# Hyper-enrichment of heavy rare earth elements in highly evolved granites through multiple hydrothermal mobilizations

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#### ABSTRACT

Highly evolved granites can be important hosts of rare earth element (REE) resources, and more importantly, they commonly serve as the protolith for regolith-hosted REE deposits to form during weathering. Highly evolved granites in the Zudong pluton, South China, are extremely rich in the heavy (H)REE (up to 8000 ppm total HREE), and display significant REE fractionation. Moreover, the HREE enrichment is positively correlated with the degree of REE fractionation, indicating a unique process in preferentially enriching the HREE during the evolution of the granites. Multiple stages of hydrothermal re-mobilization of the REE can account for the HREE mineralization, and these are recorded in the texture and composition of the zircon. In these processes, fluctuations in the F activity of the fluid caused alternating dissolution-reprecipitation and continuous growth of the zircon. REE were repeatedly mobilized and enriched in the fluid to precipitate the major HREE mineral synchysite-(Y), and partially incorporated into the growth zone of zircon, while other elements were largely lost to the fluid during the extensive dissolution of the rock-forming minerals. LREE were also likely substantially mobilized in the late hydrothermal stage and lost through complexation with Cl, causing the significant LREE depletion and, thus REE fractionation. This process continuously enriched host granites in the HREE to a potentially economic grade, making them favorable protoliths for subsequent supergene regolith-hosted HREE deposits.

**Keywords:** Rare earth element (REE), HREE mineralization, zircon, hydrothermal alteration, highly evolved granite

#### INTRODUCTION

The rare earth elements (REE) and yttrium show similar geochemical behavior but can be fractionated strongly in various geological environments (Henderson 2013). Thus, they can be used to trace various natural processes, including the evolution of melts and fluids in magmatic-hydrothermal systems (e.g., Bea 1996; Hanchar and Van Westrenen 2007; Migdisov et al. 2016; Williams-Jones et al. 2012). Recently, these elements have become increasingly important in various high-technology applications for a carbon-neutral society, especially for the heavy (H)REE. Magmatic-hydrothermal systems may form REE deposits associated with granites, carbonatites, and other alkaline complexes (Verplanck et al. 2016; Williams-Jones et al. 2012). Most of these REE-rich rocks are light (L)REE-dominated, and HREE-dominated rocks have been rarely discovered; they are essentially restricted to highly evolved granites (Li et al. 2017, 2019; Sanematsu and Watanabe 2016). The HREE-rich rocks are important HREE resources, and more importantly, through weathering, they form the regolith-hosted REE deposits (Li et al. 2017) that supply more than 85% of the global HREE production (U.S. Geological Survey 2023).

Generally, the HREE can be concentrated in highly evolved granitic melts by the removal of major elements and LREE through fractional crystallization (Bea et al. 1994; Breiter et al. 1997). Volatile-rich phases in these systems could be rich in the REE (Bau 1996; Irber 1999; Vasyukova and Williams-Jones 2018; Williams-Jones et al. 2000), and subsequent hydrothermal overprinting can enrich the granites with the HREE. Alternatively, upgrading of the HREE concentration can be achieved through metasomatism by externally derived HREErich fluids (Fan et al. 2023; Xu et al. 2017). Hydrothermal alteration is generally agreed upon as the key process for the significant HREE enrichment in these highly evolved granites necessary to reach a potentially economic grade (Li et al. 2017; Sanematsu and Watanabe 2016). However, the processes causing the HREE enrichment have not been comprehensively illustrated, nor have those responsible for the significant REE fractionation. Deciphering the mechanisms involved in the HREE enrichment and REE fractionation would be important in understanding the magmatic-hydrothermal evolution of highly evolved systems. This knowledge also sheds light on HREE mineralization and ore formation.

The Zudong pluton in South China has a sub-ore-grade HREE concentration and significant REE fractionation, both of which are at the highest and the most extreme among all granites recorded in the GEOROC database [Online Materials<sup>1</sup> Fig. S1; Sarbas (2008)]. This pluton is also the protolith of the world's largest known regolith-hosted HREE deposit (Li et al. 2019). Thus, the Zudong pluton provides a valuable opportunity to

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investigate the HREE enrichment process in a granitic system. An early study attributed hydrothermal alteration to the HREE enrichment (Huang et al. 1989), and a more recent study compared the isotopic composition of different units of different degrees of fractionation to trace the source of the hydrothermal fluid (Fan et al. 2023). However, how the HREE concentration was upgraded during the hydrothermal alteration has not yet been well illustrated.

In felsic igneous systems, zircon is a common REE-bearing accessory mineral and commonly records the magmatic-hydrothermal history (Chen and Zhou 2017; Geisler et al. 2007; Schneider et al. 2012). Both melt and fluid histories can be archived by the chemical and structural changes of zircon (Geisler et al. 2007), and under certain circumstances, REE concentrations of the coeval melts or fluids can be inferred from the zircon chemistry (Hanchar and Van Westrenen 2007). Thus, zircon can be used as a powerful tool to help reconstruct the magmatic-hydrothermal evolution of such systems. Although trace elemental compositions, combined with the crystallinity and texture, are commonly used to discriminate magmatic, metamict, and hydrothermal zircon (Wang et al. 2023; Yang et al. 2014; Zeng et al. 2017; Zhao et al. 2016), detailed characterization of consecutive growth zones in zircon that record the magmatic to hydrothermal processes is rare, but could potentially provide more in-depth illumination of the geochemical evolution of the system.

In this study, we document the highly evolved granites of the Zudong pluton in South China from mineral records. Through detailed characterization of the REE mineralization and the corresponding mineralogical and geochemical record preserved in the zircon grains, we elucidate the hydrothermal process for HREE enrichment and REE fractionation, and potential ore formation in these systems.

# **GEOLOGICAL BACKGROUND**

The Zudong granitic pluton is located in the Nanling region of SE China. In this region, multiple tectono-thermal events have taken place episodically from the Ordovician-Silurian to the late Cretaceous, generating voluminous highly evolved metaluminous to slightly peraluminous calc-alkaline I-type granites and A-type granites (Zhou et al. 2006), including the Zudong granite, which formed at  $168.2 \pm 1.2$  Ma according to a zircon U-Pb dating (Zhao et al. 2014). The Zudong pluton crops out over an area of 32.5 km<sup>2</sup> and intrudes early Jurassic volcanic rocks and late Permian coal-bearing shale and mudstone (Fig. 1). The pluton is composed of the lower unit of granodiorite and biotite granite and an upper unit of muscovite-bearing alkali-feldspar granite [Fig. 1; Fan et al. (2023)]. The world's largest regolith-hosted HREE deposit, the Zudong deposit, is derived from the weathering of the Zudong pluton, especially the muscovite-bearing alkali-feldspar granite. The deposit hosts a pre-mining resource of 131000 t of REE oxide at a grade of 0.05 wt% RE oxide in the weathering crust, whose thickness varies from a few meters to up to 30 m thick (Li et al. 2017, 2019).

In the ore-forming muscovite-bearing granites, the major minerals include quartz, K-feldspar, albite, and muscovite (Fig. 2a). Accessory minerals that host most of the REE include zircon, xenotime-(Y), Y-bearing fluorite, synchysite-(Y), gadolinite-(Y), hingganite-(Y), yttrialite-(Y), euxenite-(Y), and fergusonite-(Y). Persuasive overprinting is observed with albite largely replaced by muscovite  $\pm$  quartz (Fig. 2b) and biotite by muscovite + hematite



FIGURE 1. Simplified geological map of the Zudong pluton (after Li et al. 2019). (Color online.)



**FIGURE 2.** (a) A representative hand specimen of the Zudong granites showing the major mineral assemblage of quartz + feldspar + muscovite + hematite. (b–d) Cross-polarized light photomicrographs of the Zudong granites. (b) Alteration of albite by muscovite along cleavage plane. (c) Pseudomorph of muscovite + hematite after biotite. (d) Alteration of albite by hematite along the cleavage planes. Abbreviations: Ab = albite; Fsp = K-feldspar; Hem = hematite; Ms = muscovite; Qz = quartz. (Color online.)

(Fig. 2c). Hematite also occurs along the cleavage planes of albite (Fig. 2d). Muscovite grains show no overprinting and are presumed to represent the last stage of alteration. Most REE minerals are disseminated in the granites and regarded as hydrothermal phases showing various crosscutting and replacement relationships to the major minerals and the primary REE minerals (Li et al. 2019). The HREE mineralization has been attributed to late-stage autometasomatism during the magmatic-hydrothermal transition of the granitic magma (Huang et al. 1989) or hydrothermal overprinting by an externally derived HREE-rich fluid probably originating from the subducting slab (Fan et al. 2023).

#### SAMPLES AND ANALYTICAL METHODS

In this study, 22 samples were collected across the muscovite-bearing granite unit that hosts the sub-ore-grade HREE enrichment for petrographic and mineralogical analyses. The sampling locations are marked in Figure 1.

## Morphology and structure

Petrographic analysis was carried out with optical, electronic, and cathodoluminescence microscopy. The Hitachi S-3400N scanning electron microscope (SEM) equipped with an Oxford INCAx-sight energy-dispersive spectroscopic (EDS) detector was used at 20 kV and 60–80 µA for preliminary mineral identification. Raman spectroscopy on zircon grains was undertaken with the RISE microscopy system at the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan (CUGW). This system enables simultaneous Raman and SEM analysis, comprising an Alpha 300-R Laser Raman spectrometer and a Tescan VEGA 3 SEM. The laser wavelength was 532 nm with the power of 6 mW and an integration time of 5 s.

#### Whole-rock major and trace elements

Major element concentrations were determined using fused glass beads after the loss of ignition determination on an AxiomAX-Advanced X-ray fluorescence spectrometer at the University of Hong Kong. The analytical accuracy and precision are <0.5%. Trace element concentrations were measured with an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS) after mixed acid digestion of the fused glass beads. The uncertainties in both the accuracy and precision were <10% for all elements analyzed. Fluorine concentrations were determined potentiometrically by a specific ion electrode after potassium hydroxide fusion. The detection limit was 20 ppm. Carbon concentration hosted as carbonate minerals was measured by an ethanolamine coulometer as  $CO_2$  after digestion with HCIO<sub>4</sub>. The detection limit is 0.2%.

#### Chemical composition of zircon

Major and minor elements. Compositions of zircon grains were analyzed with a JEOL JXA-8230 electron microprobe at the University of Hong Kong under a 20 kV accelerating voltage, a 20 nA beam current, and a 1 µm beam spot diameter. The analyzing crystals were PET (Zr, Hf, Ca, U, Th, P, Y, and Cl), LiF (Gd, Dy, Er, Yb, Fe, and Ti), LED1 (F), and TAP (Si and Al). Counting times on the peak positions were 40 s for REE, Hf, Th, and U; 20 s for Zr, P, Si, Al, Ca, Fe, and Ti; and 10 s for F and Cl. Representative background intensities were measured on both sides of the peak for half of the peak time. The  $K\alpha$  line was chosen for the analyses of P, Si, Al, Ca, Fe, Ti, F, and Cl; the Lα for Zr, Hf, and Y; the Lβ line for Gd, Dy, Er, and Yb; and the  $M\alpha$  line for Th and U. The standards are zircon for Zr, orthoclase for Si and Al, apatite for Ca and P, magnetite for Fe, rutile for Ti, YP5O14 for Y, monazite for Gd and Th, DyP5O14 for Dy, ErP5O14 for Er, YbP5O14 for Yb, Hf metal for Hf, coffinite for U, topaz for F, and tugtupite for Cl. Detection limits were generally ~100-200 ppm. All data were corrected using standard ZAF correction procedures. Elemental mapping was carried out on selected zircon grains under a 20 kV accelerating voltage, a 20 nA beam current, a 1 µm beam spot diameter, and a dwell time at each location of 500 μs. Mapping was achieved by rastering the designated area with continuous spots.

Trace elements. Trace elemental analyses of zircon grains were conducted using a GeoLas 2005 laser ablation system with an Agilent 7900 ICP-MS at the State Key Laboratory of Geological Processes and Mineral Resources, CUGW. Laser pulses of 16–24 µm diameter at 5 Hz ablated the surfaces of the sample for about 50 s after monitoring the gas blank for ~20 s. All analytical spots were checked under both an optical microscope and an SEM before analysis to avoid ablating mineral inclusions. The generated aerosols were carried by a helium carrier gas and mixed with



**FIGURE 3.** BSE images of the occurrence of the REE-bearing minerals in the Zudong granites. (a) Association of gadolinite-(Y) and yttrialite-(Y) in voids of albite. (b) Hingganite-(Y) replacing albite in a mesh of veinlet. (c) A hingganite-(Y)-calcite veinlet crosscutting K-feldspar. (d) Hingganite-(Y) being cut by synchysite-(Y). (e) Hingganite-(Y) veinlets being cut by fluorite. (f) A fluorite grain interstitial to muscovite and containing inclusions of synchysite. (g) REE-enriched fluorite (FIr-1) being replaced by REE-depleted fluorite (FIr-2) with synchysite inclusions. (h and i) Inclusions of synchysite-(Ce) in fluorite being replaced by synchysite-(Y). (j) Synchysite-(Ce) being replaced by synchysite-(Y) [Syn-1] and in turn being cut by HREE-enriched synchysite-(Y) [Syn-2]. Relict magmatic grain of (k) xenotime-(Y) and (l) fergusonite-(Y) showing oscillatory zoning. Abbreviations: Ab = albite; Cal = calcite; Fgs-Y = fergusonite-(Y); FIr-1 = REE-enriched fluorite; FIr-2 = REE-depleted fluorite; Gad-Y = gadonlite-(Y); Hin-Y = hingganite-(Y); Fsp = K-feldspar; Syn = mixture of both synchysite-(Ce) and -(Y); Syn-Ce = synchysite-(Ce); Syn-1 = synchysite-(Y); Syn-2 = HREE-enriched synchysite-(Y); Xtm-Y = xenotime-(Y); Ytt-Y = yttrialite-(Y). (Color online.)

argon make-up gas via a T-connector before entering the ICP-MS instrument for the acquisition of ion-signal intensities. Rare earth element compositions of zircon were externally calibrated against various reference materials (NIST SRM 610, BHVO-2G, BCR-2G, and BIR-1G) without using an internal standard. Data reduction was carried out with the ICPMSDataCal program.

#### RESULTS

#### **Occurrence of REE-bearing minerals**

Complementary to the observations by Li et al. (2019), further petrographic examination reveals the paragenesis of various REE-bearing phases of the Zudong granite. The main REE minerals are REE fluorocarbonate [notably synchysite-(Y)], REE-bearing fluorite, and the REE silicates, mainly gadolinite-(Y), hingganite-(Y), and yttrialite-(Y), and a minor amount of zircon and thorite. Minor amounts of REE phosphates, mainly xenotime-(Y), and REE niobates, including fergusonite-(Y) and euxenite-(Y) are also observed.

**REE silicates.** Gadolinite-(Y) and yttrialite-(Y) often coexist and occur in voids in albite (Fig. 3a). Both minerals are often in

granular form but gadolinite-(Y) can also have irregular patchy shape (Fan et al. 2023), whereas hingganite-(Y) occurs in a radiating prismatic form and as mesh-textured veinlets along albite cleavage planes (Fig. 3b). The hingganite-(Y) veinlets often include rounded, anhedral calcite in the core (Fig. 3c). Occurrence of zircon will be described in the following section. The REE silicates are locally cut by fluorite and synchysite-(Y) (Figs. 3d and 3e).

**Fluorite.** Fluorite is commonly interstitial to the major minerals or, less commonly, fills veinlets and small pods where it mainly replaces albite (Fig. 3f). In some places, fluorite veinlets cut hingganite-(Y) veinlets (Fig. 3e). Two varieties of fluorite are observable under the BSE imaging. One is clean, REE-enriched, and BSE-bright (Flr-1), while the other one is porous, relatively REE-depleted, and BSE-dark (Flr-2). The Flr-2 is associated with inclusions of synchysite and cut and embayed Flr-1 (Fig. 3g).

Synchysite. From EDS analysis, both synchysite-(Y), enriched in Y and the HREE, and synchysite-(Ce), enriched in the LREE, were identified (see the Online Materials<sup>1</sup> for representative EDS spectra and analytical results). Synchysite-(Y) appears as either subhedral to euhedral laths replacing calcite, irregular-pods interstitial to feldspar and muscovite, or inclusions in fluorite. In fluorite and synchysite-(Y), inclusions of synchysite-(Ce) with variably irregular shapes and variable sizes are common. The synchysite-(Ce) inclusions are also often corroded and embayed (Figs. 3h-3j). From the BSE imaging and EDS analysis, two compositional varieties of synchysite-(Y) can be observed, one less enriched in the HREE, except Y (referred thereinafter Syn-1), and the other more enriched in the HREE (Syn-2). Syn-2 occurs as diffuse bands cutting Syn-1, whereas Syn-1 often shows a porous core and a narrow, clean rim on an individual grain (Fig. 3j).

Xenotime, fergusonite-(Y), euxenite-(Y), and thorite. Xenotime and REE niobates are often rounded and corroded (Figs. 3k–3l) and occur mainly as inclusions in mica. In some samples, anhedral xenotime and euxenite-(Y) grains are spatially associated with synchysite-(Y) and occur together as vein-filling phases. Thorite is also highly corroded and embayed, particularly when associated with fluorite and fluorocarbonates.

# Petrography of zircon

Individual zircon grains from the Zudong granites are variable in size from 20 to 150 µm long and in shape from anhedral and rounded to subhedral and tabular shape with pyramidal terminations. Complicated textures are also shown that generally include up to 5 distinct domains (Fig. 4). Domain 1 has bright cathodoluminescence (CL) but dim BSE images, rounded cores, and oscillatory zoning. Domain 2, which commonly rims Domain 1, is porous, with dark CL but bright BSE images, and contains abundant inclusions of xenotime and thorite. Domain 3 is a narrow, inclusion-free, growth zone, with dark CL and bright BSE images. It typically rims Domain 2 and, in turn, is typically rimmed by a wide overgrowth with dark CL and dim BSE images (Domain 4). In some cases, Domain 3 may be partially truncated or rimmed by another porous domain (collectively defined as Domain 2, referring to the porous texture) before being rimmed by Domain 4. Domain 4 is partially overprinted by irregular patches with dark CL and even dimmer BSE images that define Domain 5. Raman analyses reveal that Domain 1 is crystalline with strong and sharp peaks at 1004–1010, 439–442, and 355–358 cm<sup>-1</sup> for the vibration bands of Si-O antisymmetric stretching, symmetric bending, and symmetric rotation, respectively. Weak and broad bands at 995–1001 cm<sup>-1</sup>, which probably represent the vibration band of Si-O antisymmetric stretching, are only observed in Domain 2; the other domains do not show any characteristic peaks of crystalline zircon in their spectra (Fig. 5).

In the granites, zircon is often included in fluorite and synchysite-(Y) (Fig. 6). In some samples, zircon grains are highly altered and largely dissolved, with the crystal shape and internal structure largely destroyed (Fig. 4). Zircon grains with Domain 2 in the core and Domain 4 overgrowths are included in, but overall in sharp and well-defined contact with, synchysite-(Y) (Figs. 6a–6b). Also, the growth zone of zircon (Domain 4) also occasionally cuts synchysite-(Ce) (Fig. 6c), whereas it is corroded by synchysite-(Y) (Fig. 6d).

# **Elemental composition of zircon**

In total, 240 EPMA and 60 LA-ICP-MS analyses of zircon compositions were made. The entire data set for zircon compositions is provided in Online Materials<sup>1</sup> Tables S1 and S2 and presented in Figure 7. Domain 1 has the highest and most homogeneous Zr concentrations of  $63.96 \pm 1.78$  wt% ZrO<sub>2</sub>. Concentrations progressively decrease and become more dispersed in Domains 2 (57.02  $\pm$  5.11 wt%), 3 (50.45  $\pm$  7.53 wt%), and 5  $(50.05 \pm 6.03 \text{ wt\%})$ . Zirconium concentrations in Domain 4 are comparatively high and constant  $(57.94 \pm 2.45 \text{ wt\%})$  (Fig. 7). The concentrations of minor and trace elements, notably Al, P, REE, U, and Th, exhibit an opposite trend to Zr and increase from Domain 1 to the other domains, with maxima in Domains 3 and 5 (Figs. 7-9; Online Materials<sup>1</sup> Figs. S2-S4). For example, Y<sub>2</sub>O<sub>3</sub> content increases from 0.35 wt% in Domain 1 to 2.66, 6.00, 1.25, and 5.36 wt% in Domains 2 to 5, respectively. Yb<sub>2</sub>O<sub>3</sub> contents can reach up to 10 wt%, and average Al<sub>2</sub>O<sub>3</sub> contents of  $\sim$ 0.5 wt% and P<sub>2</sub>O<sub>5</sub> of 0.8 wt%, respectively. Analytical results from LA-ICP-MS analyses show similar trends (Fig. 10a). Exceptionally, Domain 4 has the highest Hf concentration, 4.72 wt% HfO<sub>2</sub> on average, although Domains 2 (2.69 wt%), 3 (2.71 wt%), and 5 (4.14 wt%) have elevated concentrations (Figs. 7-10; Online Materials<sup>1</sup> Table S1; see also the complete Online Materials<sup>1</sup> data set). From Domains 1 to 5, the zircons progressively become LREE-enriched, except Domain 4, which is relatively less LREE-enriched than Domains 3 and 5 [Average (La/Yb)<sub>N</sub> value of Domain 1: 0.0002; Domain 2: 0.0024; Domain 3: 0.0036; Domain 4: 0.0015; Domain 5: 0.0028]. The zircons are also characterized by less positive Ce anomalies [calculated as  $Ce/Ce^* = Ce_N/(\sqrt{La_N \times Nd_N})$  Domain 1: 49.6; Domain 2: 1.96; Domain 3: 2.01; Domain 4: 2.15; Domain 5: 0.98] and more negative Eu [calculated as Eu/Eu\* =  $Eu_N$ /  $(\sqrt{Sm_N \times Gd_N})$ ; Domain 1: 0.099; Domain 2: 0.0065; Domain 3: 0.0056; Domain 4: 0.014; Domain 5: 0.0081] and Y anomalies [calculated as  $Y/Y^* = Y_N/(\sqrt{Ho_N \times Er_N})$ ; Domain 1: 0.78; Domain 2: 0.65; Domain 3: 0.65; Domain 4: 0.67; Domain 5: 0.59] (Fig. 10a; Online Materials<sup>1</sup> Table S2). The Ce and Eu anomalies are also calculated using least-square polynomial fitting developed by Anenburg and Williams (2022); the results (Online Materials<sup>1</sup> Table S2) are consistent with those presented above calculated by a linear interpolation.

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(a) Domain 1

**FIGURE 4.** Occurrence of zircon of different domains. Scale bars indicate a length of 100  $\mu$ m. Abbreviations: Tr = image under transmitted light; BSE = BSE image; CL = CL image. (Color online.)

# Whole-rock geochemistry

Granites from the Zudong pluton is siliceous (SiO<sub>2</sub> content of 73–78 wt%), aluminous (Al<sub>2</sub>O<sub>3</sub> content of 12.1–14.4 wt%), alkaline (Na<sub>2</sub>O+K<sub>2</sub>O content of 6–9 wt%), and rich in F (2420– 3870 ppm) and CO<sub>2</sub> (up to 0.6 wt%) (Online Materials<sup>1</sup> Table S3). Geochemically, the granites have affinities from slightly peralkaline to peraluminous and belong to A-type granites based on the discrimination diagram of Eby (1990) (Online Materials<sup>1</sup> Fig. S5). They have total REE concentrations varying from ~150 to 7700 ppm, of which ~80–95% are HREE (Fig. 10b; Online Materials<sup>1</sup> Table S3), and all the rocks are enriched in HREE [(La/Yb)<sub>N</sub> ratio of 0.1–0.6] (Fig. 10b). In addition, the proportions of HREE are higher [lower (La/Yb)<sub>N</sub> ratio] in granites of higher total REE concentrations. All analyzed samples have negative Eu anomalies ( $\leq$ 0.02) and variable Ce and Y anomalies



**FIGURE 5.** Representative Raman spectra of different domains of zircon in the Zudong granites.

(0.18–1.55 and 0.89–1.45, respectively). Interestingly, the bulk REE concentrations of the granites of this study show a moderately to strongly positive correlation with bulk Al<sub>2</sub>O<sub>3</sub> ( $r^2 = 0.69$ ), F ( $r^2 = 0.64$ ), Rb ( $r^2 = 0.78$ ) concentrations, and LOI ( $r^2 = 0.83$ ) value (Fig. 11), but a negative correlation with the magnitude of Ce anomalies ( $r^2 = 0.65$ ) and (La/Yb)<sub>N</sub> ratios ( $r^2 = 0.83$ ); the sample with the highest REE concentration (7684 ppm) has the

most negative Ce anomaly (0.18) and the lowest  $(La/Yb)_N$  value (0.12). Furthermore, the  $(La/Yb)_N$  values show a moderately negative correlation with Al<sub>2</sub>O<sub>3</sub> ( $r^2 = 0.53$ ) and Rb ( $r^2 = 0.47$ ) concentrations (Online Materials<sup>1</sup> Fig. S6). The entire data set for whole rock geochemical compositions is provided in Online Materials<sup>1</sup> Table S3. The tetrad effect exhibited on the chondrite-normalized pattern is evaluated with the lambda shape coefficient



**FIGURE 6.** BSE images of the association of zircon with other REE-bearing minerals in the Zudong granites. (**a**) An inclusion of zircon in synchysite-(Y). (**b**) A close-up of the zircon grain in **a** showing a porous Domain 2 rimmed by a broad continuous growth zone (Domain 4); Domain 4 is not embayed by the synchysite-(Ce) and locally overgrown by xenotime-(Y). (**c**) Zircon grains included in fluorite and associated with synchysite; porous relict grains (Domain 2) are connected by subsequent hydrothermal growth (Domain 4) that cut a grain of Th-bearing synchysite-(Ce). (**d**) Zircon grain corroded and overgrown by synchysite-(Y) [Syn-1]. (**e**) A relict zircon grain (Domain 1?) embayed by the growth of synchysite-(Ce) along the margin. (**f**) Partial dissolution of a zircon grain in fluorite. Abbreviations: Zrn = zircon; other abbreviations are the same to those in Figure 3. (Color online.)

after Anenburg and Williams (2022). The tetrad coefficients ( $\tau$ ) are given in Online Materials<sup>1</sup> Table S3 and are generally positive, defining an M-type tetrad pattern. The Eu and Ce anomalies determined by this method ( $\leq 0.02$  and 0.20-1.65, respectively) are comparable to the values presented above calculated by a linear interpolation.

### DISCUSSION

# Origin and paragenesis of REE minerals

The major REE hosts in the Zudong granite, notably gadolinite-(Y), hingganite-(Y), yttrialite-(Y), synchysite-(Y), and fluorite, showed extensive replacement and veining textures with respect to the primary rock-forming minerals, suggesting a hydrothermal origin. Xenotime and REE niobates likely show two generations. The first one occurred as extensively altered, rounded, and corroded inclusions in mica. These grains were likely of a magmatic origin and represented the relict minerals that survived after hydrothermal alteration. The other generation is represented by anhedral, homogeneous grains associated with synchysite-(Y) together as vein-filling phases and is likely hydrothermal in origin and coevally precipitated with synchysite-(Y).

Regarding the hydrothermal REE mineral assemblage, REE silicates represent the earliest phase, as these minerals were often crosscut by fluorite and synchysite-(Y). Gadolinite-(Y), hingganite-(Y), and yttrialite-(Y) often occurred as veinlets crosscutting and replacing feldspars and quartz and, in turn, being crosscut by veinlets of synchysite (Fig. 3d) or pods of fluorite (Fig. 3e). Thus, both fluorite and synchysite post-dated these REE silicates. For the fluorite and synchysite, Flr-1 and Flr-2 sometimes coexisted in the same mineral grain, and when it happened, Flr-1 was either included as isolated patches or crosscut by and embayed along the contact with Flr-2 (Fig. 3g), suggesting that Flr-2 post-dated Flr-1. Synchysite could be associated with Flr-2 as inclusions, and this indicates that synchysite might precipitate slightly earlier than, or co-precipitated with, Flr-2. The synchysite inclusions are comprised of synchysite-(Ce) that was crosscut, embayed, and penetrated by synchysite-(Y). Moreover, synchysite-(Ce) only occurred as anhedral shapes, whereas some synchysite-(Y) grains were large and subhedral to euhedral in shape (Figs. 6a and 6d), indicating synchysite-(Ce) was an earlier phase pre-dating the crystallization of the synchysite-(Y).

The crosscutting relationship between zircon and synchysite



# Zircon domain

**FIGURE 7.** Variations of elemental contents in different domains of zircon in the Zudong granites. The minimum and maximum of the box and whisker plots are defined based on the  $1.5 \times IQR$  (interquartile range) value, with the minimum at  $Q1 - 1.5 \times IQR$  and maximum at  $Q3 + 1.5 \times IQR$ . Q1 and Q3 are the 25th and 75th percentiles, respectively.



FIGURE 8. Images and elemental compositions of a representative zircon grain in the Zudong granites. (Color online.)

(Fig. 6) suggests that the growth of Domain 4 was generally synchronous to synchysite-(Y) otherwise the corrosion and embayment at the margin of the zircon grain would be expected as the fluid from which the synchysite-(Y) precipitated should be F-rich and aggressive with respect to zircon (Keppler 1993). From the petrographic examination, Domains 2 and 3 were likely to be generally coeval with the precipitation of FIr-1 and/or replacement of FIr-1 by FIr-2, while Domain 4 is coeval with the precipitation of synchysite-(Y) and/or replacement of synchysite-(Ce) by synchysite-(Y).

# Zircon archive of the magmatic-hydrothermal evolution

Although zircon is generally regarded as a refractory mineral, it can be substantially altered during metasomatism to form hydrothermal zircon (Ersay et al. 2022; Geisler et al. 2003b; Soman et al. 2010; Wang et al. 2023; Yang et al. 2014). Hydro-

thermal zircon can form from the alteration of magmatic zircon (e.g., Geisler et al. 2007 and references therein) and/or direct precipitation from the hydrothermal fluids (e.g., Hoskin 2005; Zhao et al. 2016). The morphology, structure, and chemical compositions of hydrothermal zircon grains are different from those of their magmatic counterparts, enabling an easy discrimination between the two (Fu et al. 2009). In Zudong granites, Domain 1 of zircon grains is transparent and shows bright CL and oscillatory growth zones (Fig. 4), indicating a well-crystalline internal structure, which is further proved by the strong intensity and narrow, well-defined characteristic peaks in the Raman spectra (Fig. 5). The uniform chemical composition of Domain 1 with high Zr content and low Hf and other minor element contents is more commonly of magmatic origin (Hoskin and Schaltegger 2003). All these suggest that Domain 1 crystallized from a hightemperature granitic magma (Pupin 1980).



FIGURE 9. Images and variations in elemental compositions of representative zircon grains in the Zudong granites. (Color online.)

Domain 2 is murky, porous, and dark in CL (Fig. 4). Also, the lower intensity and broader, less well-defined characteristic peaks in the Raman spectra (Fig. 5) suggest that this domain is highly metamict, with lower crystallinity due to radiation damage from decay of U and Th (Geisler et al. 2003a; Wang et al. 2014). The porous and inclusion-rich texture suggests that Domain 2 likely formed via a dissolution-reprecipitation process (Chen and Zhou 2017; Geisler et al. 2007; Hay and Dempster 2009; Tomaschek et al. 2003), very often occurring during the interaction between metamict zircon and fluids (Geisler et al. 2007). Often, Domain 2 occurred in the core of zircon grains or as overgrowth on Domain 1, suggesting its formation through the interaction of Domain 1



**FIGURE 10.** Chondrite-normalized REE patterns of (**a**) different domains of zircon and (**b**) the whole-rock REE concentration of the Zudong granites. (Color online.)

with fluids. Domains 3 and 4 are transparent to slightly murky in appearance, display dark CL images, and occasionally, oscillatory growth zones (Fig. 4). Although zircon of dark CL with or without oscillatory growth zones can form from a volatile-rich residual melt at a late magmatic stage (Erdmann et al. 2013; Gagnevin et al. 2010; Kozlik et al. 2016), Domains 3 and 4 often occur as overgrowths on Domain 2 (Figs. 4, 8, and 9), suggesting that they post-dated Domain 2 and are more likely to have formed hydrothermally. In the Raman spectra, no characteristic peaks of zircon can be identified but only strong fluorescence (Fig. 5), suggesting a highly metamict and amorphous state. Metamictization-induced structural distortion facilitated signifi-



FIGURE 11. Bivariant correlations between the whole-rock REE concentrations and selected elements and elemental ratios. (Color online.)

cant incorporation of non-formula elements, such as the REE, Al, P, and Ca, into the structure of zircon (Burnham 2020; Geisler et al. 2003b). Alternatively, the elevated concentrations of these elements could be due to inclusions in the zircon grains (Burnham 2020), but this explanation seems less likely in Zudong because of the positive correlation between REE and Al concentrations in the zircon and the absence of any REE-Al-bearing inclusions of any observable size in the studied grains.

The incorporation of REE into zircon was very likely coupled with substitution of P through the reaction as  $REE^{3+} + P^{5+} = Zr^{4+}$ + Si<sup>4+</sup>, as shown by positive correlations between P and REE of coefficients being 0.70 (Fig. 12a). Aluminum also shows positive correlation coefficient with REE ( $r^2 = 0.67$ ; Fig. 12b). However, a coupled substitution of REE<sup>3+</sup> and Al<sup>3+</sup> for Zr<sup>4+</sup> and Si<sup>4+</sup> is not charge-balanced when Al<sup>3+</sup> resides at the Si site of zircon (Claridge et al. 1994), while a coupled substitution of REE<sup>3+</sup>, P<sup>5+</sup> and Al<sup>3+</sup> for Zr<sup>4+</sup> and Si<sup>4+</sup> is not site-balanced. Thus, it is likely that Al substituted through the reaction as  $Al^{3+} + P^{5+}$ =  $2Si^{4+}$ , and the positive correlation between REE and Al could be coincidentally related to the magmatic-hydrothermal fractionation of these elements. Substitution of non-formula elements into zircon is commonly attributed to the increasing involvement of fluids (Geisler et al. 2007) and found in amorphous metamict domains. In addition, the low analytical totals of these domains, often attributed to the presence of molecular H2O or OH in the structure (Nasdala et al. 2009), also indicate volatile-saturated formation conditions.

In Zudong, this process is supported by the progressive enrichment of Hf in zircon from Domains 1 to 5 (Figs. 7–9), consistent with a magmatic to hydrothermal transition because Hf is more incompatible than Zr during purely magmatic fractional crystallization and hence, tends to be enriched in the residual melt (Irber 1999; Linnen and Keppler 2002). Domains 2 to 4 of zircon likely formed under a volatile-saturated condition from the latest magmatic stage to the magmatic-hydrothermal transition. Domain 5 signifies the final re-equilibration of the zircon with the fluid. The re-equilibration of Domain 5 was likely due to a diffusion-reaction process (Geisler et al. 2007) that produced irregular and inward-penetrating patchy reaction zones overprinting previous domains.

# Fluid-mineral interaction and multiple mobilizations of **REE**

In hydrothermal systems, interactions of zircon with fluids under varying physicochemical conditions can be recorded in the textures and compositions of individual grains (Geisler et al. 2007; Hoskin 2005), and insight into the fluid chemistry can be inferred from the mineral paragenetic sequence. The results obtained from these two sources can be applied to trace the evolution of the fluid.

In Zudong, the low concentrations of Sr and Eu, also the significant negative Eu anomalies and the tetrad REE pattern (Fig. 10b), attest to the highly evolved nature of the Zudong pluton, whereas the variable REE concentrations point to a metasomatic origin. The non-chondritic Y/Ho ratio (32.7 on average, compared to the chondritic Y/Ho ratio of 28; Bau 1996) shows a strong enrichment of Y in the Zudong pluton, which also supports the involvement of an aqueous fluid (Bau 1996;



**FIGURE 12.** Correlations between REE concentrations and (a) Al and (b) P for different domains of zircon in the Zudong granites. (Color online.)

Irber 1999). Bulk geochemistry indicates that REE mineralization occurred under F-rich, volatile-rich, and highly evolved (Rbrich) conditions. From the mineral paragenesis, re-mobilization of the REE took place through the reaction of the previously deposited REE-bearing minerals, including the dissolution of the REE silicates and primary REE phosphates and niobates, for example, by the dissolution of:

Gadolinite:  $Y_2FeBe_2Si_2O_{10} + 12H^+ \rightarrow 2Y^{3+} + Fe^{2+} + 2Be^{2+} + 2H_4SiO_4 + 2H_2O$  (1)

Hingganite:  $Y_2Be(SiO_4)_2(OH)_2 + 10H^+ \rightarrow 2Y^{3+} + 2Be^{2+} + 2H_4SiO_4 + 2H_2O$  (2)

Yttrialite-(Y): 
$$Y_2Si_2O_7 + 6H^+ + H_2O \rightarrow 2Y^{3+} + 2H_4SiO_4$$
 (3)

Also, the fluid-mineral interaction promoted the dissolution of the REE-enriched fluorite (Flr-1) that was reprecipitated as REE-depleted fluorite (Flr-2). During this process, and together with the reactions 1 to 3, REE, especially the HREE, would be re-mobilized by the fluid and subsequently precipitated as REEfluorocarbonate, whereas Be was likely lost to the fluid as there are no late Be-bearing minerals observed. Here, an acidic fluid is presumed to initiate the mineral dissolution, considering that the precipitation of hematite, through oxidation of  $Fe^{2+}$  liberated from the alteration of biotite, would generate H<sup>+</sup> in an oxidizing fluid through the reaction (after Reed 1997): From the petrographic examination, synchysite is the dominant REE-fluorocarbonate phase in the Zudong granite, of which synchysite-(Ce) precipitated first, which was then replaced by synchysite-(Y) (Syn-1), and then locally further replaced by HREE-enriched synchysite-(Y) (Syn-2). The precipitation of synchysite could be produced through the following, as suggested by Ngwenya (1994):

$$REECO_{3}F_{(a0)} + Ca^{2+} + HCO_{3}^{-} \rightarrow REECa(CO_{3})_{2}F_{(s)} + H^{+}$$
(5)

This suggests that the fluid was Ca-F-CO<sub>2</sub>-REE-rich, also implied by the high-F and -CO<sub>2</sub> content of the granites (Online Materials<sup>1</sup> Table S3), and particularly Ca-rich throughout the entire mineralization because of the absence of bastnäsite or parisite precipitation, that often takes place after synchysite (Förster 2001; Ngwenya 1994). Moreover, the fluid would have become slightly HREE-enriched in the final stage to locally replace Syn-1 with Syn-2. Considering that the pH buffering ability of the major minerals, notably feldspar and quartz, is low, the H<sup>+</sup> consumed by mineral dissolution (e.g., reaction 1 to 3) could be replenished by the H<sup>+</sup> produced from reaction 4 until either REE<sup>3+</sup>, HCO<sub>3</sub>, or F<sup>-</sup> was exhausted by the precipitation of synchysite. The paragenetic sequence of the REE-bearing minerals is summarized in Figure 13a.



**FIGURE 13.** (a) Interpretations of the paragenetic sequence of the REE-bearing minerals in Zudong granites and (b) the evolution of zircon recording the mineral-fluid interaction for the HREE mineralization.

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The evolution trajectory is recorded in the zircon (Fig. 13). For instance, the coupled dissolution-reprecipitation (CDP) of zircon that formed the growth zone of Domain 2 typically involves dissolution by a F-rich fluid (Keppler 1993), after which the mobilized REE were redistributed in a highly uneven REE enrichment, whereas the repeated truncation of the porous domain by a later clean, inclusion-free domain (Domain 3) reflects fluctuating fluid chemistry between Zr under-saturation and saturation (or supersaturation). This also points to a fluctuation of the pH and F activity of the fluid, as zircon can be effectively dissolved in acidic, F-bearing fluids (Keppler 1993). Particularly when zircon is commonly spatially associated with fluorite in the Zudong granite, the CDP of fluorite (replacement of Flr-1 by Flr-2) would cause local fluctuation of the F activity of the fluid that could motivate the CDP of zircon (e.g., Han et al. 2019). The repeated re-mobilization of REE through CDP of zircon would cause the significant REE enrichment in Domain 3 and relative REE depletion in Domain 2 (Figs. 7-9; Online Materials<sup>1</sup> Figs. S2-S4). After the CDP of the fluorite ended, F activity of the fluid likely became steady and gradually decreased later due to the precipitation of synchysite. The consumption of fluoride in the fluid is manifested by the continuous growth of Domain 4, commonly rimming Domains 2 and 3 and rarely being embayed and corroded along grain boundaries. The final minor HREE metasomatism on the Syn-1 would have coevally caused the HREE enrichment in Domain 5 (Fig. 9; Online Materials<sup>1</sup> Figs. S2-S4). through a diffusion-reaction process. On the other hand, the progressive preferential enrichment of the LREEs in the zircon [indicated by (La/Yb)<sub>N</sub> value; Online Materials<sup>1</sup> Table S2] implies that the fluid was also progressively enriched in the LREE, consistent with previous experimental results showing that mobility of the LREE is higher than the HREE (Migdisov et al. 2016). In this regard, the exhaustion of fluoride would possibly be a key reason for the termination of REE mineralization in the Zudong granite. To summarize, as a refractory phase capable at the same time of being highly altered during metasomatism, the texture and composition of zircon may record the evolution of the hydrothermal system and provide further insight to the REE mineralization.

The combined mineralogical and geochemical records show that repetitive dissolution and precipitation of REE-bearing minerals took place during the hydrothermal alteration of the Zudong granites. Repeated mobilization and re-distribution caused progressive enrichment and fractionation of the REE.

#### Ce and Eu anomalies in zircon as an indicator for fluid redox

Because Ce<sup>4+</sup> can more readily substitute for Zr<sup>4+</sup> than Ce<sup>3+</sup>, magmatic zircon often shows a positive Ce anomaly. The magnitude of the anomaly is demonstrated to increase with increasing oxygen fugacity of the melt (cf. Trail et al. 2012), whereas the negative Eu anomaly shown on the chondrite-normalized pattern is attributed to preferential incorporation of Eu<sup>2+</sup> in plagioclase prior to or during the crystallization of zircon (Hoskin and Schaltegger 2003). In zircons of the Zudong granites, magmatic Domain 1 shows a typical positive Ce anomaly and a negative Eu anomaly (Fig. 10a). However, the Ce anomaly decreases from 49.6 on average for magmatic Domain 1 to ~2 in hydrothermal Domains 2 to 4. In the final phase, Domain 5, the average is 1.0, including some spots with negative anomalies (Fig. 10a). This suggests the fluid was comparatively reduced during the HREE mineralization. This interpretation is also supported by the negative correlation between the bulk REE concentration and the magnitude of Ce anomaly (Fig. 11e). The reducing conditions could be attributed to the precipitation of hematite prior to and throughout HREE mineralization that consumed  $O_2$  in the fluid. Synchronously, part of the Ce was likely oxidized to Ce<sup>4+</sup> and decoupled from the other REE. The reducing conditions are also implied by variation of the Eu anomaly from 0.1 on average for Domain 1 to 0.01 on average for Domains 2 to 4 and 0.008 on average for Domain 5 (Online Materials<sup>1</sup> Table S2). As Eu<sup>2+</sup> is unlikely to substitute Zr<sup>4+</sup> on the basis of cation charge and size (cf. Trail et al. 2012), a more reducing condition would lead to greater depletion of Eu in zircon, as manifested by the increasing negative Eu anomalies (Fig. 10a).

# IMPLICATIONS FOR HREE MINERALIZATION AND REE FRACTIONATION IN GRANITIC SYSTEMS

The Zudong granites have very high HREE concentrations. The high-HREE concentration, together with the formation of weathering susceptible REE-fluorocarbonate and silicate minerals, also would be essential to the formation of regolith-hosted ore formation during weathering (Li et al. 2019, 2022). The HREE enrichment is associated with intensifying REE fractionation, as shown by the negative correlation between the bulk REE concentration and (La/Yb)<sub>N</sub> ratio (Fig. 11f). Hydrothermal alteration is commonly thought to be the key process in boosting the HREE concentration of the granite (Fan et al. 2023; Huang et al. 1989; Li et al. 2017). The source of the fluid and HREE is most commonly attributed to either internal derivation from the granitic magma (Huang et al. 1989) or from external sources, for instance, subducted sediments (Fan et al. 2023). In this study, petrographic and mineralogical examination of the REE-bearing minerals, particularly zircon, reveals that multiple stages of mobilization of the REE happened during hydrothermal alteration. A significant amount of the major and mobile elements would be removed in this process, likewise for the LREE. The temperature of the REE mineralization was likely close to magmatic, as suggested by the coexistence of fluorite and REE-fluorocarbonates (Williams-Jones and Wood 1992). A study of a similar style of alteration at the Erzgebirge district suggested a maximum mineralization temperature of 550-600 °C (Förster 2001). Light REE would be highly mobilized through Cl complexation in this temperature range (Migdisov et al. 2016; Williams-Jones et al. 2012), and hence preferentially lost to the exsolved fluid (Bau and Dulski 1995), resulting in the observed LREE depletion in Zudong granites. In contrast, the HREE was enriched through the extensive mineralization of synchysite-(Y).

This study showcases that, apart from an HREE-rich fluid (cf. Fan et al. 2023), multiple stages of mobilization of the HREE during the hydrothermal alteration are essential in upgrading the HREE concentrations to an ore grade or a subore grade that could facilitate the creation of regolith-hosted HREE deposits subsequently formed during weathering. In this process, repeated mineral dissolution and (re)precipitation of the REE-bearing minerals would progressively fractionate the REE, with the LREE being mobilized and the HREE extensively mineralizing as newly precipitated mineral phases. At the same time, the process would cause substantial dissolution of the major minerals, like feldspars and micas, resulting in a net decrease in the major element contents with a consequent increase in the bulk HREE content of the altered rocks.

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