃	1.51	–	0.01	–	–	0.36	0.2	0.2	0.66	1.38	0.32
FeO	–	–	0.28	–	–	0.1	0.08	0.16	0.41	0.63	0.16
MnO	0.04	0.05	0.48	0.04	0.01	0.6	0.55	0.65	0.01	0.37	0.25
MgO	0.45	0.41	0.16	0.28	0.13	0.1	0.01	0.1	0.16	0.69	0.33
CaO	1.47	1.5	49.79	1.87	0.58	55.4	55	54.2	0.51	46.05	52.63
Na ₂ O	5.73	5.55	0.1	5.07	5.21	0.06	0.06	0.07	5.46	0.41	0.26
K ₂ O	4.71	5.41	0.1	4.98	4.19	0.01	0.02	0.12	3.63	0.24	0.04
P ₂ O ₅	0.08	0.1	0.05	0.07	0	0	0	0	0.02	0.74	0.36
H ₂ O +	–	–	0.3	–	–	0.7	0.85	0.43	0.18	0.74	0.82
CO ₂	1.91	1.31	38.72	2.66	0.74	40.1	38.5	40.2	0.23	32.92	22.11
SiO ₃	–	–	–	–	–	–	–	–	–	11.98	8.43
LOI	–	–	–	–	–	–	–	–	–	–	–
Total	100	98.83	91.52	98.75	100.42	99.19	99.06	99.1	99.39	100.91	87.32
La	158	1124	815.7	275	104	524	648	514	42.6	3400	3300
Ce	285	1725	1329	456	138	1143	1395	1079	63.3	4500	4300
Pr	32	188	146.4	48	12	120	142	110	5.86	337	317
Nd	94	528	487.4	151	36	468	542	422	17.5	1200	1000
Sm	14	44	63.48	15	3.3	74.3	74.7	63.5	2.03	121	91.7
Eu	3.8	4.3	16.33	0.75	5.9	16.4	16.4	14.4	0.5	32.1	21.8
Gd	9.3	31	39.3	13	2.7	53	50.3	45.5	1.33	84	67.9
Tb	1.1	2.4	4.82	1.2	0.3	6.27	5.53	5.2	0.16	7.65	5.26
Dy	4.2	4.8	20.13	3.6	0.7	29.7	25.3	24.4	0.68	28.7	18
Ho	0.6	0.6	3.9	0.5	0.1	5.04	4.16	4.33	0.13	4.71	3
Er	1.8	1.7	8.64	1.3	0.4	15.1	12.7	13.1	0.46	14.4	9.86
Tm	0.3	0.3	1.16	0.2	0.1	1.94	1.53	1.65	0.07	1.53	0.92
Yb	1.4	2.1	5.83	1.3	0.5	12	10.1	10.8	0.51	8.81	5.45
Lu	0.2	0.3	0.77	0.2	0.1	1.53	1.24	1.33	0.08	1.26	0.8
Y	22	21	86.71	20	6	149	131	133	4.62	128	94.5
Sc	–	–	–	–	–	2.45	2.03	1.91	0.16	0.52	1.05
Rb	197	–	–	172	198	0.26	0.5	1.15	135	12.4	1.03
Ba	2145	3824	–	3942	614	1629	378	1295	186	60,800	45,300
Th	53	63	–	50	54	0.65	0.23	1.03	47.2	48.7	46.1
U	9.9	12	–	13	17	0.06	0.16	0.19	6.14	2.78	1.37
Nb	21	38	–	34	17	0.33	0.07	0.04	13	3.42	0.88
Sr	728	3128	–	4691	811	10,781	14,150	11,677	181	10,600	5100
Ta	0.9	0.8	–	1.1	0.7	0.02	0.03	0.01	0.63	0.08	0.14
Zr	194	195	–	145	127	0.1	0.12	0.08	81.2	27.9	13.4
Pb	96	71	–	156	20	102	115	104	43.8	88.6	98.5
Hf	4.1	4.4	–	3.9	4.3	0.05	0.06	0.05	4.2	0.55	0.84
REE	605.7	3656.5	2942.86	967.05	304.1	2470.28	2928.96	2309.21	135.21	9741.16	9141.69
LREE	586.8	3613.3	2858.31	945.75	299.2	2345.7	2818.1	2202.9	131.79	9590.1	9030.5
HREE	18.9	43.2	84.55	21.3	4.9	124.58	110.86	106.31	3.42	151.06	111.19
LREE/HREE	31.05	83.64	33.81	44.4	61.06	18.83	25.42	20.72	38.54	63.49	81.22

(continued on next page)

Table 2 (continued)

Samples	DL102	DL103	DL105	DL107	DL109	DL112	DL113	DL117	DL120	DL123	DL124	DL128	DL136	DL137
<i>Liu et al. (2015b)</i>														
La	507	11,250	10,750	2500	7283	26,480	4096	16,250	27,400	22,920	8316	5388	400	1147
Ce	608	14,670	9538	2198	6773	20,820	3548	16,490	23,730	23,340	9219	6146	495	1375
Pr	78.9	1363	472	338	293	1418	506	1292	1743	2244	680	1355	65.5	233
Nd	234	6474	2962	697	2183	5800	1108	6234	7583	9780	3670	2626	166	550
Sm	31.4	613	240	74	198	362	146	670	615	966	491	677	25.5	72.9
Eu	15.1	157	69.4	13.6	56.6	73.5	29.1	148	131	192	82.5	139	4.77	14.7
Gd	26.7	462	255	38.8	197	261	160	392	337	470	298	357	17.8	144
Tb	2.18	49.2	19.9	3.1	11.8	17.3	5.39	30.4	24.5	36.6	18.2	26.8	1.6	3.95
Dy	10.6	120	34.5	7.16	34	36.1	15.6	85.6	54.9	80.2	48	73.6	6.84	14.9
Ho	1.87	17.5	4.66	0.92	5.1	4.71	2.62	11.8	7.34	9.65	6.36	9.07	1.19	2.39
Er	5.64	61.7	21	4.5	19	32.7	11.2	47.1	42.6	53.7	27.1	33.3	3.74	7.4
Tm	0.71	4.86	1.16	0.18	1.44	1.15	1.14	3.02	1.84	1.93	1.49	1.65	0.53	0.82
Yb	4.08	25.1	6.44	0.98	7.55	7.5	7.03	16.8	11	12	8.6	9.03	3.06	4.42
Lu	0.51	2.85	0.72	0.09	0.87	0.81	1.03	1.88	1.19	1.22	0.96	0.86	0.44	0.63
Rb	2.72	1.36	1.53	0.73	1.5	1.71	1.35	1.7	1.39	10.2	1.64	0.81	194	4.41
Sr	23,760	242,200	218,500	32,930	130,900	123,800	95,980	256,500	235,200	228,900	216,000	9796	1278	9342
Zr	1.8	0.47	1.6	0.75	2.16	3.03	4.61	0.26	0.44	1.05	0.84	2.4	562	19.5
Nb	13.1	0.38	3.41	0.11	1.78	0.49	31.5	0.11	<0.05	1.22	0.28	1.54	21.2	18.8
Ba	48,830	52,660	31,950	1938	34,160	22,470	95,000	67,750	43,760	58,960	24,220	11,740	4088	848
Hf	0.26	1.32	0.79	0.11	0.59	0.44	0.38	0.87	0.55	0.89	0.65	0.88	14.1	0.75
Ta	0.23	0.29	0.1	<0.05	0.12	0.09	0.08	0.17	0.12	0.14	0.1	0.13	0.58	0.1
U	5.91	39.2	32.3	6.51	31.8	10.4	63.2	30.9	68.3	25.5	25	35.4	13.5	8.81
Pb	214	1496	853	199	2477	675	1317	1357	2171	1289	3558	6881	162	1159
Th	2.24	221	78	1.13	63.2	102	20.7	35.3	51.2	238	56.6	17.1	89.4	11
Sc	3.62	<0.05	0.31	0.27	3.39	0.69	3.57	<0.05	<0.05	1.09	<0.05	1.45	2.71	2.14
Ni	17.5	1.39	2.17	2.34	8.85	15.8	6.07	0.48	1.16	0.6	1.74	12.7	6.85	21.5
Cu	11.9	3.83	3.45	4.44	11	4.12	4.47	6.23	1	3.39	7.95	9.08	18.7	65.4
Ga	13.2	111	54.3	44.9	58.2	245	40.2	124	192	211	61.6	331	36.8	42.8
Y	52	89.2	33	18.1	50	41.6	29.2	67.1	49.4	61.3	50	237	37.2	69.5
REE	72,926	296,824	251,512	35,146	167,768	147,369	192,501	325,872	281,495	289,693	243,983	29,066	6331	11,609
Eu*	0.52	0.3	0.28	0.25	0.29	0.24	0.19	0.29	0.29	0.28	0.22	0.28	0.22	0.14
Gd/Yb	5.26	14.78	31.8	31.8	20.95	27.95	18.28	18.74	24.6	31.45	27.83	31.75	4.67	26.16
La/Sm	9.89	11.24	27.44	20.7	22.54	44.82	17.19	14.86	27.3	14.54	10.38	4.88	9.61	9.64
La/Yb	82.05	295.96	1102.24	1684.5	636.97	2331.36	384.73	638.7	1644.79	1261.21	638.51	394	86.32	171.35
LREE	1459.3	34,370	23,962	5807	16,730	54,880	9404	40,936	61,071	59,250	22,376	16,192	1152	3377.9
HREE	52.29	743.21	343.38	55.73	276.76	361.27	204.01	588.6	480.37	665.3	408.71	511.31	35.2	178.51
L/R	27.91	46.25	69.78	104.2	60.45	151.91	46.1	69.55	127.13	89.06	54.75	31.67	32.73	18.92

“–”:not measured; (): reference value.

to illite and smectite (Fig. 10I). Weathering led to the formation of hematite but not bastnäsite (Fig. 10J).

REE minerals including bastnäsite formed during multiple events, as indicated by the occurrence of massive and fine-grained bastnäsite together (Fig. 10E), and bastnäsite together with parisite crystals (Fig. 10H). Sr-rich barite, Ca-rich strontianite, and fluorite are also present in most of the ore samples. Fractures within these minerals, and within the other gangue minerals, commonly contain aggregates of needle-like bastnäsite (Fig. 10C). This shows that at least one phase of bastnäsite formed after the formation of the Sr-rich barite, Ca-rich strontianite, and fluorite. Euhedral bastnäsite crystals are also present in fractures within K-feldspar and rutile, including where these are brecciated (Fig. 10D), which further indicates that bastnäsite mineralization occurred after the brecciation events.

5. Discussion

5.1. Mineral assemblages in the weathered ore, syenite, contact zone, and original rock types

The high levels of brecciation and weathering in the Dalucao deposit make it difficult to recognize the ore veins from the syenite–carbonatite complex or the hydrothermally altered syenite–carbonatite complex. However, based on whole-rock chemistry, petrographic studies, and XRD analyses, four rock types can be distinguished as follows: (1) ore veins, (2) partly weathered syenite–carbonatite complex, (3) the weathered contact zone between ore veins and partly weathered syenite–carbonatite complex, and (4) hydrothermal veins. Four groups of minerals are present in the weathered samples: (1) REE minerals (bastnäsite, parisite, and monazite), (2) clay minerals (smectite, kaolinite, illite, and sepiolite; Table 1), (3) hydrothermal minerals (fluorite, barite, quartz, and celestite), and (4) relict igneous minerals in the syenite or carbonatite (K-feldspar, albite, and quartz). Most of the

weathered ore samples contain significant amounts of REE (up to 10 wt.%), which most likely reflects the presence of high REE concentrations in the primary ores. The brecciated ore consists mainly of bastnäsite, parisite, monazite, fluorite, barite, and quartz, which locally contain subordinate amounts of calcite or illite. Weathered ores are characterized by up to 60 wt.% REE and are composed of bastnäsite, clay minerals, barite, fluorite, quartz, celestite, feldspar, and albite.

The weathered ores contain large amounts of clay minerals but less celestite, calcite, feldspar, and fluorite than the brecciated ore samples (Table 1). It is possibly, during weathering, primary albite and K-feldspar in syenite turned to kaolinite and smectite, meanwhile, it is also likely that aegirine–augite turned to sepiolite, muscovite turned to illite, smectite turned to kaolinite, and pyrite turned to hematite. The loss of fluorite, feldspar, calcite, barite, celestite, and sulfur, as well as the formation of clay minerals, resulted in the generation of high-grade ores. BSE images and petrographic studies of weathered samples show that the REE minerals such as bastnäsite, parisite, and monazite are closely associated with feldspar, rutile, and clay minerals (Fig. 10D and I–J). This suggests that the REE minerals had a primary igneous origin that was linked to the syenite and carbonatite intrusions. Subsequently, gangue minerals were overprinted by later generations of REE minerals during hydrothermal activity. Other REE deposits in the MD REE Belt, which include the Maoniuping, Lizhuang and Muluoizhai deposits, also contain large amounts of syenite in addition to carbonatite, although only the carbonatite has been considered as the main source of the REE (Xu et al., 2008; Xie et al., 2009). More recently, it has been suggested that both the carbonatite and the syenite contributed to the REE mineralization within the MD REE Belt (Liu et al., 2015b).

Compared with the brecciated ores, the weathered ores in the Dalucao deposit are strongly enriched in REE, particularly LREE ($\Sigma = 17,701\text{--}220,886$ ppm) (Table 3). Conversely, Sr is highly enriched in the brecciated ores (up to 256,500 ppm) and occurs with relatively low concentrations in the weathered ores (up to 4224 ppm with one

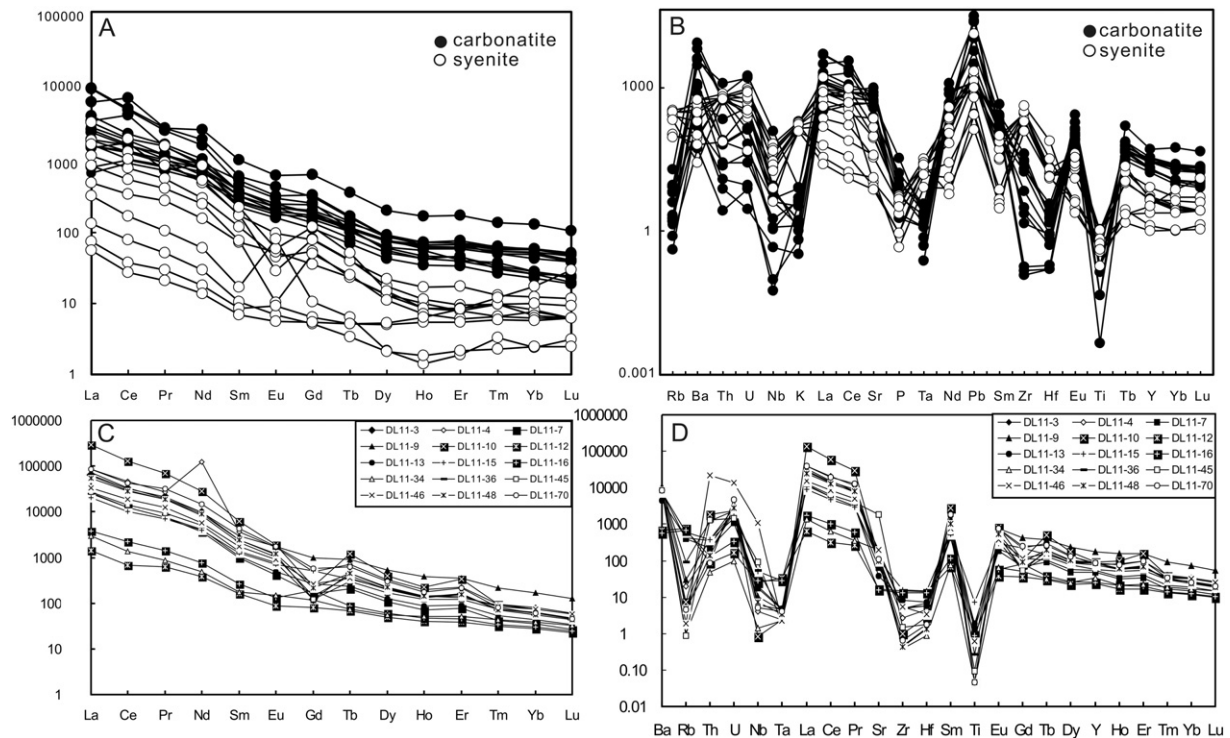


Fig. 11. A. Chondrite-normalized REE patterns of the carbonatites and associated syenites. B. Primitive-mantle-normalized trace element patterns for the carbonatites and associated syenites in western Sichuan. C. Chondrite-normalized REE patterns of weathered ore in the Dalucao deposit; D. Primitive-mantle-normalized trace element patterns for the weathered ore in the Dalucao deposit. Primitive-mantle normalizing values are from McDonough and Sun (1995) (A and B from Liu et al., 2015b).

Table 3

Whole-rock major and trace element (including REE) compositions of weathered ore, syenite, hydrothermal gangue veins, and the contact zone between syenite and ore veins.

Samples	DL11-3	DL11-4	DL11-7	DL11-9	DL11-10	DL11-12	DL11-13	DL11-15	DL11-16	DL11-34	DL11-36	DL11-45	DL11-48
Possible original rock	Ore veins	Ore veins	Contact zone	Ore veins	Ore veins	Syenite	Contact zone	Contact zone	Syenite	Hydrothermal gangue veins	Ore veins	Ore veins	Ore veins
SiO ₂	6.77	30.14	39.12	40.65	13.97	47.82	47.74	40.99	49.37	3.02	17.46	5.01	6.25
Al ₂ O ₃	0.25	1.14	11.93	0.76	0.36	13.35	11.67	10.79	12.81	3.75	2.79	0.11	0.21
Fe ₂ O ₃	0.94	4.10	5.46	8.01	3.84	12.78	6.06	10.70	11.59	1.07	1.38	1.31	0.81
CaO	41.89	0.64	9.4	0.34	0.21	1.35	5.23	1.84	1.18	29.29	31.37	38.19	44.84
MgO	0.05	0.17	2.75	0.45	0.13	7.45	3.12	5.19	7.73	0.04	0.29	0.06	0.04
K ₂ O	0.08	0.34	4.25	0.27	0.06	3.45	3.54	4.41	3.71	0.02	1.65	0.01	0.06
Na ₂ O	0.19	0.44	1.36	0.28	0.41	3.46	1.59	0.52	2.89	0.33	0.26	0.21	0.16
TiO ₂	<0.01	<0.01	0.29	0.03	<0.01	2.03	0.42	1.57	1.86	<0.01	0.06	0.02	<0.01
MnO	0.39	1.44	0.36	4.21	1.14	0.29	0.47	0.64	0.35	0.59	0.36	0.48	0.38
P ₂ O ₅	0.05	0.45	0.14	0.24	0.21	0.23	0.10	0.48	0.20	0.18	0.20	0.12	0.05
H ₂ O +	1.32	2.20	3.84	4.05	3.2	5.24	4.36	5.32	4.58	2.78	1.44	1.54	0.96
CO ₂	1.71	0.94	0.60	0.73	0.94	0.26	0.43	1.11	0.81	0.77	2.31	11.23	2.49
LOI	6.94	5.76	10.56	7.94	11.44	5.93	8.89	8.32	5.92	4.99	7.14	14.86	6.60
Total	60.58	47.76	90.06	67.96	35.91	103.64	93.62	91.88	103.00	46.83	66.71	73.15	62.85
Y	382.00	351.00	219.00	819.00	425.00	105.00	252.00	392.00	117.00	149.00	390.00	258.00	390.00
La	20,520.00	26,750.00	7947.00	22,630.00	92,390.00	450.00	8158.00	6326.00	1216.00	927.00	19,180.00	8612.00	17,040.00
Ce	25,980.00	37,230.00	10,140.00	26,570.00	103,500.00	552.00	10,260.00	8263.00	1835.00	1126.00	23,820.00	11,380.00	22,530.00
Pr	2453.00	3118.00	867.00	2234.00	8006.00	72.60	884.00	806.00	163.00	99.40	2142.00	1094.00	2163.00
Nd	5777.00	73,338.00	2122.00	5879.00	16,990.00	223.00	2419.00	2306.00	451.00	294.00	4939.00	3057.00	5289.00
Sm	473.00	706.00	190.00	580.00	1221.00	30.80	208.00	241.00	51.70	33.30	411.00	267.00	465.00
Eu	83.60	122.00	30.50	128.00	134.00	6.19	35.30	50.00	9.46	10.80	73.70	55.80	88.30
Gd	31.00	129.00	41.10	249.00	60.60	20.70	67.10	130.00	48.60	29.60	37.00	31.50	56.00
Tb	20.80	32.80	9.66	41.80	56.00	3.16	11.00	15.70	4.15	3.44	18.60	14.20	21.10
Dy	71.00	104.00	35.30	169.00	128.00	16.00	41.00	65.80	19.70	18.30	65.00	55.60	73.90
Ho	9.78	13.60	5.07	26.20	15.60	2.79	5.99	9.90	3.35	3.54	9.32	8.46	10.10
Er	34.40	47.60	16.60	74.80	73.00	8.09	19.30	28.30	9.59	10.80	33.20	26.10	33.40
Tm	2.17	2.90	1.26	6.59	2.88	0.96	1.60	2.72	1.04	1.35	2.30	2.22	2.17
Yb	11.50	16.80	7.30	34.90	15.40	5.75	9.16	15.50	6.14	8.09	12.90	12.80	11.50
Lu	1.40	1.97	0.87	4.06	1.84	0.74	1.09	1.88	0.78	1.07	1.51	1.53	1.38
Be	14.70	6.14	31.50	19.70	12.90	16.40	24.70	26.10	17.80	2.34	61.50	10.70	16.00
Sc	3.87	15.10	21.40	14.00	9.93	37.80	29.80	29.70	36.50	3.14	6.59	5.47	3.15
V	37.20	123.00	108.00	98.90	115.00	315.00	201.00	284.00	329.00	16.80	31.90	9.53	32.90
Cr	5.17	31.50	76.90	49.60	71.80	566.00	148.00	614.00	794.00	1.99	8.39	4.94	5.56
Ni	14.20	20.10	25.80	25.60	7.35	190.00	44.30	147.00	193.00	12.00	15.20	10.00	16.60
Cu	45.60	36.80	115.00	184.00	114.00	71.70	96.50	122.00	109.00	206.00	40.20	18.20	38.90
Zn	209.00	158.00	240.00	301.00	227.00	235.00	223.00	332.00	277.00	210.00	264.00	282.00	152.00
Ga	469.00	668.00	151.00	487.00	1673.00	31.90	155.00	136.00	46.20	17.90	435.00	119.00	394.00
Rb	3.72	12.90	254.00	19.00	4.63	474.00	264.00	393.00	434.00	0.61	58.90	0.57	3.10
Sr	2246.00	2544.00	1364.00	1720.00	2671.00	356.00	815.00	2322.00	331.00	4224.00	3660.00	37,850.00	2052.00
Zr	5.21	29.50	58.30	53.20	10.90	170.00	91.80	171.00	147.00	4.29	52.90	16.50	4.74
Nb	4.42	2.93	12.90	7.25	0.60	18.20	14.10	35.60	20.30	1.01	38.20	66.80	5.22
Mo	244.00	40.70	9.22	96.80	52.20	2.60	10.30	6.13	1.63	17.00	14.70	5.34	140.00
Cd	1.07	4.31	0.41	2.20	0.95	0.35	0.40	0.49	0.30	1.34	2.92	2.39	0.79
In	<0.05	<0.05	0.05	0.09	<0.05	0.09	0.07	0.08	0.08	<0.05	<0.05	<0.05	<0.05
Cs	0.33	0.55	7.74	0.69	0.31	45.40	11.00	19.00	31.90	0.07	2.98	0.10	0.32
Ba	57,990.00	61,120.00	53,890.00	76,950.00	55,150.00	4746.00	31,300.00	53,188.00	4075.00	62,390.00	62,210.00	57,530.00	58,890.00
Hf	0.43	1.43	1.75	2.17	0.89	4.41	2.24	4.59	3.96	0.27	1.79	0.55	0.41
Ta	0.19	0.10	0.19	0.18	0.10	1.37	0.20	1.15	1.13	0.09	0.16	0.08	0.14
W	0.73	1.38	2.60	1.36	0.52	1.70	3.63	5.76	2.94	0.84	0.87	0.79	0.48
Tl	0.17	0.72	1.97	1.64	0.58	6.02	1.82	3.13	4.32	0.20	0.59	<0.05	0.14
Pb	6351.00	5641.00	2542.00	25,000.00	22,780.00	146.00	1480.00	2511.00	237.00	9930.00	3580.00	581.00	6016.00
Bi	0.32	4.19	3.23	92.60	19.40	0.39	1.38	6.69	0.77	26.10	0.53	<0.05	0.24
Th	22.10	15.50	19.10	32.20	156.00	7.19	30.90	31.40	11.40	4.13	103.00	112.00	12.00
U	45.90	43.30	22.60	59.80	48.60	3.50	29.70	42.90	6.89	2.08	49.90	29.90	58.10
Li	31.80	40.40	239.00	145.00	55.60	50.30	351.00	332.00	195.00	0.60	93.90	8.19	34.70
REE	55,469.00	141,613.00	21,414.00	58,627.00	222,594.00	1393.00	22,121.00	18,262.00	3820.00	2567.00	50,746.00	24,618.00	47,785.00
LREE	54,730.00	140,436.00	21,076.00	57,313.00	220,886.00	1297.60	21,721.00	17,701.00	3665.00	2446.40	50,081.00	24,143.00	47,022.00
MREE	689.18	1107.40	311.63	1194.00	1615.20	79.64	368.39	512.40	136.96	98.98	614.62	432.56	714.40
HREE	49.47	69.27	26.03	120.35	93.12	15.54	31.15	48.40	17.55	21.31	49.91	42.65	48.45
LREE%	0.99	0.99	0.98	0.98	0.99	0.93	0.98	0.97	0.96	0.95	0.99	0.98	0.98
MREE%	0.01	0.01	0.01	0.02	0.01	0.06	0.02	0.03	0.04	0.04	0.01	0.02	0.01
HREE%	0.00	0.00	0.01	0.01	0.00	0.04	0.01	0.01	0.02	0.03	0.00	0.01	0.00
Eu*	0.69	0.40	0.35	0.34	0.49	0.25	0.30	0.28	0.19	0.34	0.60	0.61	0.55
Gd/Yb	2.16	6.17	4.52	5.73	3.16	2.89	5.88	6.74	6.36	2.94	2.3	1.98	3.91
La/Sm	26.58	23.21	25.63	23.91	46.36	8.95	24.03	16.08	14.41	17.06	28.59	19.76	22.45
La/Yb	1178	1051	719	428	3961	52	588	269	131	76	982	444	978

exception of 37,850 ppm). Calcite is not present in the weathered samples, whereas the brecciated ores contain up to 83% calcite, which suggests that calcite was removed during weathering (Table 1). Since Sr²⁺ can replace Ca²⁺ in the calcite lattice or some aragonite, the loss

of calcite during weathering may also lead to a large reduction in whole-rock Sr concentrations. Consequently, weathering processes are important factors that lead to the formation of high-grade REE ores and can also lead to a significant decrease in Sr.

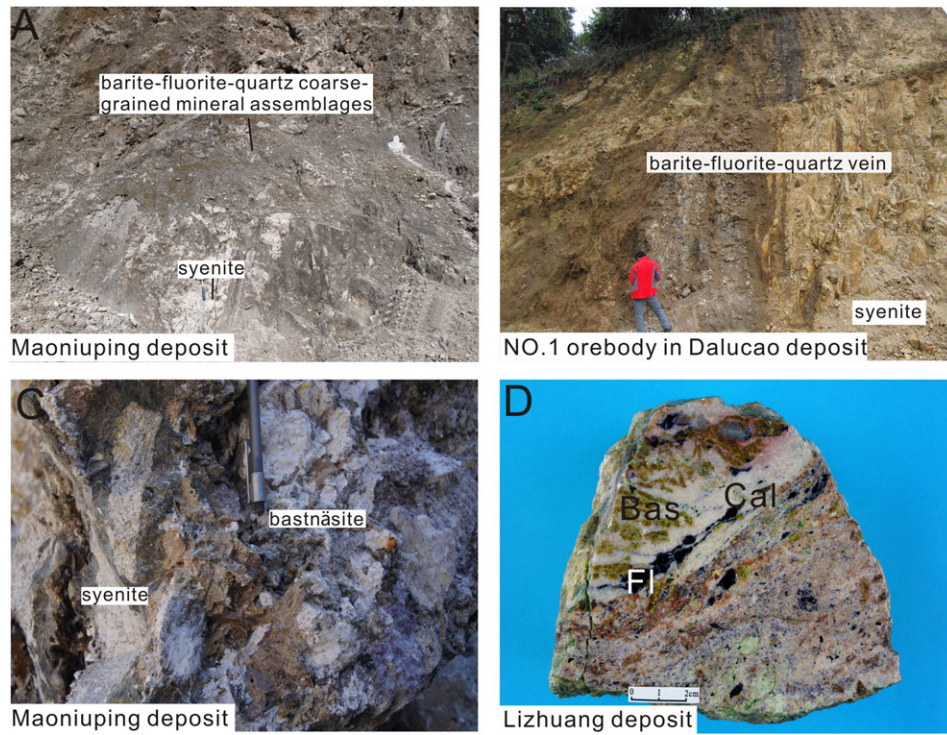


Fig. 12. A. Coarse-grained barite–fluorite–quartz mineral assemblages associated with the syenite–carbonatite complex in the Maoniuping deposit. B. Coarse-grained barite–fluorite–quartz veins cross-cutting the syenite–carbonatite complex in orebody No. 1 in the Dalucao deposit. C. Coarse-grained mineral veins in fractures within syenite at the Maoniuping deposit, hosting bastnäsite–aegirine–fluorite–barite. D. Coarse-grained bastnäsite associated with fluorite and calcite in altered red carbonatite. Cal = calcite. Fl = fluorite. Bas = bastnäsite (A from Liu et al., 2015a and B from Liu et al., 2015b).

5.2. Source of the weathered ore

Alkaline complexes consisting of syenite and carbonatite are widely developed along the western margin of the Yangtze Craton in the Himalayan MD REE Belt (Fig. 1). At Dalucao, the carbonatite and syenite have similar geochemical compositions. Both are strongly enriched in LILE (particularly Sr and Ba) and LREE (up to 4329 ppm), but are relatively depleted in HFSE (Na, Ta, and Zr). The carbonatite samples have higher overall REE concentrations (2910–4422 ppm) than the syenite samples (62.6–77.1 ppm) in Dalucao deposit (Table 2). The syenite, carbonatite, and REE mineralization have overlapping emplacement ages (Tian et al.,

2008b; Liu et al., 2015a). They also possess similar Sr–Nd isotope compositions, display similar mantle-normalized trace element patterns, and occur in close spatial relationship to one another. These observations suggest the existence of a genetic relationship between the carbonatite, the syenite, and the REE mineralization. The carbonatites and syenites in western Sichuan are thought to have been generated by partial melting of the subcontinental lithospheric mantle, which was previously metasomatized by Li-rich fluids derived from subducted oceanic crust and marine sediments (Tian et al., 2015). This melting was most likely triggered by the upwelling of an asthenospheric mantle diapir related to India–Asia continental collision in the Cenozoic, or

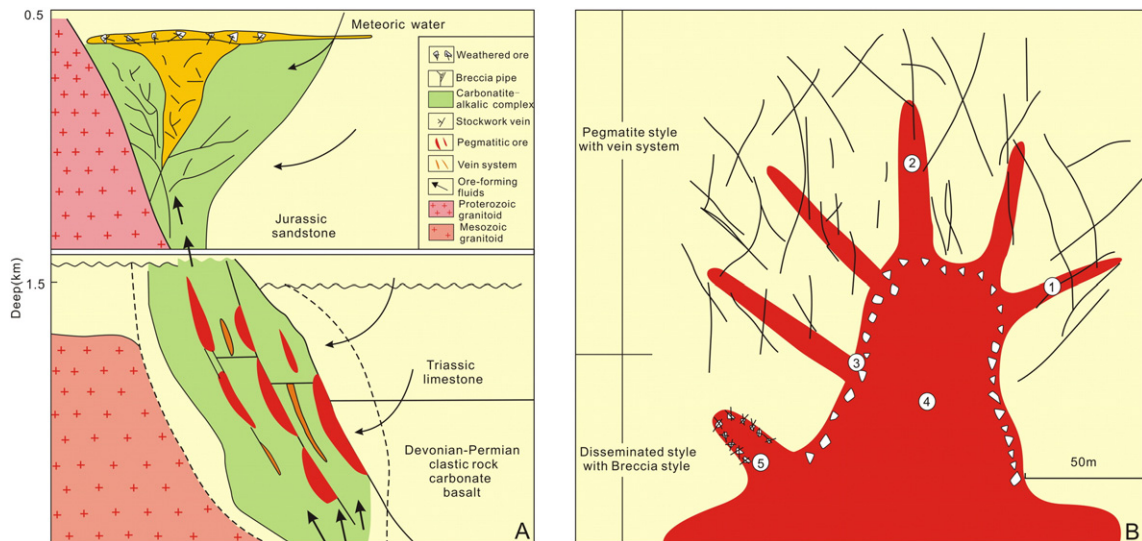


Fig. 13. A. Model of the formation of REE deposits in the MD REE Belt. See the text for details. B. Carbonatite-related REE deposit model showing different mineralization styles in different parts of the system. 1—Vein and stock-work systems at the outer and top zone; 2—pegmatite in the middle of the upper zone; 3—banded and breccia style at the contact zone between carbonatite and wall-rock; 4—disseminated mineralization in the carbonatite (lower zone) (A from Hou et al., 2009 and B from Xie et al., 2015).

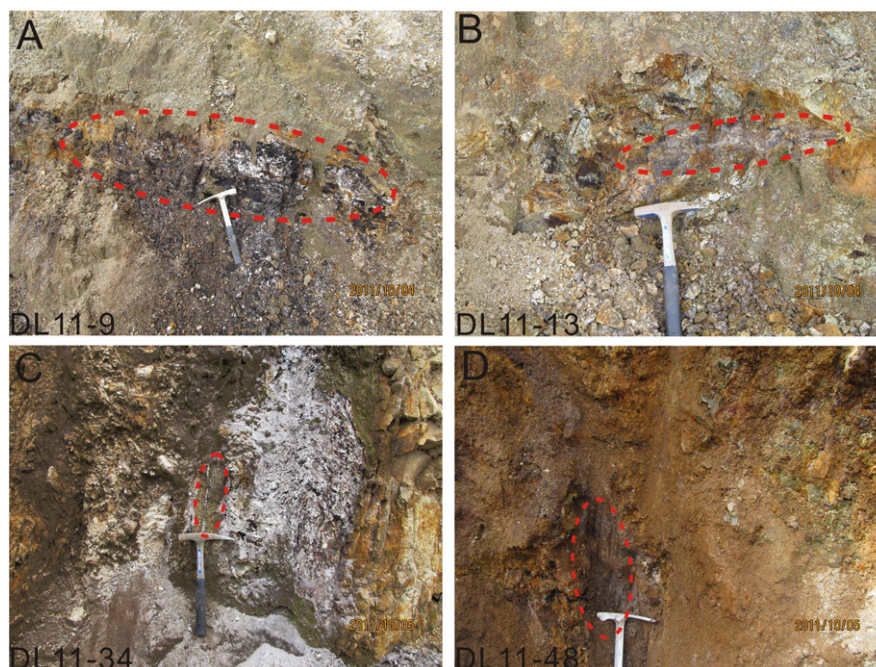


Fig. 14. A. Sample DL11-9: powdery, purple-weathered sample with fluffy texture in altered syenite. B. Sample DL11-13: silty gray-purple weathered sample with fluffy texture. C. Sample DL11-34: powdery, brownish-yellow weathered sample with fluffy texture along a coarse-grained quartz-celestite-fluorite-barite vein. D. Sample DL11-48: powdery, purple-weathered sample with fluffy texture surrounded by altered syenite.

possibly late- or post-collisional stress relaxation in the Oligocene (Hou et al., 2014; Tian, 2005; Hou et al., 2006; Liu et al., 2015a).

The carbonatites at Dalucao contain high REE concentrations (Table 2) and are thought to be the main REE source and the wall-rocks of the three known REE deposits at the Dalucao deposit within the Mianning–Dechang REE Belt, as well as significant contributors of REEs to the Dalucao orebodies and other deposits in the Himalayan MD REE Belt (Xu et al., 2008; Xie et al., 2009). However, the contribution of the syenite to the REE deposit has not been studied in detail, although its alteration and REE content have been analyzed. Five lines of evidence suggest that the syenite was also a source of the REE mineralization, as follows.

1. The syenite in the whole REE Belt has higher total REE contents (62–3656 ppm, with one value of 5356 ppm) than many other rocks such as granite.
2. The occurrence of bastnäsite as one of the main accessory minerals in syenite suggests that the syenite is one of the sources of REE that subsequently formed the orebodies at Dalucao.
3. In the No. 1 orebody, syenite forms the main wall-rock to the REE ore veins and occurs with much greater volumes than the carbonatite, as also observed in the Maoniuping (Fig. 12B) and Lizhuang deposits.
4. The syenite is extensively hydrothermally altered (Liu et al., 2015b), and areas of highly altered syenite are cut by REE-bearing ore veins (Fig. 12C, D).
5. The syenite, carbonatite, and REE mineralization in the No. 1 and 3 orebodies have overlapping emplacement ages of 11–12 Ma (Tian et al., 2008a,b; Liu et al., 2015a).

5.3. Genesis of the weathered ore in the No. 1 Dalucao orebody

Because of its high grade and large size, weathered ore in the No. 1 orebody is the main ore type currently being mined in the Dalucao deposit. In contrast, only minor amounts of weathered ore occur in the No. 3 orebody at Dalucao, or in the Maoniuping and Lizhuang deposits. Although the various deposits in the MD REE Belt are related to syenite and carbonatite intrusions, the

degree of alteration, mineralization style, and ore types are different, which indicates substantial differences in the pressure, temperature, fluid flux, and duration of fluid activity within each of the mineralizing systems (Fig. 13) (Hou et al., 2009; Kynicky et al., 2012; Xie et al., 2015). At the Maoniuping REE deposit, the extensive carbonatite–syenite complex is associated with large amounts of hydrothermally altered rocks composed of coarse-grained quartz–fluorite–barite–celestite (Fig. 12). This suggests that the igneous complexes provided the REE as well as magmatic fluids with a high fluid flux. This inference is consistent with the occurrence of extensive coarse-grained bastnäsite (Fig. 12C) and bastnäsite veinlets or veinlet swarms within the ores, which constitute one of the largest REE deposits in the world. Hou et al. (2009) and Xie et al. (2015) proposed models to explain the geographic distribution of deposits in the Mianning–Dechang REE Belt and their ore types (Fig. 13). However, their models did not consider the effects of weathering in generating the high-grade ores, although from our work it appears that weathered ores are closely associated with the brecciated ores.

In the Lizhuang district, carbonatite–syenite complexes intrude a 1000-m-thick sequence of Silurian–Triassic volcano-sedimentary rocks. This, combined with the brecciated nature of the lower part of the deposit, is evidence that REE mineralization formed at a greater depth compared with the Dalucao and Maoniuping deposits. At Dalucao and Maoniuping, REE mineralization occurs mainly as small lenses of bastnäsite within cross-cutting veins and fractures in the complex, rather than the coarse-grained bastnäsite in the Lizhuang deposit (Fig. 12D). Compared with Maoniuping, the Dalucao deposit has a smaller syenite–carbonatite complex and narrow fluorite–quartz–barite–calcite veins that cut the complex, which suggest a small-scale ore-forming system with a relatively low fluid flux. Furthermore, the presence of two breccia pipes at Dalucao and the absence of coarse-grained bastnäsite or REE veinlets, may indicate a shallow depth of REE mineralization (Liu et al., 2015b).

At Dalucao, the emplacement of a carbonatite–syenite complex at shallow crustal levels would have led to extensive boiling of magmatic fluids, resulting in cryptoexplosive events and the formation of the

breccia pipes. Our study suggests that both the No. 1 and No. 3 orebodies underwent at least four episodes of cryptoexplosive brecciation (Fig. 6), resulting in the formation of fine-grained gangue and wall-rock hosted REE mineralization. It is also apparent that the location of the No. 1 orebody is controlled by two main faults, in addition to controlling the location of the cryptoexplosive breccia, whereas the No. 3 orebody has experienced less faulting and cryptoexplosive brecciation. Petrographic studies show that the No. 1 orebody contains more generations of bastnäsite and other REE minerals, and has a finer grain size of the REE and gangue mineralization than the No. 3 orebody (Liu et al., 2015b).

The occurrence of cryptoexplosive breccia and faulting in the No. 1 orebody led to favorable conditions for alteration of the syenite–carbonatite complex and subsequent overprinting by hydrothermal fluids, which led to the deposition of fine-grained REE minerals in ore veins. In addition, brecciation led to an increase in weathering that led to upgrading of the ores. Field observations also show that weathered ores developed mainly along fractures in the No. 1 orebody, which increases in width from several centimeters at the top (Fig. 8A) to 1 m towards the bottom (Fig. 14D). Consequently, multiple stages of REE mineral formation are related to faulting and brecciation, which facilitated the introduction of ore-forming fluids. During later stages of weathering, large amounts of clay minerals formed, which, together with the removal of calcite, led to the generation of high-grade ores.

6. Conclusions

Rocks from the Dalucao REE deposit can be grouped into four types: (1) weathered syenite, (2) hydrothermal mineral veins, (3) ore veins, and (4) the contact zone between syenite and ore veins. The latter two types represent the main ores targeted for mining because of the large amounts of contained REE minerals (up to 60 wt.%), whereas the first two types are unsuitable for mining because of their low grade. Bastnäsite, parisite, and monazite are the main REE minerals in the weathered ore. The REE mineralization developed during the late stages of hydrothermal evolution and overprinted the brecciated fluorite–quartz hydrothermal veins. Subsequent weathering led to an enrichment in the REE contents and consequently the generation of high-grade ores, primarily through the removal of fluorite, barite, celestite, and calcite.

The petrographic characteristics of the weathered ores are similar to those of the brecciated ore, which indicates that no further REE mineralization developed as a consequence of weathering and that further refertilization of REE occurred in situ, as REE minerals are immobile. During the weathering process, large amounts of clay minerals formed, including illite, smectite, kaolinite, and chlorite. Most of the weathered samples contain little or no calcite, barite, feldspar, celestite or fluorite, but instead commonly contain large amounts of clay and REE minerals. Although the concentrations of La, Ce, Pr, and Nd are higher in the weathered ores, Sr concentrations are appreciably lower due to the loss of celestite or Sr-bearing calcite.

Two main factors explain the extensive occurrence of weathered high-grade ores within the No. 1 orebody at Dalucao compared with other deposits in the MD REE Belt. Firstly, the No. 1 orebody is hosted within a breccia pipe that contains evidence of at least four episodes of brecciation. The REE mineralization also formed at shallower crustal levels than the other deposits in the MD REE Belt, such as at Maoniuping and Dalucao. Secondly, the No. 1 orebody experienced more faulting and brecciation than did the No. 3 orebody and other deposits within the whole Mianning–Dechang REE Belt, which resulted in additional REE mineralization and enabled a high degree of weathering, and consequently the generation of high-grade ores.

Conflict of interest

On behalf of all authors including “Yan Liu, Zhimin Zhu, Chao Chen, Shuping Zhang, Xiang Sun, Zhusen Yang, Wei Liang,” in this manuscript

“Geochemical and mineralogical characteristics of weathered ore in the Dalucao REE deposit, Southwestern China”, we declare that there is no conflict of interest among them and their identities. If anything, please do not hesitate to contact me.

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