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Rare-Earth Mineralization in Dong Pao Deposit, Laichau Province, Vietnam

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ABSTRACT

The Dong Pao deposit in northern Vietnam is associated with the Paleogene Dong Pao Syenite Complex, which intruded into the limestone of the Triassic age. Although the Dong Pao deposit has been attracting exploration for decades as a promising rare earth deposit, it has not been well studied in terms of mineralization style and formation process until recently. We describe the occurrence of the orebodies of the deposit and the mineralogy of collected samples to discuss the mineralization style and process that formed the huge rare earth resource at Dong Pao. The deposit is composed of 60 orebodies, which occur where the syenite of the Eocene Dong Pao Complex contacts with the limestone of the Dong Giao Formation. Most of the orebodies exhibit a lenticular shape, situated at the boundary between the syenite and limestone along the margin of the complex, with the exception of the F3 orebody, where carbonatite is located. The F3 carbonatite consists mainly of calcite, which has carbon and oxygen isotope ratios slightly to moderately deviated from primary igneous carbonatites, due possibly to the assimilation of limestone. Two distinct styles of rare earth mineralization, metasomatized carbonatite and metasomatized limestone, are observed. The F3 metasomatized carbonatite is characterized by the replacement of calcite by synchysite-(Ce) and parisite-(Ce) in addition to fluorite, barite, celestine, and sulfides. The metasomatic limestone orebodies contain dolomite overprinted by the assemblage of barite, fluorite, bastnäsite-(Ce), parisite-(Ce), quartz, and sulfides. The metasomatic limestone zone at the F9 orebody is intruded by hydrothermal veins, which contain similar mineral assemblage to the metasomatic zone, although HREE-enriched minerals such as xenotime and synchysite-(Y) are present. The REE mineralization in these metasomatized rocks is interpreted to have formed by the reaction of carbonate-rich metasomatic fluids with carbonatite at F3 and fluorine-rich fluids at the other orebodies with limestone. Such different fluids possibly exsolved from carbonatite magma and syenite magma, respectively. The Dong Pao deposit is an analogue of skarn deposits, although instead of calc-silicate minerals, the metasomatic rocks at Dong Pao contain fluorite, barite, and REE-bearing fluorcarbonate minerals, because of the scarcity of silica and alumina in the hydrothermal fluids and host rocks. A large tonnage of the resource (> 4.7 Mt. of REO) is estimated at Dong Pao because of many orebodies scattered around the complex. In addition, the present semi-tropical climate of northern Vietnam accelerates surface weathering of orebodies, upgrading the REE ores.

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1 | Introduction

The global demand for rare earth elements (REEs), crucial for various applications such as permanent magnets in electric vehicles and renewable energy technologies, has been increasing in recent years as part of the global effort to achieve decarbonization objectives. This increasing demand has driven the search for new supply sources of REEs in addition to China, the world's largest producer of REEs.

The United States Geological Survey (USGS 2024) reported that Vietnam hosts 22 Mt. of REE (as oxides: REO) reserve, which is the second largest reserve after China. Vietnam yields various types of REE deposits, such as alkaline rocks and/or carbonatite-related (Dong Pao, Nam Xe, Muong Hum, and Yen Phu), ion-adsorption type (Ben Den), and placer deposits (Kušnir 2000; Khoi 2014; Chiba 2023; Figure 1). Most of the magmatic intrusion-related deposits are concentrated in the northern provinces along the Red River Fault Zone (Figure 1). Among these, Dong Pao is the largest deposit with reserves of 7 Mt. of REO (Orris and Grauch 2002).

The Dong Pao deposit was discovered in 1959 by Geological Division No. 16 of Vietnam with help from Soviet geological experts. Subsequent geological exploration works by the Vietnamese government discovered many orebodies in the 1960s. During the 1980s, major orebodies (F1, F3, F7) were explored in detail, and 288 Mt. at 6%–41% of barite resources were calculated (Hirano, Kamitani, and Sudo 1996). The deposit was explored by the Japan International Cooperation Agency (JICA) and the Metal Mining Agency of Japan (MMAJ) in 2001–2002 for the most promising F3 orebody (Fujii et al. 2010). Currently, the deposit is managed by VIMICO, a subsidiary company of Vietnam National Coal-Mineral Industries Holding Corporation Limited. According to the latest exploration reports, the total REO resource is more than 4.7 Mt. In addition, the deposit hosts > 24.5 Mt. barite and > 13.7 Mt. fluorite (Nguyen 2010).

The Dong Pao deposit is associated with the Paleogene Dong Pao Syenite Complex, which intruded into the limestone of the Triassic age (Fujii et al. 2010). Although the Dong Pao deposit has been attracting exploration for decades as a promising rare earth deposit, it has not been well studied in terms of mineralization style and formation process until recently.

JICA and MMAJ (2002) confirmed the presence of a high-grade orebody between the syenite and carbonate rocks by drilling. The report described the carbonate rocks as limestone and argued that the rare earth mineralization occurred by the reaction between the limestone and the fluids exsolved from the syenite magma. However, Fujii et al. (2010) described the coarse-grained carbonate rock below the F3 orebody as carbonatite on the basis of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions of the carbonate minerals. Li et al. (2023) also analyzed carbon and oxygen isotopes of calcite of the carbonate rock and confirmed that it has $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions similar to the primary igneous carbonatites with slight to moderate deviation toward the marine carbonates. Such a deviation is interpreted to have been caused by the assimilation of limestone by carbonatite magma (Li et al. 2023) or overprinted hydrothermal alteration (Fujii et al. 2010). Since then, many authors have assigned Dong Pao as a carbonatite deposit (e.g., Smith et al. 2016; Li et al. 2023), although such carbonatite has not been confirmed except the F3 orebody.

We conducted field surveys in 2011 and 2022, described outcrops, and collected samples from major orebodies (F7, F9) in addition to F3 in the Dong Pao deposit. In this paper, we describe the occurrence of these orebodies and the mineralogy of the collected samples to discuss the mineralization style and process that formed the huge rare earth resource at Dong Pao.

2 | Geological Setting

Northern Vietnam is situated within the Sino-Vietnam composite terrane, also known as the Yangtze terrane, a part of the larger South China block. This region is distinctly separated from the Indochina block by the Song Ma Suture Zone to the southwest (Figure 1; Thanh, Janvier, and Phuong 1996; Lan et al. 2003; Wakita and Metcalfe 2005). The Northern Vietnam region is further subdivided into southwest and northeast Vietnam by the lengthy Red River Fault Zone (Figure 1), which is more than 900-km long. This fault zone comprises narrow (<20-km wide) high-grade metamorphic zones of Xuelong Shan, Diancang Shan, and Ailao Shan in China and Ailao Shan and Day Nui Con Voi in Vietnam. All these metamorphic zones consist largely of Oligocene–Miocene metamorphic-age gneiss formed from Precambrian protolith (e.g., Leloup et al. 1995).

The Dong Pao deposit, together with the Nam Xe and Muong Hum deposits, is located in the Son La–Lai Chau Zone, bounded in the northeast by the Red River Fault Zone and southwest by the Song Ma Suture Zone (Figure 1). The Son La–Lai Chau Zone includes mafic suites of gabbro, pillow basalt, and volcanic breccia of Permian to Triassic in age (Polyakov et al. 1999; Tran et al. 2008; Tran 2010). These mafic suites are overlain by an Upper Permian formation, which consists of shallow marine limestone, coal, bauxite, and iron units in ascending order (Metcalf 2012). This Upper Permian formation is conformably overlain by Lower to Middle Triassic submarine sedimentary rocks, and unconformably covered by Upper Triassic conglomerate and sandstone, or by Cretaceous continental red beds (Faure et al. 2014).

During the Paleogene, alkaline igneous magmas intruded in the Son La–Lai Chau Zone to form the large 34–35-Ma Ye Yen Sun batholith and the smaller 49–51-Ma Ban Xeo alkali granite complex (Pham et al. 2020). In addition to the batholith and igneous complex, swarms of small dikes of potassic and ultrapotassic rocks are distributed in the Son La–Lai Chau Zone (Thi et al. 2014). These alkaline rocks vary from alkaline mafic (lamproite, trachyandesite, minette) to alkaline felsic rocks (trachyte and syenite). These alkaline rocks are dated in the range from 42 to 30 Ma by Ar–Ar and Rb–Sr methods and are related to the late Paleogene intraplate extension activities in northwest Vietnam (Tran 1995; Tran et al. 1998, 2016; Tran and Vu 2011).

3 | Geology and Orebodies in the Dong Pao Area

In the Dong Pao deposit area, limestone and fine clastic sedimentary rocks of the Lower to Middle Triassic Dong Giao Formation are distributed (Figure 2). This limestone is covered by Cretaceous conglomerate and siltstone in the southwestern part of the area.

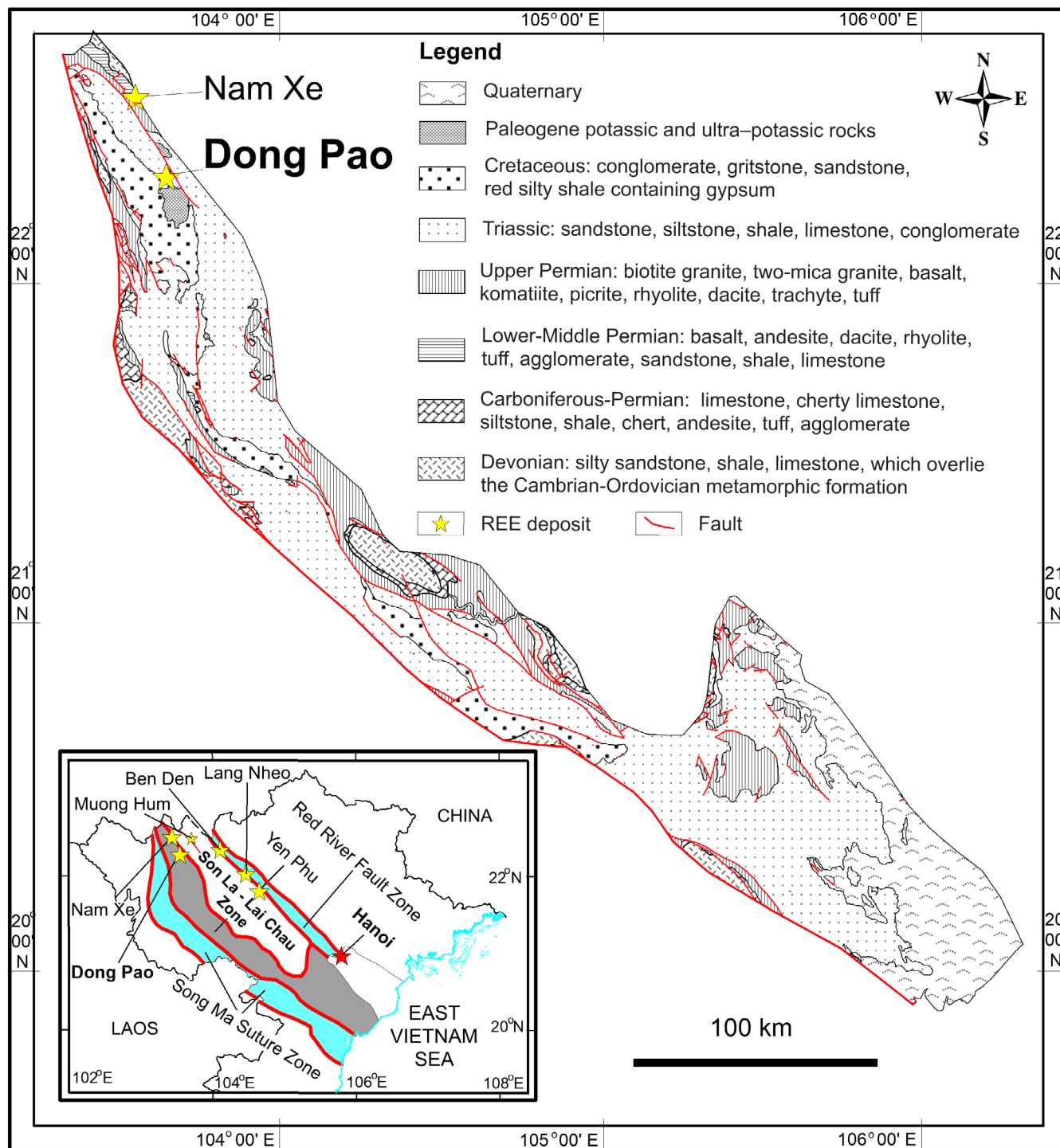


FIGURE 1 | Geologic map of the Song Da structure, modified from Tran (2010).

The Triassic limestone is intruded by the Dong Pao Syenite Complex, which measures 3.5 km by 5.5 km in plan view and occupies an area of 8.9 km². The complex is located at a gentle NW-trending anticline axis and is put between two major faults of the same trend. The complex is slightly extended in an NW direction and has a form of laccolith. This intrusive complex is covered in some places by alkaline volcanic rocks. The complex is intruded by small lamprophyre dikes in NE and NW directions. The complex is mainly composed of syenite and quartz syenite and includes a “carbonatite” body in the F3 orebody. Li et al. (2023) reported U–Pb zircon ages of the syenite as 51.6 ± 0.4 Ma and 52.4 ± 0.4 Ma.

The syenite and quartz syenite are enriched in orthoclase (> 80 vol.%) with plagioclase, biotite, clinopyroxene, and rare quartz. Titanite, garnet, apatite, and magnetite occur in trace amounts in the syenite. The rocks in the area are heavily weathered (~100 m), and limestone forms a karst landscape with sinkholes and pinnacles.

The Dong Pao deposit consists of about 60 orebodies. These orebodies have an averaged REO grade of 5.96 wt% (Nguyen 2010). Large-sized orebodies have the shape of vein and lens and are distributed near the contacts between the intrusive rocks of

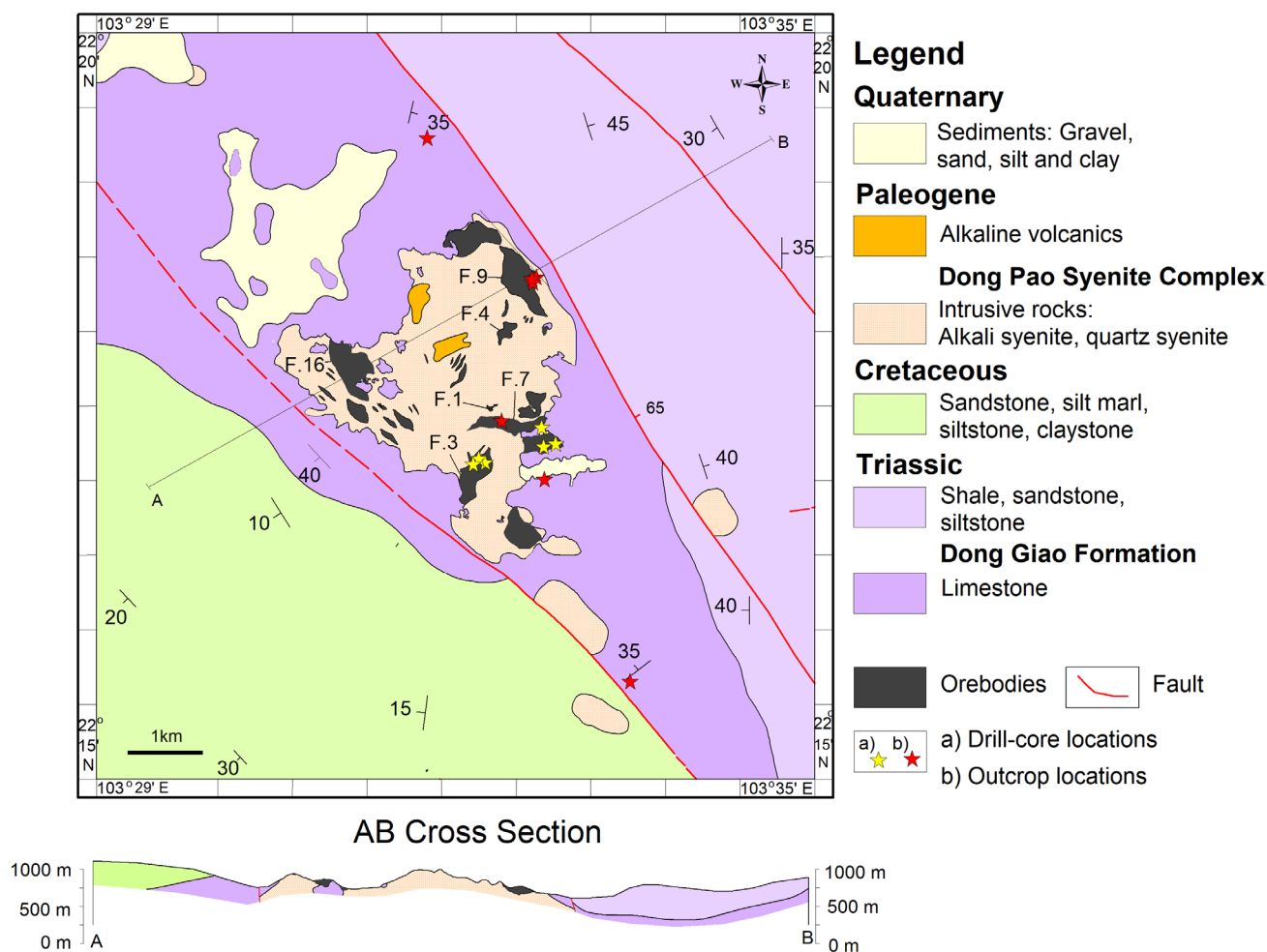


FIGURE 2 | Geological map of the Dong Pao deposit (Nguyen 2010).

the Dong Pao Complex and the limestone of the Dong Giao Formation (Figure 2; Khang 2002; Nguyen 2010). Small-sized orebodies are composed of dissemination, veins, and stockwork veinlets in the limestone (Nguyen 2010).

Major ore minerals of these orebodies are bastnäsite, parisite, allanite, barite, and fluorite. The ore grades $\sum\text{REO}$ vary from 0.5 wt% to 39 wt% and are enriched in light REEs. The fluorite (CaF_2) content ranges from 2.7% to 61% and barite (BaSO_4) from 1.8% to 55%. Radioactive elements such as U and Th are 0.006%–0.010% U_3O_8 and 0.011%–0.033% ThO_2 , respectively (Khang 2002; Nguyen 2010; Bui and Trinh 2017).

4 | Analyzed Samples and Methods

Rock samples were collected from the surface outcrops of the F3 and F9 orebodies and drill cores of the F3 and F7 orebodies. Carbonatite samples were collected at a depth of 52–83 m of the F3 orebody.

We used a Rigaku MultiFlex x-ray diffractometer with $\text{CuK}\alpha$ tube (30 kV, 16 mA, receiving slit = 0.3 mm, step = 0.01, 2° $2\theta/\text{min}$) for the identification of constituent minerals of the samples at

the Graduate School of International Resource Sciences, Akita University, Japan. Randomly oriented whole-rock powdered samples were scanned from 2° to 60° 2θ .

To identify minerals based on chemical compositions and to observe mineral texture, we use a JEOL JSM-IT300 scanning electron microscopy (SEM) equipped with an Oxford Instruments X-Max 50 mm² energy-dispersive spectroscope (EDS) attachment. Calibration was done using the pure cobalt standard. SEM-EDS analysis was operated at 15 kV, ~80 nA, and WD = 10 mm at Akita University.

Chemical compositions of minerals were analyzed using an electron probe micro analyzer (EPMA), a JXA-8230 EPMA model at Akita University, and a JXA-8530F Field Emission EPMA at the Institute for Geo-Resources and Environment, AIST, Japan. At Akita, for imaging and determining mineral compositions, backscattered electron (BSE) images were captured. The analytical condition is a 15-kV accelerating voltage, a 20-nA beam current, and a 2- μm beam size. Both natural minerals and synthetic oxides were employed for calibration. The correction for matrix effects was performed utilizing the ZAF program provided by the manufacturer. Specific standards were employed for the EPMA analyses: Periclase for Mg, plagioclase for Al, barite for

Ba, fluorite for F and Ca, celestine for Sr., quartz for Si, tugtupite for Cl, pyrite for S, LaF_3 (LIFH), CeF_3 (LIFH), NdF_3 (LIFH), and PrF_3 (LIFH) for La, Ce, Nd, and Pr, respectively.

Major and trace element compositions of representative ores were analyzed by x-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) after a lithium metaborate/tetraborate fusion technique. These analyses were conducted at the Activation Laboratories, Ontario, Canada.

Six calcite samples of “carbonatite” and limestone were analyzed for C–O isotopes. Samples were pulverized to a grain size of 180–320 μm . Then, heavy minerals such as barite were separated by using a heavy liquid. After separation, samples were washed with distilled water and dried in an oven at 50°C. Samples were checked by XRD to confirm that they were pure calcite before hand-picking calcite grains. Finally, the samples were crushed with an agate mill to a grain size of less than 100 μm and retested with XRD before being sent for isotopic analysis at the Activation Laboratories, Ontario, Canada.

5 | Results

5.1 | Field Observation

We observed outcrops and drill cores obtained from the F3 orebody and outcrops at the F9 orebody in detail. The F3 orebody occurs in carbonate rocks, which were first described as

limestone (JICA and MMAJ 2002) but reinterpreted as carbonatite based on carbon and oxygen isotopic studies (Fujii et al. 2010; Li et al. 2023). This carbonatite, which exhibits 300 and 400 m in plan view, is distributed in the syenite of the Dong Pao Complex. Relatively unaltered parts of the carbonatite that occur near the contact with the syenite are mainly composed of calcite and barite with fluorite dissemination. The central portion of the carbonatite is heavily metasomatized and weathered, characterized by the decomposition of calcite and a high concentration of barite and Mn oxides. This alteration zone extends down to 100 m below the surface (Figure 3a).

In the F9 orebody, syenite contacts with limestone through the metasomatic zones of tens to several tens of meters in thickness. These metasomatic zones consist of a mixture of syenite and carbonate rocks. This zone mainly contains fluorite, barite, quartz, and REE carbonates, as well as REE phosphates. The most eastern metasomatic zone close to limestone includes 5 cm-thick banded veins consisting of fluorite, barite, REE carbonates, and phosphates. The metasomatic zone also contains a few meter-sized dolostone blocks, which are the alteration product of limestone. The top surface of the orebody is heavily weathered, resulting in purple-colored fluorite-rich soil with barite covering the syenite. A similar relation is observed at the outcrops of the F1 and F4 orebodies (Figure 3c,d; JICA and MMAJ 2002).

On the surface of the F1 orebody, two veins, 2–3-m thick, extend in a west–northwest direction. Those veins are fluorite-rich and very soft due to weathering.

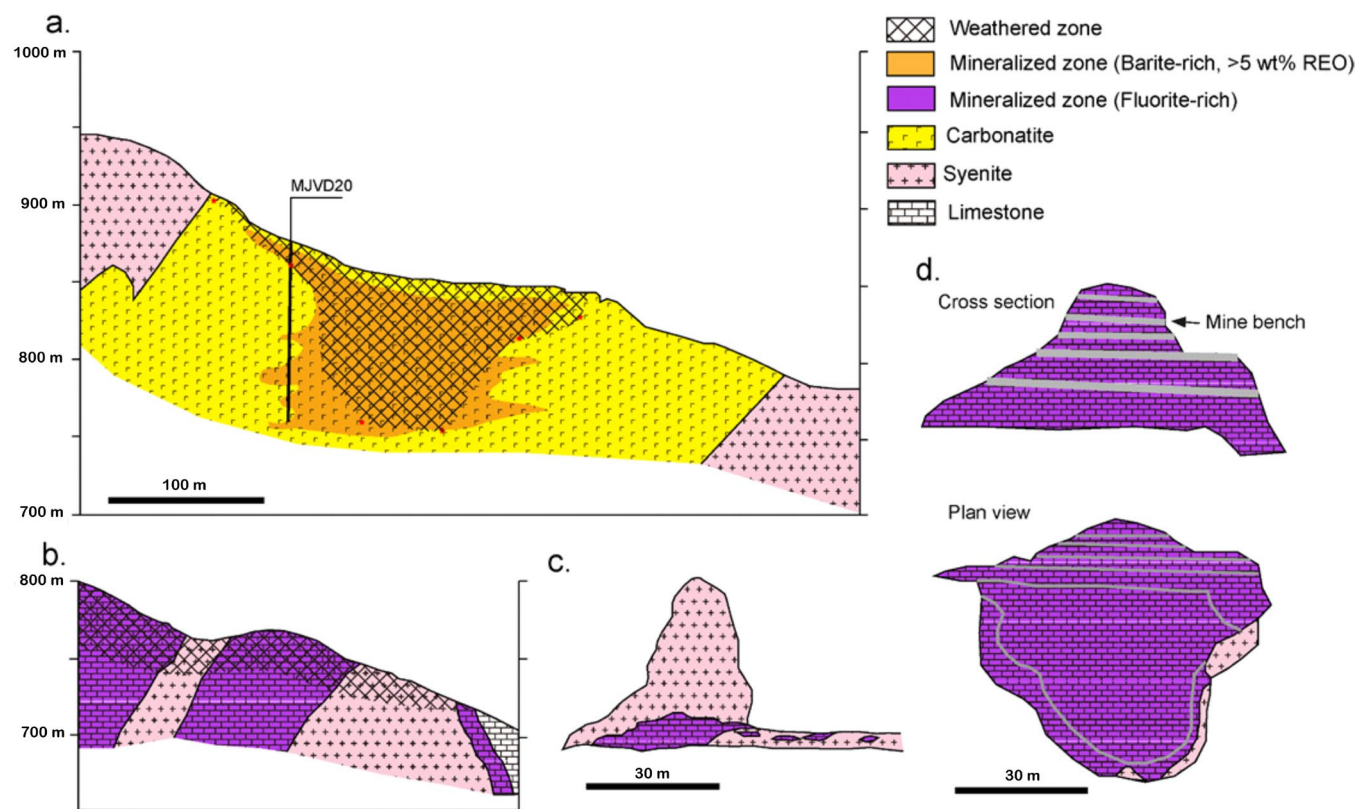


FIGURE 3 | Occurrence of REE orebodies in the Dong Pao deposit. (a) A cross section of the F3 orebody modified from JICA and MMAJ (2002). MJVD20 drill hole location is shown. (b) A cross section of the F9 orebody (This study). (c) A sketch of the F1 orebody (JICA and MMAJ 2002), (d) A sketch of the F4 orebody (JICA and MMAJ 2002).

5.2 | Lithology

5.2.1 | Limestone and Dolostone

The limestone of the Dong Giao Formation is exposed around the Dong Pao Complex forming pinnacles as high as 800 m. The limestone is compact and fine-grained, dark gray in color. The contact between the syenite and the limestone is clearly observed in several outcrops. The limestone is composed mainly of calcite (92%–99% in volume) and includes orthoclase fragments (Figure 4a,b). It is commonly crushed, cracked,

marbleized, or transformed into dolostone (Figure 4c). In some places, the limestone and marble have calcite veins and veinlets (Figure 4b).

Dolostone occurs along the contact between limestone and syenite. The representative rock samples collected from the drill holds KE257 (41 m) and KE272 (30 m) are located below the F7 orebody. They are yellowish brown in color and characterized by banded and/or porous textures of dolomite (Figure 4c,d), which may represent the original bedding plane and volume reduction by dolomitization, respectively (Amthor and

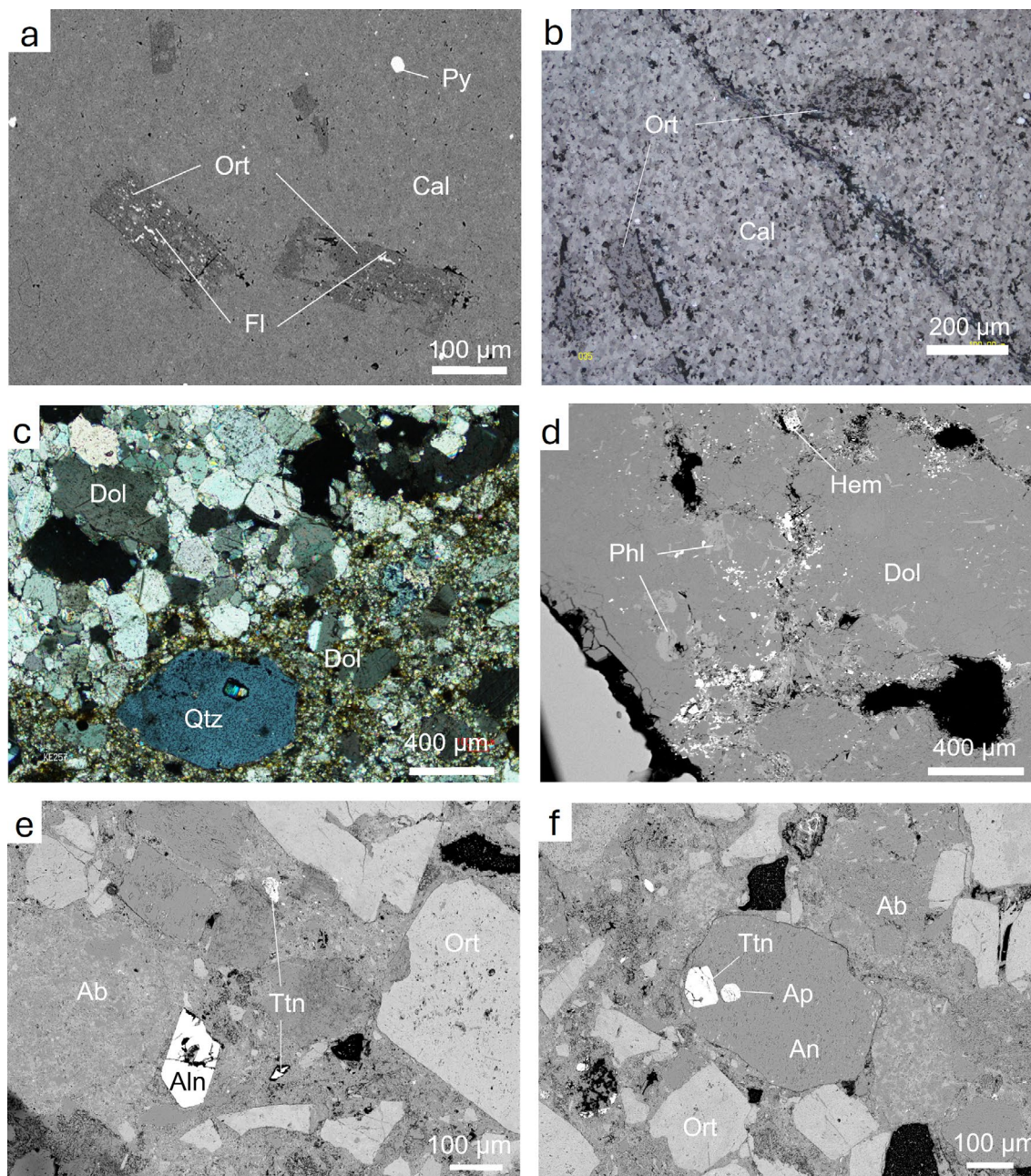


FIGURE 4 | (a, b) Microphotograph of limestone, containing mineral fragments of orthoclase, is included. Small pyrite (Py) also occurs in the calcite (Cal) matrix. (c, d) Microphotograph and back-scatter image of dolostone. Dolostone consists of layers of large grains and small grains of dolomite (Dol). Quartz (Qtz) grain is included in the layer of small dolomite layer (c). Dolostone is porous, and hematite (Hem) and phlogopite (Phl) occur in dolostone (d). (e, f) Back-scattered electron microscope images of porphyritic syenite containing phenocrysts of albite (Ab), orthoclase (Ort), and anorthoclase (An) in a groundmass of albite and K-feldspar. Allanite (Aln) and titanite occur as phenocrysts (e). Anorthoclase includes titanite (Ttn) and apatite (Ap) (f).

Friedman 1991). The dolostone consists mainly of dolomite, and includes feldspar, quartz, and titanite (Figure 4c). The banded fine-grained dolomite layers contain oriented phlogopite and feldspar. Occasionally, quartz grains are included in the layers. In the porous dolostone, fluorite and hematite occur in the dolomite grain boundaries, which suggests metasomatic alteration, although no rare earth mineral is included in these samples (Figure 4a,d).

5.2.2 | Syenite

Syenite is the major lithofacies of the Dong Pao Complex. It is fine-grained pinkish-gray or yellowish-brown in color. The syenite is composed of orthoclase, albite, anorthoclase, biotite, pyroxene, and quartz. Accessory minerals are titanite, apatite, allanite, zircon, and monazite (Figure 4e,f). It shows a porphyritic texture with feldspar phenocrysts, 0.5–1 mm in length. Some anorthoclase is decomposed into K-feldspar and albite. Quartz is anhedral and usually interstitial to feldspar. The minor minerals are small (5–50 μm) in size and associated with or included in anorthoclase. Biotite is small in size and commonly occurs along the grain boundaries of feldspar. Most biotite grains are decomposed into secondary minerals. Pyroxene is completely weathered to secondary iron minerals. Most albite grains are also decomposed into secondary albite and K-feldspar.

5.2.3 | Carbonatite

Carbonatite is white in color and coarse-grained. It is dominantly composed of calcite with minor phlogopite; however, calcite is replaced by fine-grained minerals ($< 5 \mu\text{m}$) including apatite, carboxenite $[\text{Ca}(\text{Sr}, \text{Ba})(\text{CO}_3)_2]$, celestine $[(\text{Sr}, \text{Ca}, \text{Ba})\text{SO}_4]$, strontianite $[\text{SrCO}_3]$, and phlogopite along anastomosing fractures (Figure 5a). At the shallow depth (52 m), veinlets consisting of fluorite, barite, and synchysite-(Ce) are present in carbonatite. Large euhedral to subhedral crystals of fluorite (0.5–2 cm) and barite appear at a depth of 76–78 m in the drill core MJVD20 (Figure 5c). Barite includes sulfide minerals such as sphalerite, galena, and pyrite. Calcite is replaced by euhedral, tabular, and acicular synchysite-(Ce), celestine, barite, and fluorite. Strontium concentration in barite is variable, exhibiting different brightnesses of barite in the backscatter images (Figure 5b). Parisite-(Ce) and bastnäsite-(Ce) occur as acicular needles that overprint synchysite-(Ce).

5.2.4 | Weathered Materials

The rocks exposed on the surface are heavily weathered to form soft clayey materials, and occasionally, their protoliths are hard to identify. However, they can be separated into three protolith types based on their color and constituent minerals. Brown-colored clayey materials are mainly composed of orthoclase, quartz, and mica, and heavily weathered materials are enriched in kaolinite, halloysite, and smectite together with gibbsite and zeolite group minerals. These brown-colored materials are widespread on the syenite of the Dong Pao Complex. The abundance of silicate minerals of this type indicates that their protolith is syenite.

Another type is deep purple-colored materials. They commonly form REE orebodies, which are scattered in the areas where the syenite of the Dong Pao Complex is exposed. The orebodies (F9, F16) are exposed in areas about 1.5 km by 0.5 km on the surface (Figure 2). These orebodies are lenticular in shape and ~100-m thick, present near the contact between syenite and limestone (Figure 3). These orebodies change either into fresh limestone or syenite at depth. The constituent minerals of the purple-colored materials are dominated by fluorite and barite (fluorite > barite) together with minor quartz, bastnäsite, mica, and trace amounts of phosphate minerals. This mineralogy is distinctly different from the brown-colored materials and suggests that they are the weathered products of limestone, which underwent metasomatic alteration.

The last type is black-colored materials. They typically occur at elevations higher than 850 m, covering yellowish-brown clayey materials in the F3 orebody. The black-colored material is enriched in barite together with a lesser amount of fluorite and Mn oxides. Carbonate minerals are scarcely observed except bastnäsite. This type contains cryptocrystalline florencite-(Ce) $[\text{CeAl}_3(\text{PO}_4)_2(\text{OH})_6]$, cerianite $[\text{CeO}_2]$, bastnäsite-(La), and bastnäsite-(Ce). The protolith of this type is carbonatite because the presence of carbonatite is confirmed by the drill cores at depth.

5.3 | Ore Mineralogy

5.3.1 | Ore Mineralogy in the Metasomatized Rocks

XRD, SEM-EDS, and EPMA analyses of typical ores from veins and metasomatic rocks in the F7 and F9 orebodies indicate that the common REE minerals are bastnäsite-(Ce), parisite-(Ce), monazite-(Ce), xenotime-(Y), and florencite-(Ce), with gangue minerals comprising mainly quartz, barite, fluorite, hematite, orthoclase, pyrite, galena, and sphalerite. Parisite-(Ce) in the F9 ores is minor in amount compared to that in the F7.

The samples (017LM, 017) from the metasomatic zone between the syenite and limestone in the F9 orebody are massive and are comprised of dolomite, orthoclase, barite, fluorite, rare earth minerals, quartz, and sulfides. These samples show a brecciated texture with large fragments (0.1–2 cm) of dolomite and orthoclase set in the matrix of fluorite, barite, quartz, and rare earth carbonates [bastnäsite-(Ce), parisite-(Ce)] (Figure 6a,b,d). Closing to the limestone, the matrix changes into calcite or a mixture of orthoclase and dolomite, which are overprinted by the assemblage of barite, fluorite, REE minerals, and quartz (Figure 6c). These metasomatized rocks are cut by hydrothermal veins. Sulfide minerals in the zone are sphalerite, pyrite, and galena, which are enclosed in fluorite (Figure 6b). Bastnäsite-(Ce) is subhedral and tabular in shape (100–500 μm) (Figure 6a,b).

This metasomatic zone includes 5-cm-thick banded veins (017–3, 017–4, 017–5). The veins contain fluorite, barite, REE carbonates bastnäsite-(Ce), parisite-(Ce), REE phosphates [monazite, xenotime, and florencite-(Ce)] (Table S1, S2), and quartz. In addition, the vein samples include synchysite-(Y), which are secondary and small (1–2 μm) grains occurring with florencite-(Ce) along the grain boundaries of barite and

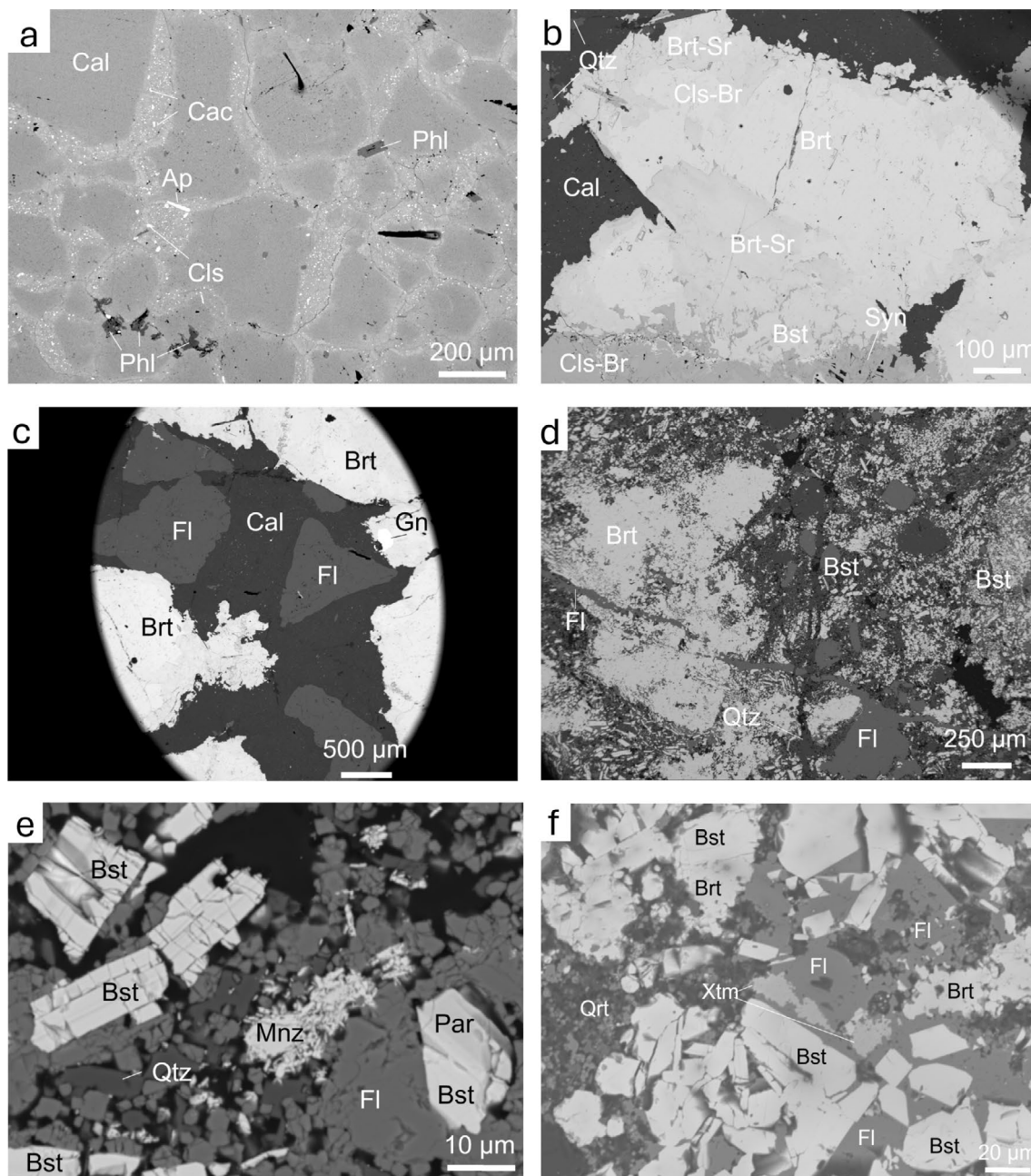


FIGURE 5 | Back-scattered electron image of fresh carbonatite. (a) Coarse-grained calcite is replaced by carbocernaite (Cac), celestine (Cls), apatite (Ap), and phlogopite (Phl) along anastomosing fracture (MJVD18 (52 m)). (b, c) Metasomatized carbonatite (MJVD20 (68 m)), showing calcite replaced by fluorite (Fl), barite (Brt), strontium-bearing barite (Brt-Sr), barium-bearing celestine (Cls-Br), synchysite (Syn), and quartz (Qtz). Barite includes galena (Gn). (d) Banded vein (KE252 (9.5 m)) containing bastnäsite (Bst) hosted by barite and fluorite. (e, f) Close-up images of bastnäsite-Ce occurring with parisite-Ce, monazite (Mnz), xenotime (Xtm), and quartz.

fluorite, as well as in seams cutting large grains of barite and bastnäsite-(Ce), together with xenotime (Figure 6e). These veins also contain sulfides (sphalerite, galena) and hematite. Todorokite $[(\text{Na}, \text{Ca}, \text{K}, \text{Ba}, \text{Sr})_{1-x}(\text{Mn}, \text{Mg}, \text{Al})_6\text{O}_{12} \cdot 3-4\text{H}_2\text{O}]$ fills the voids of the samples or forms thin seams cutting barite and bastnäsite-(Ce) grains, indicating the latest mineral in the paragenetic sequence (Figure 6f).

In the F7 orebody, the ores (KE252, 9.5 m) consist of strongly weathered syenite intruded by banded veins of barite and fluorite, with REE carbonates and phosphates. The ore contains quartz, feldspar, and Fe oxides. Major vein minerals are barite

and fluorite (Figure 5d), together with euhedral bastnäsite-(Ce) and parisite-(Ce). Minor amounts of anhedral to subhedral fine-grained (1–7 μm) xenotime and monazite are included. Euhedral bastnäsite-(Ce) and monazite are hosted by fluorite and barite, suggesting the earlier precipitation of REE minerals than barite and fluorite (Figure 5e). Thin quartz veinlets cut the grains of fluorite and barite at the latest (Figure 5d). Minor pyrite is disseminated.

In the F3 orebody, carbonatite ore samples contain synchysite-(Ce) as the major REE mineral (Table S1, Figure 7a–d). Parisite-(Ce) and bastnäsite-(Ce) are minor. The gangue minerals are calcite, fluorite, barite, Sr-barite,

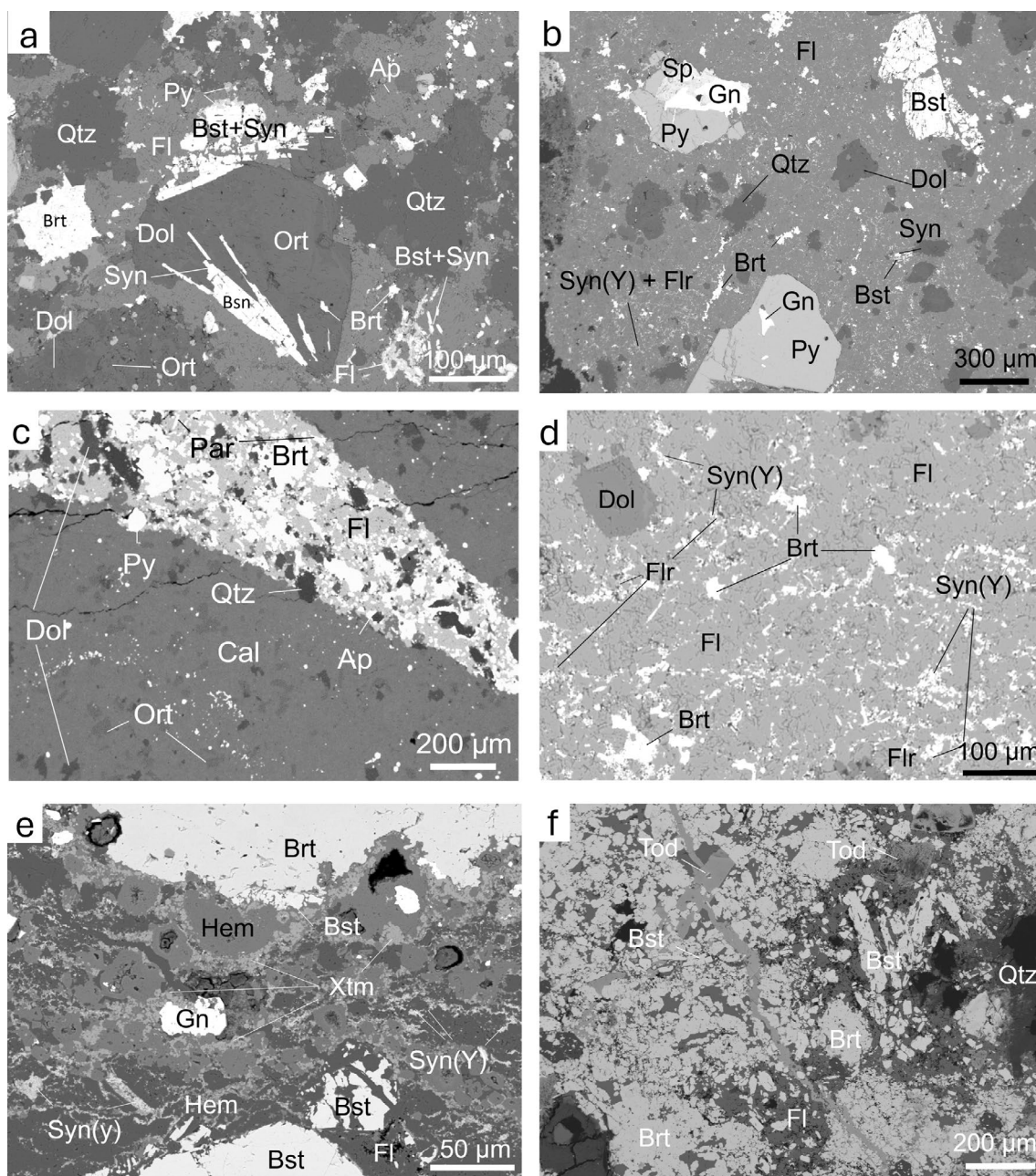


FIGURE 6 | (a–c) Back-scattered electron images of metasomatized limestone (017LM, 017). Dolomite (Dol) and orthoclase (Ort) are set in the matrix of fluorite (Fl). Calcite (Cal) and a mixture of orthoclase (Ort) and dolomite (Dol) are overprinted by an assemblage of barite (Brt), fluorite (Fl), bastnäsite (Bst), parisite (Par), and quartz (Qtz). Fluorite is overprinted by galena (Gn), sphalerite (Sp), and pyrite (Py). (d) Close-up images of the fluorite matrix. Florencite (Flr) and synchysite-(Y) (Syn(Y)) overprinted fluorite (Fl). (e, f) Back-scattered electron images of banded veins (017–3, 017–5), bastnäsite (Bst), occurring with barite (Brt), fluorite (Fl), and quartz (Qtz). Synchysite-(Y) is associated with florencite (Flr) and xenotime (Xtm) overprinted fluorite (Fl). Galena (Gn) overprinted fluorite. Torodokite (Tod) cut barite and bastnäsite.

celestine, strontianite, carbocernaite, apatite, hematite, phlogopite, and quartz (Figure 7a–d). The matrix part of the rock consists of micron-sized barite, fluorite, calcite, synchysite, and bastnäsite (Figure 7e). Some calcite is porous and filled with barite, celestine, and synchysite (Figure 7f). Synchysite-(Ce) is typically euhedral, having platy crystals intergranular to calcite (Figure 7a–d), and occurs together with barite, fluorite, and bastnäsite (Figure 7d). Relatively large synchysite crystals co-exist with barite, suggesting that it precipitated with barite at the same time or slightly later (Figure 7a–d).

The mineralogy of the carbonatite is quite homogeneous throughout the body, although the mineral proportions vary (Figure 8). The chemical mapping results show that synchysite is most dominant, followed by barite or calcite. Fluorite is an accessory amount.

The chondrite-normalized REE patterns of these rare earth minerals are shown in Figure 9. Synchysite, bastnäsite, and monazite all show LREE-enriched patterns, although the monazite and synchysite at F9 are depleted in La, and

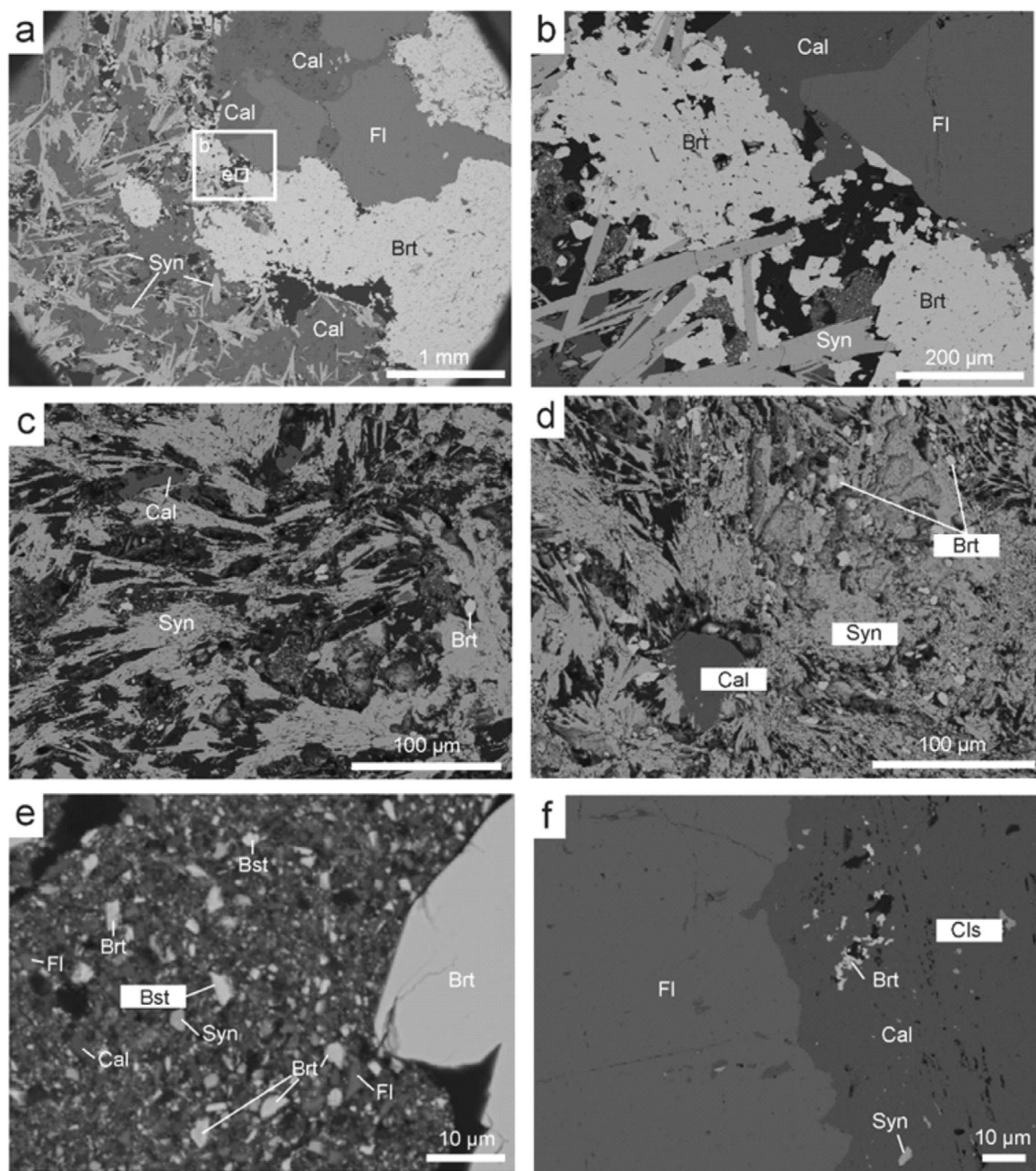


FIGURE 7 | SEM images of metasomatized carbonatite (MJVD 82.7 m). (a) Occurrence of calcite, replaced by fluorite, barite, and euhedral platy synchysite. (b) Close-up image showing the occurrence of calcite, fluorite, barite, and synchysite. The image area is shown in panel (a). (c) Occurrence of synchysite, barite, and calcite in the fine-grained matrix. (d) Occurrence of synchysite and barite co-existing with calcite. (e) Close-up image of the matrix part, which consists of micro-sized grains of barite, fluorite, calcite, synchysite, and bastnäsite. The area is shown in panel (a). (f) Porous calcite, in which pores are filled with barite, synchysite, and celestine.

some are relatively enriched in middle REEs. No difference is found between the bastnäsite in the metasomatic rock and veins.

5.3.2 | Ore Mineralogy in the Surface Weathered Rocks

The results of XRD analysis determined that clayey surface weathered samples at F3 mainly contain barite, quartz, bastnäsite-(Ce), and fluorite, in addition to minor or trace amounts of mica, orthoclase, and gibbsite.

The yellowish-brown surface materials mainly consist of fragments of barite and fluorite, cemented by very fine-grained secondary barite, fluorite, bastnäsite-(Ce), and quartz (Figure 10a–c). Secondary quartz forms a compact matrix, whereas bastnäsite-(Ce) shows a network texture, in which pores are commonly occupied by florencite and/or cerianite (Figure 10e). Goethite fills the fragments of barite and fluorite (Figure 10f). Bastnäsite also occurs in the pseudomorphs of synchysite (Figure 10c).

Black clayey samples show that barite grains are dominant together with goethite and cemented by Mn oxides, Fe oxides

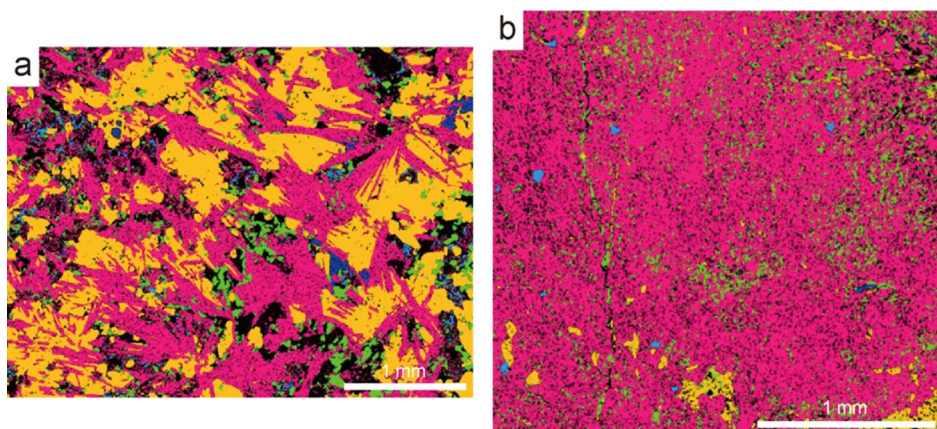


FIGURE 8 | Chemical mapping of the metasomatized carbonatite by SEM-EDS (MJVD 82.7 m). Red, green, blue, and yellow represent REE minerals, barite, fluorite, and calcite, respectively. (a) Coarse-grained part consisting of REE minerals (37.8%), barite (5.0%), fluorite (0.4%), calcite (26.7%), and others (30.1%). (b) Fine-grained part consisting of REE minerals (53.0%), barite (10.5%), fluorite (0.1%), calcite (1.9%), and others (34.5%).

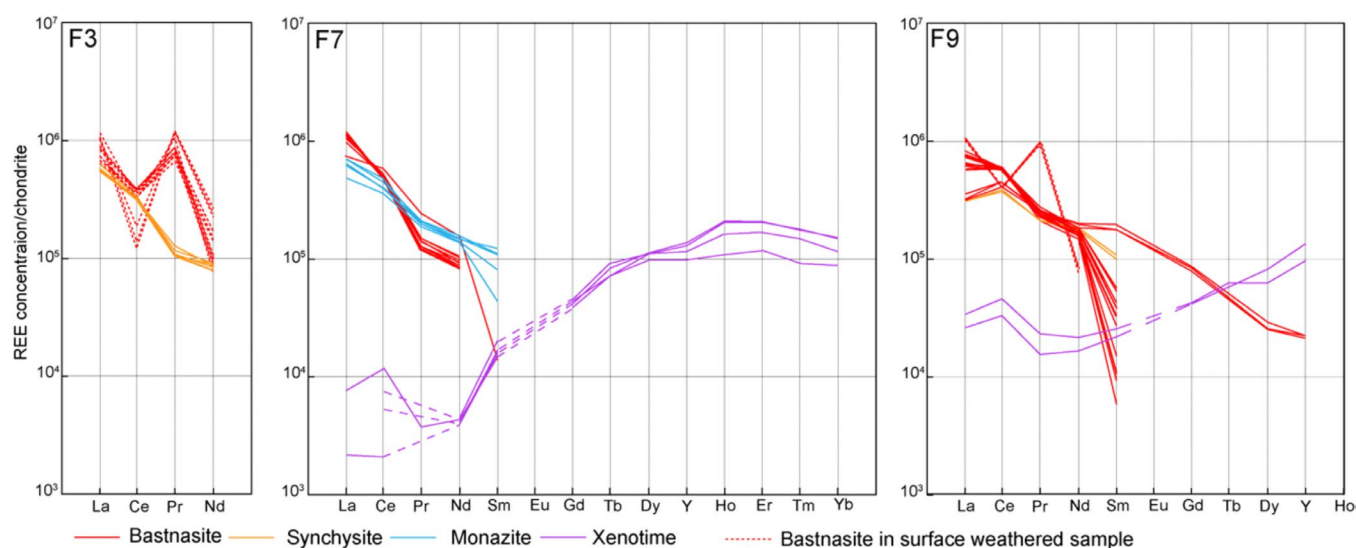


FIGURE 9 | Chondrite-normalized REE patterns of rare earth minerals in F3, F7, and F9 orebodies of the Dong Pao deposit. The chondrite data are after McDonough and Sun (1995).

quartz, and REE minerals. These samples do not contain fluorite (Figure 11a,b). In the matrix, bastnäsite-(La) occurs with Mn oxide, goethite, cerianite, quartz, and gibbsite (Figure 11c–e). Some of the Mn oxides contain Al and Fe, having a chemical composition of galaxite [(Mn, Fe)Al₂O₄]. A trace amount of monazite-(La) is also present (Figure 11f). These samples are characterized by the separation of Ce-rich minerals (cerianite) and Ce-poor rare earth minerals [bastnäsite-(La) and monazite-(La)].

5.4 | Geochemistry

The syenite samples collected have compositions SiO₂ (66.20 wt%–67.59 wt%), Al₂O₃ (16.55 wt%–17.72 wt%), Na₂O (0.21 wt%–3.35 wt%), K₂O (6.96 wt%–10.12 wt%), Fe₂O₃* (* total iron as Fe₂O₃) (0.76 wt%–1.98 wt%), CaO (0.08 wt%–0.34 wt%), and MgO (0.19 wt%–0.45 wt%). Normative orthoclase and quartz are 41.1%–59.8% and 20.7%–33.0%, respectively, indicating that the calculated amounts of quartz are not consistent with the petrographic observation. This may be due to the dissolution of feldspars and

mafic minerals by weathering. The amount of albite is consistent with the observation; one sample (036) contains a certain amount of albite (3.8%), whereas the other two are scarce in albite.

The syenite samples are relatively high in Zr (213, 302, 370 ppm) and lower U/Th ratio (0.11, 0.13, 0.15) compared to fresh carbonatite (3, 4 ppm) and (1.23, 1.27). Niobium concentrations are generally low (11, 32, 17 ppm) (Table 1).

These rocks contain 1209–4637 ppm Ba, 294–1120 ppm Sr, and 303–1166 ppm ΣY + REEs. The sample 011 is higher in Ba (1120 ppm), Sr (1120 ppm), and ΣY + REEs (1166 ppm) than the other two, suggesting that this sample is slightly mineralized. Because of weathering and hydrothermal mineralization, detailed geochemical interpretation of syenite is not possible.

The non-mineralized carbonatite samples (MJVD18, 52 m, 78 m) in the F3 orebody exhibit high concentrations of CaO (51 wt%–53 wt%), and other elements are minor: MgO (0.43, 1.46 wt%), Na₂O + K₂O (0.09, 0.32 wt%), Fe₂O₃ (0.44, 0.37 wt%), MnO (0.16, 0.09 wt%),

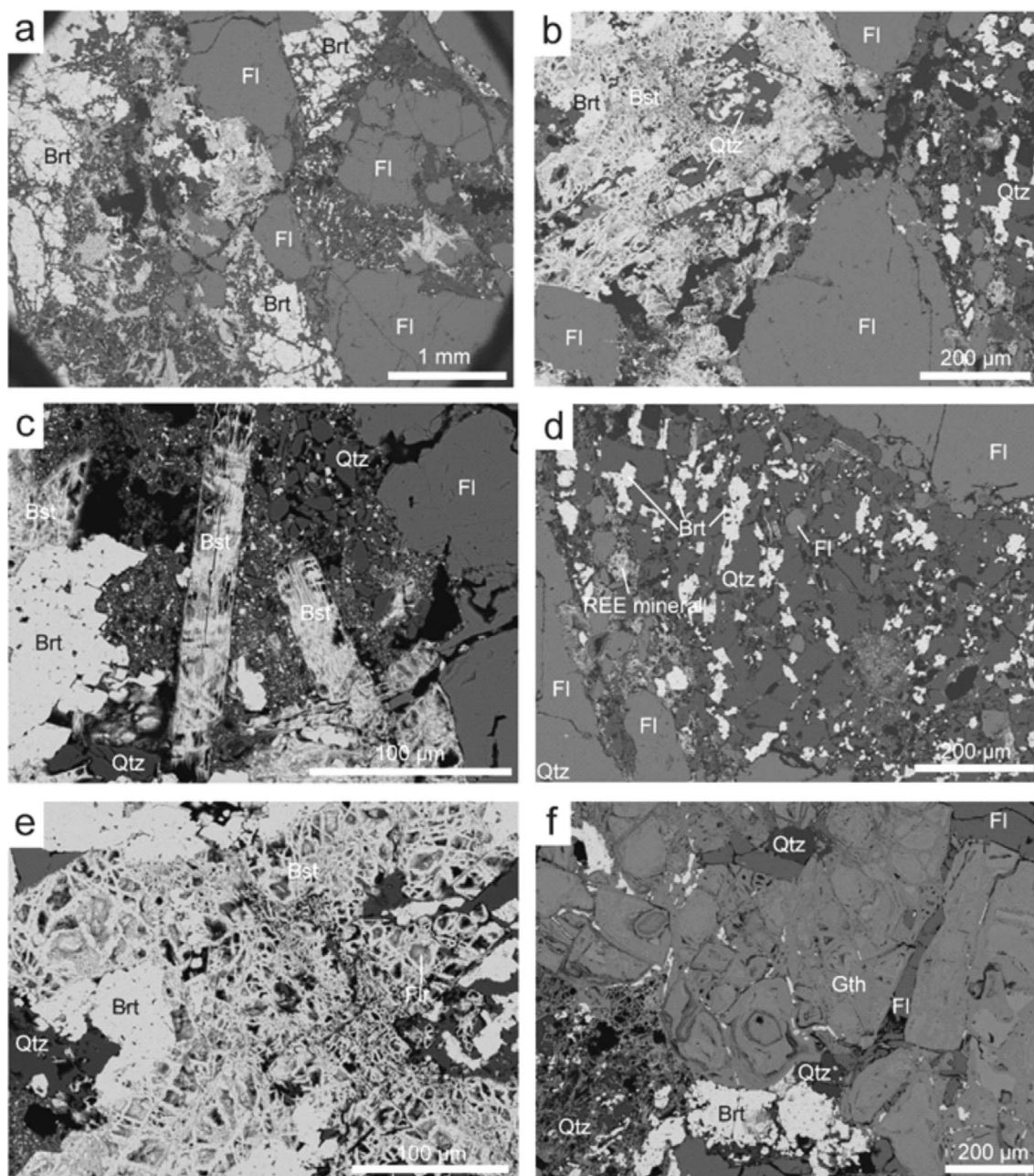


FIGURE 10 | SEM images of surface weathered carbonatite (P301). (a) Occurrence of weathered carbonatite, including fragments of fluorite and barite cemented by fine secondary minerals. Fluorite contains minor amounts of Y and Sr in the rim parts. (b) Close-up image showing cementing minerals (barite, bastnäsite, and quartz) around fluorite fragments. The location of the area is shown in panel a. (c) Close-up image showing the occurrence of bastnäsite-(Ce) replacing possibly primary synchysite. (d) Close-up image showing fluorite cemented by minerals (barite, quartz, fluorite, and REE mineral). (e) Occurrence of secondary bastnäsite-(Ce) crystals, including florencite in the porous parts. (f) Occurrence of zoned goethite together with fluorite, quartz, and barite.

and TiO_2 (0.03 wt%). These carbonatite samples consist of calcite mainly, corresponding to calcic carbonatite (Woolley 1982). The carbonatite has a low SiO_2 content (1.41, 1.90 wt%) and Ba (2354, 4980 ppm) and Sr (1808, 1972 ppm), compared to the mineralized carbonatite samples. These two samples contain 433 and 492 ppm $\Sigma\text{Y} + \text{REEs}$, respectively. The barite-rich sample (003 white: Ba 21.6%) is also enriched in Sr (1.02 wt%), suggesting the presence of Sr-barite as well as celestine and carboternite. These rocks are characterized by lower Zr concentrations (3–4 ppm), higher U/Th ratio (1.23–1.27), and low Nb concentrations (3–9 ppm).

The slightly and heavily mineralized carbonatite samples (MJVD2–76.7 m, MJVD20–67 m, MJVD20–68 m, 005) have elevated $\Sigma\text{Y} + \text{REE}$ concentrations (0.91, 1.49, 1.50, 2.83 wt%) compared to the non-mineralized ones. These carbonatites are variable in CaO (26.62, 33.68, 50.34, 33.92 wt%) and have higher amounts of Ba (18.2, 15.5, 3.3, 13.4 wt%), which show a negative correlation with CaO. Strontium concentrations of these samples are 10,870, 42,780, 59,370, and 5960 ppm, which are more than 10 times higher than those of the non-mineralized samples except the sample collected on the surface. These samples have slightly higher Nb

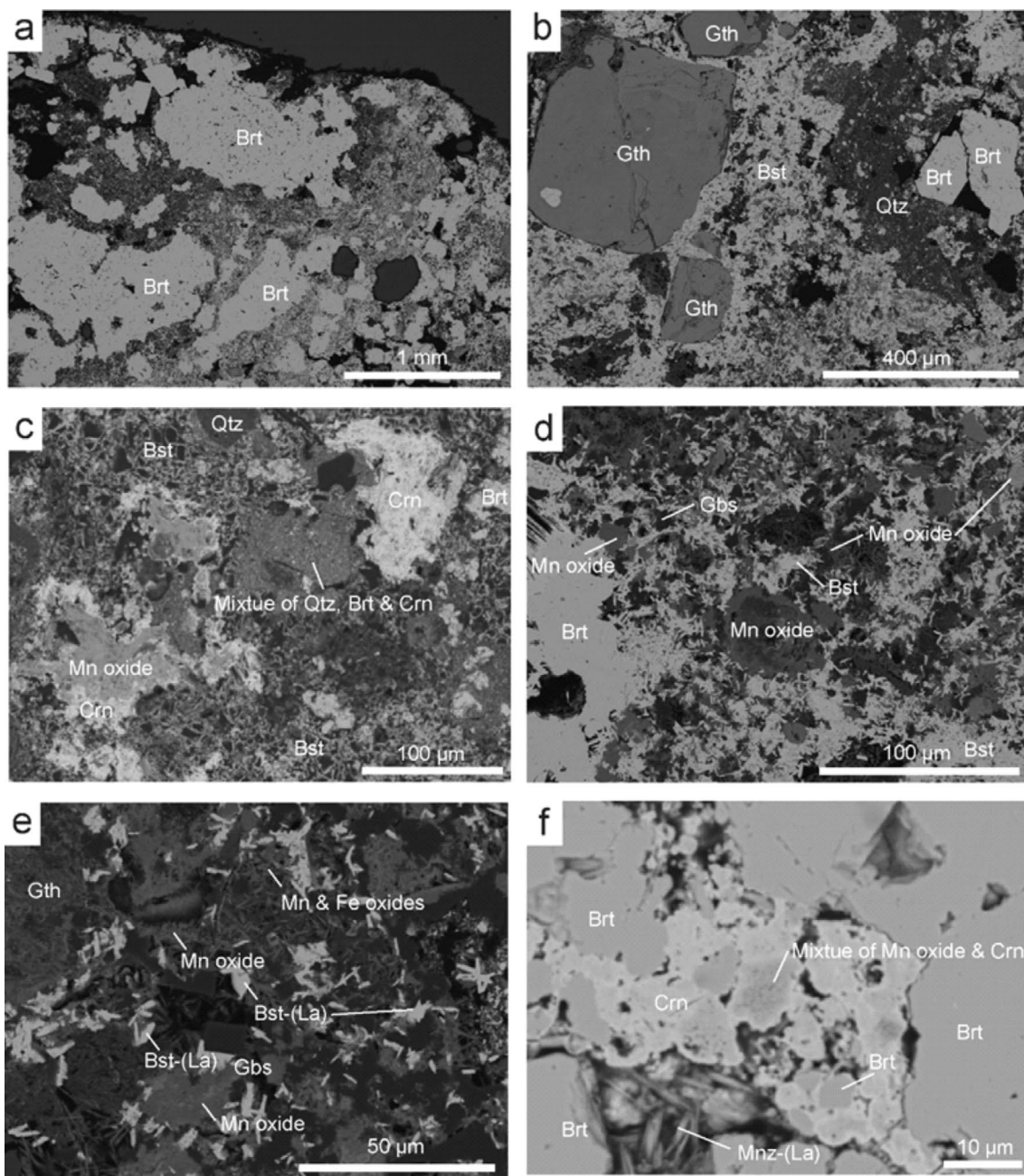


FIGURE 11 | SEM images of surface black weathered carbonatite (a–e: P305, f: 306). (a) Occurrence of weathered carbonatite including fragments of barite and quartz in a fine-grained matrix (P305). (b) Occurrence of goethite and barite in a fine-grained matrix of barite and quartz. (c) Occurrence of cerianite (Crn) fringing manganese oxide. Network bastnäsite-(La) also present. (d) Barite fragment cemented by Mn oxide, bastnäsite-(La), and gibbsite. (e) Close-up image of the cement composed of Mn-oxide, bastnäsite-(La), goethite, and gibbsite. (f) Close-up image of barite cemented by Mn-oxide, cerianite, and monazite-(La) (Mnz-(La)).

(66, 3, 15 and 8 ppm) and Zr concentrations (4, 8, 24, and 12 ppm) compared to those of fresh carbonatite (Figure 12, Table 1).

The highly mineralized carbonatite sample (004) contains $\Sigma Y + REE$ concentrations (8.96 wt%). This sample is extremely low in CaO concentrations (0.11 wt%), and high in MnO (1.35 wt%), TiO_2 (0.06 wt%), $Fe_2O_3^*$ (2.13 wt%), and P_2O_5 (0.23 wt.%) compared with those of the non-mineralized and mineralized carbonatites, suggesting the dissolution of calcite and concentrations of refractory minerals by weathering. Strontium concentration (3842 ppm) is lower than mineralized

samples but higher than non-mineralized samples. This sample also contains higher Nb (91 ppm) and Zr concentrations (20 ppm) compared to the fresh and mineralized carbonatites. This sample is characterized by a low U/Th ratio (0.28) compared to the fresh and mineralized carbonatites (Table 1).

In the F7 orebody, the lower dolostone (KE272 30 m) contains 21.41 wt% MgO and 27.44 wt% CaO and only 12 ppm of $\Sigma Y + REEs$ and 40 ppm Ba, indicating that the dolostone consists of almost pure dolomite. However, the vein sample above the dolostone (KE252 9.5 m) is highly mineralized with 13 wt%

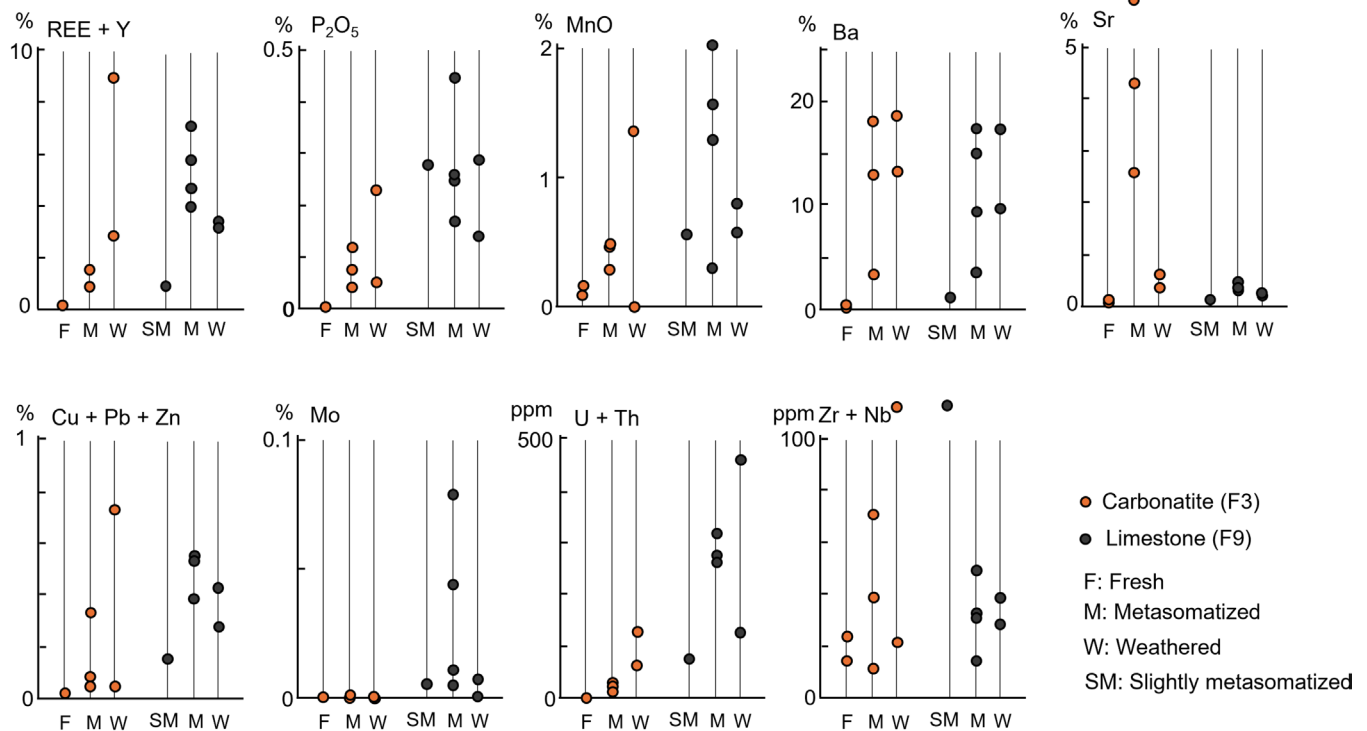


FIGURE 12 | Minor and trace element concentrations in the fresh, metasomatized, and weathered carbonatite (F3) and limestone (F9) in the Dong Pao deposit.

$\Sigma Y + \text{REEs}$. This sample contains 8.11 wt% SiO₂, 20.96 wt% CaO, 21.39 wt% Ba, and 0.521 wt% MnO, concordant with the petrographic observation of a high concentration of fluorite and barite. The high concentration of MnO suggests that the sample is weathered and affected by supergene alteration.

In the F9 orebody, the metasomatic rocks between limestone and syenite are well mineralized. The metasomatic rocks (017 (LM), 017) are slightly and moderately mineralized with $\Sigma Y + \text{REEs}$ of 8467 and 46649 ppm, respectively. The slightly mineralized sample (017 (LM)) contains 25.63 wt% SiO₂, 5.72 wt% MgO, and 22.33 wt% CaO, concordant with the petrographic observation of a mixed protolith of limestone and syenite. This sample contains 1.3 wt% Ba and 1113 ppm Sr, suggesting a slight influence of metasomatic alteration. The moderately mineralized rock from the metasomatic zone (017) contains 5.73 wt% SiO₂, 2.69 wt% MgO, 42.79 wt% CaO, 9.5 wt% Ba, and 2910 ppm Sr, indicating that the metasomatic alteration becomes stronger compared to the sample 017(LM). The decrease in MgO and an increase of CaO are concordant with the change of matrix mineralogy from dolomite dominant to calcite with dolomite overprinted by the assemblage of barite, fluorite, REE minerals, and quartz.

The veins intruding in the metasomatic zone (017–3, 017–4, 017–5) contain 3.97 wt%, 5.84 wt%, and 7.13 wt% of $\Sigma Y + \text{REEs}$, respectively. These samples contain 0.298 wt%, 1.566 wt%, and 2.03 wt% MnO, 32.31 wt%, 28.73 wt%, and 19.61 wt% CaO, 0.26 wt%, 0.23 wt%, and 0.17 wt% P₂O₅, 17.5 wt%, 15.1 wt%, and 16.7 wt% Ba, and 3914, 3470, and 4729 ppm Sr, concordant with the presence of REE carbonates and phosphates. The dominance of BaSO₄ and the decrease of CaO concentrations indicate that barite dominated over fluorite in these samples. These vein samples are scarce in MgO (0.01 wt%–0.02 wt%), reflecting rare

dolomite in the samples. The chemical compositions of the veins are similar to that of the moderately mineralized host metasomatic rock, although the veins contain more Th (210, 218, and 262 ppm) and Pb + Zn + Cu (5050, 4880, and 3810 ppm) than the host rock (Th 139 ppm; Pb + Zn + Cu 1930 ppm), suggesting the enrichment of thorite and sulfides. These vein samples contain high concentrations of Mo (790, 54, 109 ppm) and moderate amounts of Nb (21, 23, 6 ppm) and Zr (12, 26, 8 ppm) and have low U/Th ratios (0.29, 0.26, 0.21) (Figure 12 and Table 2).

Chondrite-normalized REE patterns of the F3 carbonatite samples show that mineralized carbonatites are more enriched in LREEs (La–Sm) than unmineralized ones (Figure 13). The enrichment of LREEs is due to the presence of synchysite-(Ce) in the mineralized samples. Higher mineralization is the replacement of synchysite-(Ce) by bastnäsite-(Ce) in the surface samples. The surface samples (003 Black) show a positive Ce anomaly, while the most mineralized surface sample (004) shows a strong negative Ce anomaly. The positive anomaly is ascribed to the presence of florencite-(Ce), detected by XRD and SEM–EDS. The heavy enrichment of REEs with a strong negative Ce anomaly may have been caused by the formation of secondary bastnäsite-(La) by a descending surface solution. The sample (005) that shows a positive Y anomaly is enriched in fluorite, whereas the samples (003, 004, MJVD2 76 m) that show negative Y anomalies are absent or scarce in fluorite, suggesting the presence of yttrifluorite.

Chondrite-normalized REE patterns of the F7 mineralized sample show LREE enrichment, concordant with the abundant occurrence of bastnäsite-(Ce) and parisite-(Ce).

At F9, the chondrite-normalized REE pattern of the slightly mineralized sample shows enrichment of LREEs (La–Nd).

TABLE 1 | Whole rock chemical compositions of the samples.

Sample no.	MJVD2 (76.7 m)	MJVD18 (52 m)	MJVD18 (78 m)	MJVD20 (67 m)	MJVD20 (68 m)	KE252 (9.5 m)	KE272 (30 m)	036	17/4	17/3	17 (LM)	017	17/5
Orebody	F3	C	F3	C	F3	V	D	F7	F9	V	F9	F9	F9
Rock type	C	C	C	C	C	C	C	S	V	V	M	M	V
SiO ₂ (wt%)	0.24	1.41	1.90	0.98	1.07	8.11	3.56	67.56	8.85	0.87	25.63	5.73	2.88
Al ₂ O ₃	0.01	0.26	0.44	0.08	0.04	0.07	0.76	16.55	2.04	0.37	7.03	0.69	0.24
Fe ₂ O ₃ *	0.06	0.44	0.37	0.08	0.25	0.48	0.61	1.38	2.68	7.50	5.17	0.93	2.71
MnO	0.289	0.161	0.088	0.475	0.487	0.521	0.009	0.014	1.566	0.298	0.584	1.297	2.03
MgO	0.09	0.43	1.46	0.50	0.24	0.01	21.41	0.19	0.02	0.01	5.72	2.69	0.01
CaO	26.62	52.74	51.16	33.68	50.34	20.96	27.44	0.34	28.73	32.31	22.33	42.79	19.61
Na ₂ O	0.01	0.01	0.03	0.02	0.03	<0.01	0.02	3.35	0.02	0.02	0.04	0.01	0.01
K ₂ O	0.01	0.08	0.29	0.03	0.01	0.08	0.34	6.96	0.82	0.02	6.03	0.10	0.04
TiO ₂	0.003	0.029	0.034	0.004	0.03	0.024	0.080	0.318	0.074	0.036	0.870	0.042	0.023
P ₂ O ₅	0.12	0.01	0.01	0.04	0.08	0.14	0.04	0.11	0.23	0.26	0.28	0.45	0.17
LOI	20.91	42.47	41.54	17.21	20.47	8.07	44.49	1.71	6.42	3.36	18.20	9.30	4.61
Total	52.08	98.05	97.32	53.49	73.85	42.99	98.75	98.48	51.92	48.82	91.92	65.12	37.29
Sc (ppm)	2	<1	1	4	3	28	1	4	17	9	10	13	23
Be	<1	2	1	2	2	8	1	5	12	11	5	11	9
V	6	14	30	7	17	36	35	27	52	51	111	67	57
Cr	<20	<20	<20	<20	<20	<20	<20	30	40	<20	180	20	20
Co	<1	<1	<1	<1	<1	<1	<1	2	<1	<1	23	<1	<1
Ni	<20	<20	<20	<20	<20	<20	<20	<20	30	<20	110	<20	50
Cu	10	10	10	10	<10	<10	<10	<10	130	210	40	10	30
Zn	70	80	70	540	70	160	30	40	550	460	510	440	630
Ga	<1	1	1	<1	<1	<1	1	21	<1	<1	7	<1	<1
As	<5	13	<5	<5	<5	26	15	<5	35	88	71	29	36
Rb	<2	7	29	3	<2	<2	9	257	26	<2	262	5	<2
Sr	10,870	1808	1972	42,780	59,370	4876	503	1048	3470	3914	1113	2910	4729

(Continues)

TABLE 1 | (Continued)

Sample no.	MJVD2 (76.7 m)		MJVD18 (52 m)		MJVD18 (78 m)		MJVD20 (67 m)		MJVD20 (68 m)		KE252 (9.5 m)		KE272 (30 m)		036		17/4		17/3		17 (LM)		017		17/5	
Orebody	F3	C	F3	C	F3	C	F3	C	F3	C	F7	V	F7	D	F7	S	F9	V	F9	V	F9	M	F9	M	F9	V
Rock type	C		C		C		C		C		V		D		S		V		V		M		M		V	
Zr	4		3		4		8		24		12		15		213		26		12		93		7		8	
Ba	181,900		2358		4980		155,100		32,920		213,900		40		4637		151,100		175,000		13,250		95,480		166,800	
Nb	66		9		3		3		15		50		2		11		23		21		20		24		6	
Mo	2		2		3		12		3		5		<2		<2		54		790		55		440		109	
Sb	1.9		<1		<0.5		3.5		1.1		12.4		2.2		<0.5		56.8		187		22.4		20.6		21.3	
Y	67		43		50		219		240		519		2		29		1945		3527		211		1340		929	
La	3110		89.4		99.6		5510		5100		57,200		2.2		88.9		15,200		8100		3170		12,200		20,800	
Ce	4270		164		183		6710		6890		58,700		4		154		28,300		18,200		3840		22,700		35,300	
Pr	364		17.8		20.3		533		585		4000		0.44		18.2		2630		1730		288		2140		3140	
Nd	1080		66.1		78.3		1510		1790		9570		1.5		65.2		7540		5300		759		6130		8820	
Sm	115		16.1		20.7		160		210		623		0.4		11.4		1210		1080		75.5		960		1160	
Eu	25.6		5.08		6.36		36.5		49.5		125		0.1		2.54		327		332		19.5		253		283	
Gd	51.6		12.6		14.6		81		96.8		246		0.3		8.1		623		669		41.4		492		518	
Tb	5.2		1.8		2		10.3		10.7		28.4		<0.1		1		73.2		85.7		5.5		58.1		49.6	
Dy	18.9		9.1		9.7		43.8		42.5		94		0.3		5.4		299		383		26.7		233		172	
Ho	2.8		1.4		1.4		7.0		6.6		14.6		<0.1		0.9		44.6		61.8		4.8		34		24	
Er	6.8		3.4		3.2		17.6		15.9		41.4		0.2		2.6		99.5		140		13.1		73.3		57.7	
Tm	0.66		0.41		0.41		1.94		1.71		3.93		<0.05		0.35		10.2		14.5		1.64		6.34		5.56	
Yb	3.8		2.3		2.1		10.4		8.7		20.7		0.2		2.2		48.7		69.4		9.3		26.4		27.1	
Lu	0.42		0.29		0.27		1.37		1.08		2.79		0.03		0.34		5.80		8.01		1.17		3.21		3.51	
W	2		8		2		2		7		13		5		<1		19		13		43		13		30	
Tl	0.3		0.2		0.5		0.6		0.1		8.3		1.1		1.7		3.6		0.7		8.5		1.1		8.0	
Pb	339		83		<5		1100		176		146		<5		27		4120		4380		241		1480		3150	
Th	13.4		1.3		3.0		7.5		11.5		499		0.6		23.6		218		210		46.8		139		262	

(Continues)

TABLE 1 | (Continued)

Sample no.	MJVD2 (76.7 m)	MJVD18 (52 m)	MJVD18 (78 m)	MJVD20 (67 m)	MJVD20 (68 m)	KE252 (9.5 m)	KE272 (30 m)		036		17/4	17/3	17 (LM)		017	17/5
	F3	F3	F3	F3	F3	F7	F7	D	S	F7	F9	F9	F9	F9	F9	F9
Rock type	C	C	C	C	C	V					V	V		M	M	V
U	19.8	1.6	3.8	8.3	10.9	103	1.7	1.7	5.7	56	60.5	60.5	26.5	129	54.9	
ΣY + REEs	9122	433	492	14,852	15,041	131,189	12	390	58,356	39,700	8467	46,649	71,289			
U/Th	1.48	1.23	1.27	1.11	0.95	0.21	2.83	0.11	0.26	0.29	0.57	0.93	0.21			
Sample no.	005	004	011	001	003 (Black)	003 (White)		Black	Mix	Brown	Clay	023	022			
Orebody	F3	F3	F7	F7	F3	F3	WC	F9	F9	F9	F9	F9	F9			
Rock type	WC	WC	S	S	WC	WC	WC	BS	BS	BS	BS	BS	FS			
SiO ₂ (wt%)	6.3	3.49	66.69	66.20	22.50	0.60	63.56	50.00	38.81	50.28	9.23	3.83				
Al ₂ O ₃	0.03	6.83	16.81	17.72	0.28	0.02	9.74	19.63	26.59	18.03	4.28	0.19				
Fe ₂ O ₃ *	0.51	2.13	0.76	1.98	37.85	0.06	4.53	7.69	8.78	9.34	1.73	1.90				
MnO	0.01	1.353	0.015	0.013	0.050	0.021	3.214	1.333	2.035	0.187	0.582	0.795				
MgO	<0.01	0.14	0.27	0.45	0.15	0.01	0.08	0.11	0.27	0.16	0.01	0.01				
CaO	33.92	0.11	0.12	0.08	0.06	0.03	0.15	0.37	0.09	0.05	38.64	37.7				
Na ₂ O	0.01	<0.01	0.23	0.21	<0.01	<0.01	0.03	0.08	0.08	0.16	0.01	0.01				
K ₂ O	<0.01	0.15	10.12	8.22	<0.01	<0.01	2.58	6.87	6.93	11.91	0.02	0.02				
TiO ₂	0.005	0.062	0.357	0.364	0.018	0.001	0.538	1.004	1.113	1.488	0.015	0.015				
P ₂ O ₅	0.05	0.23	0.15	0.13	0.06	0.02	0.75	0.75	0.84	0.67	0.29	0.14				
LOI	4.08	7.92	2.29	2.74	4.70	0.14	9.53	8.40	10.86	4.02	6.92	3.78				
Total	44.94	24.57	97.82	98.09	65.91	6.47	94.68	96.24	96.38	96.30	63.92	51.03				
Sc (ppm)	6	4	1	2	2	<1	14	22	33	12	8	12				
Be	3	4	6	4	30	<1	67	12	14	7	15	10				
V	14	77	57	39	240	<5	166	209	385	262	60	43				
Cr	<20	40	<20	<20	190	<20	100	120	130	160	<20	<20				
Co	<1	6	<1	1	4	<1	17	22	29	10	1	<1				
Ni	<20	70	<20	<20	30	<20	960	230	270	60	20	<20				

(Continues)

TABLE 1 | (Continued)

Sample no.	005	004	011	001	003 (Black)	003 (White)	Black	Mix	Brown	Clay	023	022
Orebody	F3	F3	F7	F7	F3	F3	F9	F9	F9	F9	F9	F9
Rock type	WC	WC	S	S	WC	WC	BS	BS	BS	BS	BS	FS
Cu	<10	420	<10	<10	920	<10	150	90	90	100	<10	20
Zn	30	530	30	60	2650	<30	2300	1860	3400	870	230	250
Ga	<1	17	29	28	2	<1	17	19	24	25	<1	<1
As	13	74	11	13	967	<5	33	57	62	91	22	16
Rb	<2	9	375	411	<2	<2	104	297	322	602	<2	<2
Sr	5960	3842	1120	294	2680	10,190	2075	907	524	410	2101	2368
Zr	12	20	302	370	6	4	96	160	187	233	18	148
Ba	133,500	187,000	1209	3908	146,600	216,500	19,670	18,150	10,890	11,630	140,900	171,000
Nb	8	91	32	17	18	18	19	31	30	40	31	21
Mo	<2	9	3	<2	50	4	151	60	49	65	7	7
Sb	6.3	34.3	5.6	3.5	310	3	19.9	28.1	21.9	29.8	8.9	75
Y	430	1169	24	13	68	<1	656	487	517	479	157	148
La	8800	50,000	457	95.8	1180	13.3	566	645	426	350	13,500	13,600
Ce	13,300	5990	312	119	3500	17.3	626	797	437	502	14,400	15,500
Pr	1210	6810	54.5	14.2	112	2.04	92.8	96.8	63	64	995	1130
Nd	3840	20,500	161	44.8	322	6.6	328	312	212	218	2440	3000
Sm	366	2590	18.1	6.1	39.7	1.0	91.9	74.1	61.8	67.6	172	220
Eu	72.5	646	4.06	1.52	9.62	<0.05	32.3	24.7	23.9	22.7	41.4	48.7
Gd	133	1160	8	3.3	20.8	0.7	82.7	62.6	62.3	53.3	69.8	85.5
Tb	13.7	124	0.8	0.4	3.3	<0.1	13.2	10.3	11.2	9.3	7.3	8.2
Dy	51.7	423	3.8	1.9	17.2	0.4	72.6	56.7	64.5	54.1	25.8	25.0
Ho	7.8	49.3	0.6	0.3	2.9	<0.1	14.1	10.7	12.4	10.5	4.2	3.6
Er	19.1	105	1.8	1.1	8.0	0.2	39.4	30.3	35.5	30	11.9	10.6
Tm	1.44	9.05	0.23	0.16	1.1	<0.05	5.41	4.12	5.12	4.15	1.24	1.03

(Continues)

TABLE 1 | (Continued)

Sample no.	005	004	011	001	003 (Black)	003 (White)	Black	Mix	Brown	Clay	023	022
Orebody	F3	F3	F7	F7	F3	F3	F9	F9	F9	F9	F9	F9
Rock type	WC	WC	S	S	WC	WC	BS	BS	BS	BS	FS	FS
Yb	6.1	43.1	1.4	1.0	7.1	0.1	31.9	25.2	31.8	24.5	6.6	5.5
Lu	0.64	5.29	0.21	0.16	0.85	<0.01	4.19	3.27	4.16	3.17	0.96	0.79
W	6	27	34	19	103	1	77	78	48	80	18	24
Tl	0.1	8.4	4.6	8.5	0.4	<0.1	31.7	12.6	15	7.3	7.7	4.1
Pb	199	6420	21	13	3040	66	238	712	426	794	3590	3890
Th	41.9	33.2	51.9	35.6	27.7	<0.1	13.4	24.2	16.8	26	386	45.9
U	26.4	117	6.7	5.3	31.7	4.4	20.3	32.1	31.8	39	72.5	83
Total REEs	28,252	89,624	1166	303	5293	41.64	2657	2640	1968	1892	31,833	33,787
U/Th	0.63	0.28	0.13	0.15	1.14		1.51	1.33	1.89	1.50	0.19	1.81

Abbreviations: BS, brown soil; C, carbonatite; D, dolomite; FS, fluoride-rich soil; M, metasomatized limestone; S, syenite; V, hydrothermal vein; WC, weathered carbonatite.

TABLE 2 | Analytical results of oxygen and carbon isotopes.

Sample No.	Mineral	$\delta^{18}\text{O}_{\text{SMOW}}$	$\delta^{13}\text{C}_{\text{VPDB}}$
017	Calcite	14.01	0.1
033	Dolomite and calcite	16.90	−1.4
035	Calcite	21.33	1
MJVD2	Calcite	11.54	−4.4
MJVD18	Calcite	12.26	−0.8
MJVD20 (68 m)	Calcite	10.09	−1.2

This LREE enrichment is enhanced with mineralization in the metasomatized rocks. However, the late-stage veins are relatively enriched in HREEs, reflecting the presence of phosphate minerals and synchysite-(Y). Surface fluorite-rich weathered materials show heavy enrichment of LREEs compared to the patterns of the veins, and the weathered material shows positive Y anomaly due to enrichment of fluorite.

5.5 | Carbon and Oxygen Isotope

Analytical results of carbon and oxygen isotopic ratio measurements of the carbonatite and limestone are shown in Table 2 and Figure 14. The fresh carbonatite (MJVD18) and heavily mineralized carbonatite (MJVD20–68 m) from the F3 orebody have $\delta^{18}\text{O}_{\text{SMOW}}$ values of 12.3‰ and 10.1‰ and $\delta^{13}\text{C}_{\text{PDB}}$ values of −0.8‰ and −1.2‰, respectively. These values are similar to those reported by Fujii et al. (2010) and are shifted toward a heavier $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{SMOW}}$ region from the “primary carbonatite” fields defined by Taylor Jr., Frechen, and Degens (1967) and Demény, Sitnikova, and Karchevsky (2004). The slightly mineralized carbonatite sample (MJVD2) has a relatively heavier $\delta^{18}\text{O}_{\text{SMOW}}$ value (11.5‰) compared to the primary carbonatite, whereas its $\delta^{13}\text{C}_{\text{PDB}}$ value (−4.4‰) is similar to the primary carbonatite. This value is similar to those reported by Li et al. (2023).

The limestone sample (35) has the highest $\delta^{18}\text{O}_{\text{SMOW}}$ and $\delta^{13}\text{C}_{\text{PDB}}$ values of 21.3‰ and 1.0‰, respectively, among the analyzed samples. These values are similar to those of the limestones in the Dong Pao area and other areas in the Son La–Lai Chau Zone, as reported by Li et al. (2023). Another limestone sample (33) is a mixture of dolomite and calcite, having $\delta^{18}\text{O}_{\text{SMOW}}$ and $\delta^{13}\text{C}_{\text{PDB}}$ values of 16.9‰ and −1.4‰, respectively. This sample is plotted between the primary carbonatite and the fresh limestones. The metasomatized limestone (017) from the F9 orebody has an intermediate $\delta^{18}\text{O}_{\text{SMOW}}$ value (14.0‰) and $\delta^{13}\text{C}_{\text{PDB}}$ value (0.1‰) between the fresh carbonatite (MJVD18) and limestone (35).

6 | Discussion

6.1 | Geological Setting of the Dong Pao Deposit

The Dong Pao deposit is composed of abundant numbers of orebodies, which occur where the syenite of the Dong Pao Complex contacts with the limestone of the Dong Giao Formation.

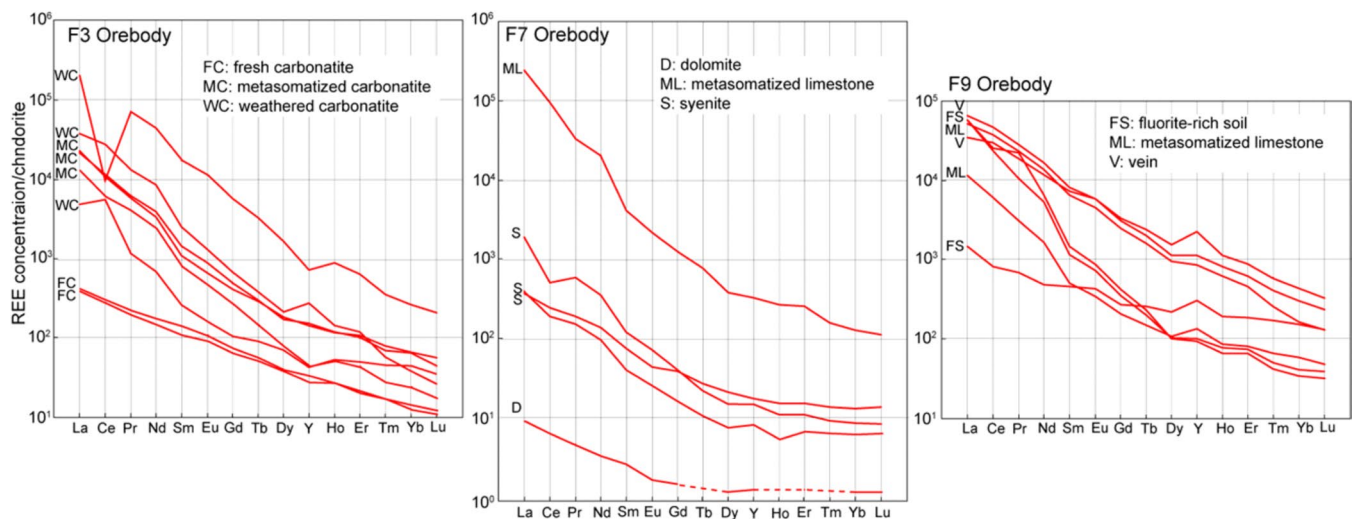


FIGURE 13 | Chondrite-normalized REE patterns of rare earth elements for mineralization and related rocks in F3, F7, and F9 orebodies of the Dong Pao deposit. The chondrite data are after McDonough and Sun (1995).

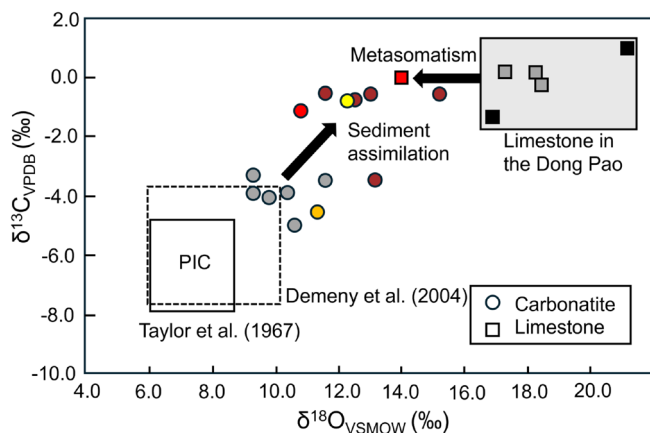


FIGURE 14 | $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ correlation diagram for carbonatite and limestone in the Dong Pao area. The compositional fields of primary igneous carbonatite (as defined by Taylor Jr., Frechen, and Degens 1967, and Demény, Sitnikova, and Karchevsky 2004) are also shown for comparison. The yellow, orange, and red circles represent fresh, slightly mineralized, and heavily mineralized carbonatites, respectively. The black and red squares represent fresh and metasomatized limestones, respectively. The data with gray color and brown colors are from Li et al. (2023) and Fujii et al. (2010), respectively.

Although the deposit has been regarded as a carbonatite-related REE deposit (Smith et al. 2016; Li et al. 2023), carbonatite is found only at the F3 orebody. The reported ages of syenite (51.6 ± 0.4 Ma and 52.4 ± 0.4 Ma) and bastnäsite (51.4 ± 0.8 Ma) at Dong Pao by Li et al. (2023) confirm that rare earth mineralization occurred simultaneously with the intrusion of the syenite magma.

The Dong Pao Syenite Complex is one of the oldest Eocene alkaline complexes in the Son La–Lai Chau Zone, together with Ban Xeo granites in the Muong Hum complex (Pham et al. 2020). Li et al. (2023) discussed that the Dong Pao deposit is enigmatic because it formed during the period of the collision between the Indian and Asian continents. They assigned that the carbonatite magma ascended in a local dilational jog associated with the

left-lateral strike-slip faulting along the Red River Fault System. However, recent studies show that the collision was completed by 50 Ma, and it was followed by extension because of the subducted Indian slab steepening and breakoff (Zhu et al. 2015). Such extension is also recorded as rifting related to left-lateral faulting along the Red River Fault System since the Eocene in Vietnam (Fyhn et al. 2018).

The syenite magma that formed the Dong Pao Complex intruded into the limestone at the very shallow crustal level, because the complex includes effusive facies. Most of the orebodies exhibit a lenticular shape, situated at the boundary between the syenite and limestone along the margin of the complex (Figure 2). The exception is the F3 orebody, where carbonatite is located.

The average ore grades of these orebodies are 2.7 wt%–6.2 wt% REO (F4, F7, F10, F14, F16, F17, F19) (Chau et al. 2017), while that of F3 is high and the largest (5.2 wt%, 7.4 Mt.; JICA and MMAJ 2002). Thus, the F3 orebody is quite different in terms of the grade and total reserve from other orebodies.

6.2 | Carbonatite at F3 Orebody

The white coarse-grained carbonate rock that occurs ca. Fifty meter below the surface in the F3 orebody consists mainly of calcite. Although this rock was described as limestone by JICA and MMAJ (2001, 2002), it does not show any sedimentary structure and is heavily depleted in silicate minerals although it contains a minor amount of phlogopite. It also contains trace apatite, carbocernaite $[\text{Ca}(\text{Sr}, \text{Ba})(\text{CO}_3)_2]$, celestine $[(\text{Sr}, \text{Ca})\text{SO}_4]$, and strontianite $[\text{SrCO}_3]$ along anastomosing fractures. This texture and mineralogy suggest that this carbonate rock is calcite carbonatite (Mitchell and Gittins 2022), and later Sr- and carbonate-rich melt intruded into the grain boundaries of calcite in the carbonatite, replacing calcite to celestine and carbocernaite together with secondary igneous calcite. Similar Sr-rich melt is reported in the Kamthai carbonatite complex in India (Pastel et al. 2023).

The oxygen and carbon isotopic values of the slightly mineralized sample (MJVD2) ($\delta^{13}\text{C}_{\text{PDB}}$: -4.35% ; $\delta^{18}\text{O}_{\text{SMOW}}$: 11.5%) are similar to those reported by Li et al. (2023) for the same rock type at Dong Pao ($\delta^{13}\text{C}_{\text{PDB}}$: -4.0% to -3.3% ; $\delta^{18}\text{O}_{\text{SMOW}}$: 9.3% to 11.5%). These values are slightly deviated from those of the primary igneous carbonatite (Figure 14), defined by Taylor Jr., Frechen, and Degens (1967) and Demény, Sitnikova, and Karchevsky (2004). However, the values of our fresh sample MJVD18 ($\delta^{13}\text{C}_{\text{PDB}}$: -0.8% ; $\delta^{18}\text{O}_{\text{SMOW}}$: 12.3%) and heavily mineralized sample MJVD20 ($\delta^{13}\text{C}_{\text{PDB}}$: -1.2% ; $\delta^{18}\text{O}_{\text{SMOW}}$: 10.1%) have lighter $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ value than those reported by Li et al. (2023) and are similar to the values of the carbonatites reported by Fujii et al. (2010). This deviation of the MJVD18 and MJVD20 may be explained by the assimilation of carbonaceous sedimentary rocks (Demény, Sitnikova, and Karchevsky 2004; Li et al. 2023; Figure 14) rather than hydrothermal alteration (Fujii et al. 2010), because (1) heavily mineralized sample (MJVD20) has lighter oxygen and carbon isotope values than that of the fresh sample (MJVD18), which excludes the effect of metasomatism, and (2) these values are plotted between the limestone of the Dong Giao Formation in the Dong Pao area and the primary magmatic carbonatite fields (Figure 14). The heavier and lighter carbon isotope data of the F3 carbonatite may have ascribed to the different degree of host rock assimilation because heavier and lighter carbon isotope samples were collected from the different parts (northern part and western part, respectively) of the F3 orebody, regardless of the different authors (Fujii et al. 2010; Li et al. 2023; this study).

6.3 | Rare Earth Mineralization Styles at Dong Pao

We observed two distinct styles of rare earth mineralization at Dong Pao (Figure 15). They are (1) metasomatized carbonatite and (2) metasomatized limestone. The metasomatized carbonatite is limited only to the F3 orebody, and the metasomatized limestone is observed in the other orebodies.

6.3.1 | Metasomatized Carbonatite

The mineralization style changes from the deeper zone to the shallower zone at the F3 orebody. At the deepest zone, carbonatite is fresh, and rare earth mineralization is hardly observed. However, the calcite carbonatite at depth changes into the metasomatized one at the center of the body, which is characterized by the replacement of calcite by barite, fluorite, and rare earth carbonate minerals such as synchysite-(Ce) and parisite-(Ce) (Figure 5b,c). This is reflected in the sudden decrease of Ca contents less than 15 wt% and the increase of Ba more than 10 wt%, typically more than 20 wt% (JICA and MMAJ 2001, 2002) as well as the increase of REE concentration from <0.05 wt% to 1.5 wt% (Table 1) in the metasomatized carbonatite at each drill holes ~ 100 m.

Such Ba–Sr–REE mineralization is reported to occur commonly in the late orthomagmatic and post-magmatic hydrothermal stages (Dey et al. 2024). Enrichment of these incompatible elements in a late-stage melt usually takes place either due to fractionation or reworking of primary magmatic phases such as apatite, burbankite, etc. Alternatively, carbonatite-derived late-stage fluids are responsible for the formation of Ba–Sr–REE mineralization in carbonatite complexes (Zaitsev, Wall, and Le 1998; Wall, Zaitsev, and Mariano 2001; Giebel et al. 2019; Mitchell and Gittins 2022; Louvel et al. 2022; Bhattacharjee et al. 2024). At Dong Pao, carbonatite metasomatism and REE mineralization are ascribed to the post-magmatic fluid because of the absence of the fractionated magmatic stage, such as dolomite carbonatite as well as burbankite, although trace carbocearnite is detected.

This metasomatic mineralization was caused by the carbothermal fluid, rich in CO_3^{2-} , F^- , PO_4^{3-} , and SO_4^{2-} as well as Ba^{2+} , Sr^{2+} , and REEs^{3+} , resulting in crystallization of barite, fluorite, synchysite-(Ce), parisite-(Ce), celestine, and sulfides. Further, synchysite-(Ce) is replaced by bastnäsite-(Ce) at the latest stage. The change from synchysite-(Ce) to bastnäsite-(Ce) may have been related to an increase in H_2O and a subsequent decrease in

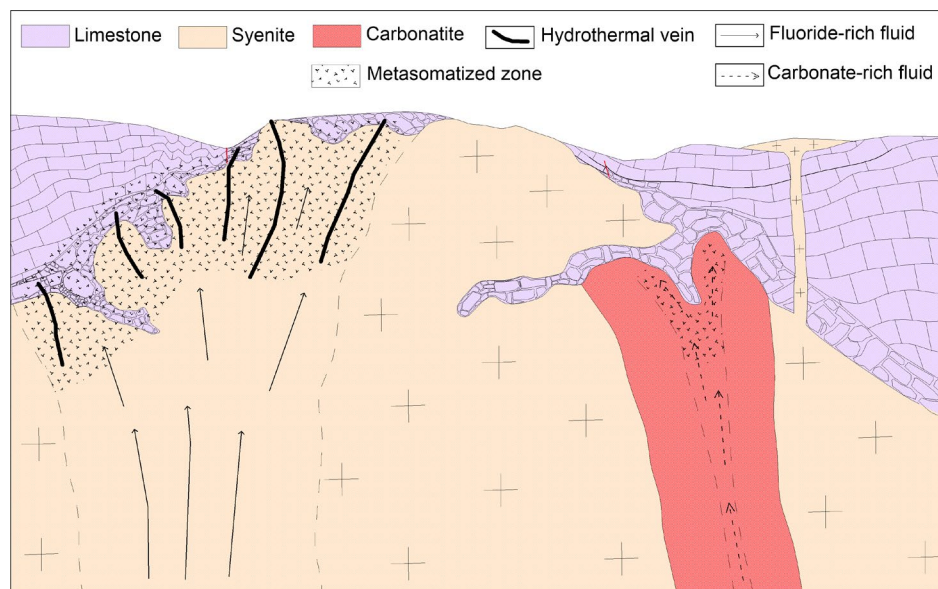


FIGURE 15 | A schematic sketch outlining the genesis of the Dong Pao deposit.

CO_3^{2-} activities in the carbothermal fluid (Migdisov et al. 2016; Dey et al. 2024) and/or a decrease of SO_4^{2-} triggered by crystallization of barite due to the decrease of fluid temperature (Zhang et al. 2022).

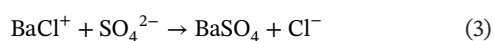
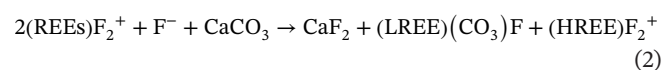
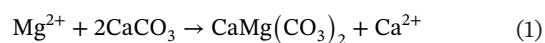
6.3.2 | Metasomatized Limestone

At the orebodies at F7 and F9 as well as F1 and F4 (Figure 3), rare earth orebodies occur in the limestone along the contact between the syenite and limestone, where the limestone is heavily metasomatized to form lens-shaped orebodies in dolostone. In the F9 orebody, the metasomatic orebody contains dolomite overprinted by the assemblage of barite, fluorite, bastnäsite-(Ce), parisite-(Ce), quartz, and sulfides such as sphalerite, pyrite, and galena. This metasomatic zone is intruded by hydrothermal veins, which contain fluorite, barite, REE carbonates [bastnäsite-(Ce), parisite-(Ce), REE phosphates [monazite-(Ce), xenotime-(Y), and florencite-(Ce)], as well as synchysite-(Y)]. The abundance of bastnäsite-(Ce) coexisting with fluorite indicates that these minerals precipitated at the same time.

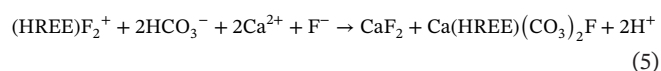
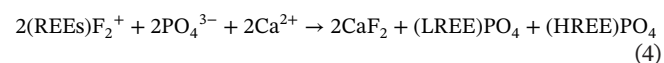
The REE mineralization in these orebodies is interpreted to be formed by the reaction between the fluorine-rich metasomatic fluids and limestone. This mineralization is explained by (1) dolomitization replacing calcite by dolomite Equation (1). (2) decrease of fluorine activity in the fluid by fluorite precipitation, leading to destabilization of the rare earth fluoride complex to precipitate bastnäsite-(Ce) (Equation (2); Migdisov et al. 2016). Such reactions occurred during the decrease of fluid temperature, leading to the precipitation of barite Equation (3). Barium may occur as BaCl^+ in the fluids at a higher temperature ($> 200^\circ\text{C}$) and precipitate as barite when the temperature and/or Cl molarity decreases (Hanor 2000; Jamieson et al. 2016). Barite at F9 is low in Sr, suggesting a lower temperature of formation, because Sr substitution in barite increases with temperature (Hanor 2000). This barite precipitation may have destabilized REE $(\text{SO}_4)_2^-$ species, also promoting the precipitation of bastnäsite-(Ce) (Migdisov et al. 2016).

The late veins are more enriched in phosphate minerals (monazite and xenotime), as well as bastnäsite-(Ce) and synchysite-(Y). This late-stage mineralization is relatively enriched in HREE (Figure 13), resulting in the precipitation of xenotime and synchysite-(Y) Equations (4) and (5). Such a mineralization sequence may be explained by the addition of phosphate ions from the host rocks (Migdisov et al. 2016), in this case, syenite, which contains much higher amounts of apatite than fresh carbonatite. This explains the minor REE phosphate minerals in the hydrothermal vein.

Early stage



Late stage



The late-stage phosphate mineralization was possibly triggered by a decrease in temperature because the solubility of monazite and xenotime decreases with decreasing temperature (Migdisov et al. 2016). The change from LREE-enriched fluorides to HREE-enriched fluorides with decreasing temperature can be explained by differences in the solubility of minerals (Migdisov et al. 2016). Recently, Louvel et al. (2022) discussed that a gradual change from the LREE dominant fluorcarbonate metasomatic mineralization to relatively HREE-enriched phosphate-bearing mineralization is caused by the sudden decrease of LREE solubility with lowering the temperature at around 400°C in alkaline fluids and a decrease of F^- in the fluids due to precipitation of fluorite. This change is observed at the F9 orebody at Dong Pao, as well as Tundulu and Kangankunde carbonatites in Malawi (Broom-Fendley et al. 2016).

The assemblage of barite + hematite + sphalerite + galena + pyrite (Figure 6b,e) suggests that the fluids were neutral pH and relatively high oxidation state ($\log f\text{O}_2 = \text{ca. } -55$) (Cooke et al. 1998; Hanor 2000). The $\delta^{18}\text{O}_{\text{SMOW}}$ value decreases from the host limestones to metasomatized limestone, suggesting that the metasomatic fluids have a low $\delta^{18}\text{O}_{\text{SMOW}}$ value similar to the fresh carbonatite.

The metasomatic rocks are enriched in LREE, in particular, La and Ce (Figure 13). These rocks are also enriched in REE + Y, TiO_2 , P_2O_5 , MnO, Cu + Pb + Zn, Mo, Th, and U but depleted in Sr (Figure 12). The abundance of incompatible elements such as U and Th suggests that the metasomatic fluid was exsolved from highly differentiated magma (Song et al. 2016).

The above-mentioned occurrence of the orebodies indicates that dolomitic metasomatism and subsequent mineralization occurred by the fluid exsolved from the syenite. The dominant occurrence of fluorite and barite at F9 indicates that the hydrothermal fluid was fluorine-rich. Such fluorine-enriched fluid might have formed from fluoride melt, formed by silicate-fluoride immiscibility (Veksler et al. 2005; Shu and Liu 2019; Kynicky et al. 2019), although the evidence showing such immiscibility is not observed at Dong Pao.

6.4 | Origin of Metasomatic Fluids

In the Dong Pao deposit, two distinct metasomatic fluids were observed: (1) carbonate-rich fluid at F3, associated with carbonatite, and (2) fluorine-rich fluid at F9 and other orebodies, associated with syenite. These two fluids are enriched in LREEs, although there are significant differences in major ligands, metasomatized host carbonates, REE mineralogy and geochemistry, minor and trace element geochemistry (Sr, HFSE, base metals), and REE concentrations, discussed above.

The carbonate-rich fluid at F3 was relatively low in $\text{F}^-/\text{CO}_3^{2-}$ and salinity, deduced from the dominant precipitation of synchysite-(Ce), which replaced calcite of the magmatic carbonatite. The enrichment of Sr in this fluid suggests that this fluid directly exsolved from carbonatite because Sr is one of the elements that partition into fluid phase relative to the crystallizing carbonatite melt (Bühn and Rankin 1999). The mineralizing

fluids have similar $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{SMOW}}$ compositions to the associated carbonatites (Figure 14). The fluorine-rich fluid at F9 may have been relatively high in $\text{F}^-/\text{CO}_3^{2-}$, originally, although CO_3^{2-} became dominant due to the reaction with carbonate rocks, deduced from dominant precipitation of bastnäsite-(Ce) in the early stage. This fluid was possibly relatively higher in salinity, suggested by the presence of sulfide minerals in the late stage. This mineralizing fluid may have similar $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{SMOW}}$ compositions to that of the western part of the carbonatite.

Kynicky et al. (2019) speculate that volatile-rich F-rich carbonatitic melt may form by separating from volatile-rich silicate melt (resulting in nepheline syenite) and subsequently the F-rich carbonatitic melt unmixed into REE-rich carbonate melt and REE-poor fluoride melt, based on the study of Lugin Gol nepheline syenite body in Mongolia. However, this is not the case at Dong Pao, where carbonate-rich and fluorine-rich fluids occur individually at F3 and F9 (and others). At Dong Pao, both fluids contain high amounts of carbonate and fluorine, although the relative abundance is different. These fluorine-rich and carbonate-rich fluids may have exsolved from different magmas, syenite and carbonatite, in which carbonate amounts were different (syenite < carbonatite).

6.5 | Weathering Effect

Weathering is an important effect for upgrading the ores at Dong Pao (Chau et al. 2017). Chau et al. (2017) confirmed that the ore grades of the surface weathered ores above the syenite reach up to 10wt%. Our analytical results also confirmed that the weathered vein sample in the F7 orebody, which is composed mainly of fluorite, barite, quartz, and bastnäsite-(Ce) with minor monazite and xenotime (Figure 5d–f), contains 13wt% (Table 2, Figure 13). The atomic ratios of La and Ce in the bastnäsite-(Ce) in the sample are nearly equal, suggesting that some Ce precipitated as Ce-enriched minerals such as cerianite. Other gangue minerals include hematite and todorokite in the ore veins, which overprinted fluorite.

At F3, the black-colored Mn-oxide-rich materials that occur at elevations higher than 850m are enriched in barite together with a lesser amount of fluorite and Mn oxides. This material contains Ce-rich minerals such as florencite-(Ce), cerianite, and bastnäsite-(Ce), although some bastnäsite is enriched in La [bastnäsite-(La)]. Because this material formed just above the carbonatite body, it is highly depleted in silica, resulting in the formation of supergene bastnäsite. Some of the weathered samples are heavily enriched in REEs (~11wt% REO), but depleted in Ce (Figure 13), due to the separation of insoluble Ce-rich minerals such as florencite-(Ce) and cerianite above. This could become a preferable ore because the relative abundance of Nd + Pr, which are the main elements used for the production of Nd magnets among REEs, is higher (~30%) than the non-weathered metasomatized ores.

6.6 | Implications for the Formation of a Large REE Deposit

The Dong Pao deposit is different from the typical REE-bearing carbonatite deposits in the world because of the association of

many orebodies occurring along the boundary of the syenite of the Dong Pao Complex and the limestone of the Dong Giao Formation, in addition to the F3 carbonatite orebody. Rather, this deposit is an analogue of skarn deposits, which form orebodies in the carbonate rocks where volatile-rich silicate magmas intrude. Instead of calc-silicate minerals, the metasomatic rocks at Dong Pao contain fluorite, barite, and REE-bearing fluorcarbonate minerals because of the scarcity of silica and alumina in the hydrothermal fluids and the host rocks. Carbonatites generally have either a form of cylindrical shape, up to a few kilometers in diameter, or a form of dike, up to several tens of meters thick, with an exception of Sulfide Queen at Mountain Pass, which is ~210-m thick (Olson et al. 1954). In contrast, the Dong Pao Syenite Complex is 3.5 km by 5.5 km in plan view size, much larger than a typical carbonatite body. And it yields many orebodies around the complex. The large reserves estimated at Dong Pao are a result of this widespread, large-scale mineralization. In addition, the present semi-tropical climate of northern Vietnam accelerates surface weathering of the orebodies, upgrading REE ore grades. Such an unusual style of mineralization and climate has produced a large REE deposit at Dong Pao, making Vietnam the second largest reservoir of REE in the world.

7 | Conclusion

The Dong Pao deposit in northern Vietnam is composed of abundant orebodies along the contacts of the syenite of the Eocene Dong Pao Complex and the limestone of the Dong Giao Formation. Although most of the orebodies exhibit a lenticular shape and are situated at the boundary between the syenite and the limestone, the F3 orebody occurs in the calcite carbonatite intruding the syenite. This carbonatite has carbon and oxygen isotopic ratios, slightly to moderately deviated from primary igneous carbonatites, due possibly to the assimilation of limestone.

Two distinct styles of rare earth mineralization, metasomatized carbonatite and metasomatized limestone, are observed at Dong Pao. The F3 metasomatized carbonatite is characterized by the replacement of calcite by REE-bearing fluorcarbonate minerals such as synchysite-(Ce) and parisite-(Ce) in addition to fluorite, barite, celestine, and sulfides. The metasomatic limestone orebodies contain dolomite overprinted by the assemblage of barite, fluorite, bastnäsite-(Ce), parisite-(Ce), quartz, and sulfides. This metasomatic zone is intruded by hydrothermal veins, which contain fluorite, barite, bastnäsite-(Ce), parisite-(Ce), REE phosphates, as well as synchysite-(Y). The REE mineralization in these metasomatized rocks is interpreted to have formed by the reaction of carbonate-rich metasomatic fluids with carbonatite at F3 and fluorine-rich fluids at the other orebodies with limestone. Such different fluids possibly exsolved from carbonatite magma and syenite magma, respectively.

The Dong Pao deposit is an analogue of skarn deposits, although instead of skarn minerals, the metasomatic rocks at Dong Pao contain fluorite, barite, and REE-bearing fluorcarbonate minerals, because of the scarcity of silica and alumina in the hydrothermal fluids and the host rocks. A large tonnage is estimated at Dong Pao because of the presence of many orebodies scattered around the syenite complex in addition to the

carbonatite-associated orebody at the F3. Furthermore, the present semi-tropical climate of northern Vietnam accelerates surface weathering of orebodies, which upgrade the REE ores.

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Conflicts of Interest

Dr. Takuya Echigo and Dr. Mihoko Hoshino are Editorial Board members of RGE Journal and a co-author of this article. Also, the co-author Dr. Yasushi Watanabe is the Editor-in-Chief of the journal. To minimize bias, they were excluded from all editorial decision-making related to the acceptance of this article for publication.

Data Availability Statement

The data that supports the findings of this study are available in the [Supporting Information](#) of this article.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.