1   **Revision 1:**

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3   **Nanostructure reveals REE mineral crystallization mechanisms in**

4   **granites from heavy-REE deposit, South China**

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ABSTRACT

Weathering crusts after granites are the most important source of heavy rare-earth elements (HREE) worldwide. Although HREE in these deposits are known to be inherited from parental rocks, the origin of HREE enrichment and reasons why it is rare outside of China remain unclear. Here, we report the occurrence of variably organized nanoparticles of Ce-poor (<0.2 wt.%), Nd-Y-rich bastnäsite-(La) and associated cerianite in parental granites from a HREE deposit, South China. The mineral contains high HREE abundances (up to 13 wt.% Y_2O_3). Synchrotron radiation-induced X-ray diffraction and high-resolution transmission electron microscopy analyses suggest that the mineral grew as disordered nanocrystals, and coaligned, or nearly coaligned nanoparticle aggregations, thus supporting "nonclassical" crystallization mechanisms by particle attachment under hydrothermal conditions. The nanocrystalline Ce-poor, Nd-Y-rich bastnäsite-(La) precipitated at rapidly decreasing temperature related to the influx of externally derived fluids, which caused CO_2-H_2O immiscibility and REE supersaturation. This interpretation is supported by petrographic data and microthermometric analysis of fluid inclusions in quartz. Unusually high $f(O_2)$ resulted in Ce oxidation and decoupling from trivalent lanthanides, producing polycrystalline mineralization, which decomposed easily during late weathering stages to release HREE.

46

47   **INTRODUCTION**

48   The rare-earth elements (REE), generally defined as the lanthanides plus

49   yttrium (Y), are considered critical raw materials because of their extensive

50   applications in renewable energy solutions and modern technologies (Kalvig

51   and Machacek 2018). Recently, concerns over the perceived imbalance

52   between the increasing demand for these resources and their supply

53   shortages have led to a surge in REE exploration worldwide, since China, the

54   largest REE producer in the past 30 years, reduced its REE export quota

55   (Gulley et al. 2018). Heavy REE (HREE = Gd-Lu + Y) are much less abundant

56   than light REE (LREE = La-Eu) and are anticipated to be associated with the

57   highest supply risk in the foreseeable future (Balaram 2019). The majority of

58   economically exploitable HREE resources are associated with regolith-hosted

59   ion-adsorption deposits (IAD) in South China (Martin et al. 2020). The HREE

60   are adsorbed as ionic complexes onto clay minerals in weathering crusts

61   developed over igneous, mostly granitoid rocks (Bao et al. 2008). These

62   deposits account for about 80% of the global HREE supply (Bernhardt and

63   Reilly 2020). The forms of REE adsorption on clays reported to date primarily

64   include readily leachable eightfold- to ninefold-coordinated outer-sphere

65   hydrated complexes, dominantly attached to the clays kaolinite and halloysite

66   (Borst et al. 2020). Although weathering of granitoids under warm and humid

67   conditions plays an important role in REE fractionation and enrichment, this

68   process is expected to yield high LREE/HREE ratios in IAD because LREE are

69   hosted in phases relative more susceptible to weathering in comparison with

70   HREE-enriched phases (Estrade et al. 2019; Prameswara et al. 2021).

71   Geologically similar IAD were identified elsewhere in Southeast Asia

72   (Sanematsu et al. 2013) and Madagascar (Janots et al. 2015), and these

73   deposits generally exhibit stronger enrichment in LREE than HREE. The

74   extent of relative enrichment and fractionation among leachable REE is

75   believed to be controlled by the nature of precursor bedrock and REE-hosting

76   minerals in that rock (Martin et al. 2017; Estrade et al. 2019). Therefore, one

77   essential question that needs to be addressed to understand the origin of IAD

78   is how HREE-rich minerals form in their precursor granitoid rocks.

79   Xu et al. (2017) reported three types of previously unidentified, Ce-poor,

80   LREE- and HREE-enriched minerals in the South China granites. The

81   weathering profiles inherited the REE signature of their parental granites,

82   reflecting the depletion in Ce and enrichment in both LREE and HREE.

83   Different horizons within the weathering profile show variable enrichment

84   levels in LREE and HREE. Uncommon REE minerals were interpreted to have

85   served as the principal source of HREE incorporated in the mineralized

86   weathering crusts (Xu et al. 2017); however, the exact nature and genesis of

87   these minerals were not very clear. Understanding their origin and paragenetic

88   role in the parental granites has become a priority in explaining why HREE-rich

89   clays are particularly abundant in South China. This work also has practical

90   implications for mineral exploration as it provides criteria for the identification of

91   similar HREE-rich IAD elsewhere. Here, we report unusual nanostructures

92   observed in a Ce-poor, REE fluorocarbonate mineral [referred to hereafter as

93   Ce-poor, Nd-Y-rich bastnäsite-(La)] from the Zhaibei granites, which

94   weathered to give rise to the famous HREE deposits of South China (also

95   known as "South China clays"). Our results provide evidence for a

96   crystallization mechanism novel among REE minerals, which involves crystal

97   growth by oriented and disoriented attachment of nanoparticles, and further

98   supports the idea that HREE enrichment in the parental granites was related to

99   rapid crystallization in a highly oxidized environment.

100

101   **GEOLOGICAL BACKGROUND**

102   Vast quantities of granitic rocks, associated with subordinate gabbros and

103   basalts, were emplaced in the South China Block during the Mesozoic. Mao et

104   al. (2008) suggested that these rocks were products of three episodes of

105   magmatic activity: Late Triassic (230-210 Ma), Middle-Late Jurassic (170-150

Ma) and Early Cretaceous (134-90 Ma). The Early Mesozoic intrusions were confined mostly to intracontinental areas, whereas the Cretaceous granites were distributed mainly towards the South China Sea coast (Fig. 1). Many studies identified subduction of the Paleo-Pacific plate beneath the Eurasian plate as responsible for the Mesozoic granitic magmatism in the region (Li and Li 2007; Zhou et al. 2006; Zhou et al. 2015). The Triassic episode produced voluminous S-type granites with high modal contents of Al silicates, in particular muscovite, garnet and tourmaline (Wang et al. 2013). Jurassic granites are widespread in the Nanling region and primarily composed of biotite and two-mica varieties. These rocks include calc-alkaline I-type, alkaline A-type and subordinate S-type granites (Zhou et al. 2015). Cretaceous granites are mostly of A- and I-types, and tend to occur closer to the coast (Sun et al. 2015).

Ore deposits are quite abundant in the South China granitic belt and include W, Sn, Sb, Bi, Cu, Pb, Zn, Nb, Ta and REE targets. More than 90% of the HREE-rich IAD are located in Jiangxi, Guangdong and Guangxi provinces (Fig. 1). The examined weathering profiles in Zhaibei, southern Jiangxi, have a thickness ranging from 5 to 30 m, and are developed after Middle-Jurassic peraluminous biotite and muscovite granites (Li et al. 2003; Wang et al. 2015). The mineralized laterites show moderate LREE enrichment levels and negative Ce and Eu anomalies; their REE budget (215-1334 ppm) is made up

of ~30-50% HREE (57-542 ppm; Xu et al. 2017). The Jurassic (188 Ma; Xu et al. 2017) granites intruding Paleozoic granitoids have intrusive contacts with Jurassic volcanic rocks in the western part of the study area, and are separated by a fault from Cambrian metamorphic rocks in its northern part. The parental rock of the Zhaibei REE-rich clays is medium- to coarse-grained and composed of alkali feldspar (25-30%), plagioclase (25-32%), quartz (30-35%), biotite (3-10%) and muscovite (< 2%) (Online Material[1] Fig. S1). The accessory mineral assemblage includes REE phases, zircon, fluorapatite, magnetite and ilmenite. The REE minerals are represented by monazite-(Ce), xenotime-(Y), Ca-REE fluorocarbonates, allanite-(Ce), cerianite-(Ce) and three HREE-rich minerals described in our earlier work as "REE-1, 2, 3". Both REE-1 and REE-2 apparently formed by alteration of fluorapatite, which is highly susceptible to fluid-induced chemical and textural changes under natural and experimental conditions (Fig. 2a; Harlov and Förster 2003; Harlov 2015; Chakhmouradian et al. 2017). The Ce-poor, Nd-Y-rich bastnäsite-(La) ("REE-3") occurs as fracture fillings in feldspar and disseminated anhedral grains up to 200 μm in size developed interstitially to quartz, biotite and feldspar (Fig. 2b, c). Cavernous samples contain thin encrustations of Ce-poor, Nd-Y-rich bastnäsite-(La) lining cavities (Fig. 2c). The mineral did not form at an early stage of the weathering event, and is in direct contact with biotite, quartz and feldspar, or separated from them by a rim of unidentified hydrous

148 Al-Fe-rich silicate (Fig. 2c, d) in the fresh parental rock. The cerianite veinlets

149 are observed in the granite, where they are intimately intergrown with an

150 unidentified hydrous Al-Fe-rich silicate (Fig. 2e). Ilmenite in this granite was

151 partially converted to hematite, which was confirmed by Raman

152 microspectroscopy (Fig. 2f and Online Material[1] Fig. S2).

153

154 **ANALYTICAL METHODS**

155 **Mineral analysis**

156 The major-element compositions of mineral phases in the granites were

157 analyzed by wavelength-dispersive X-ray spectrometry (WDS) using a JEOL

158 JXA-8230 electron microprobe at the East China University of Technology.

159 According to the chemical composition and grain size of individual minerals,

160 each of them was analyzed with a set of appropriate matrix-specific standards

161 (both natural and synthetic) and optimized instrumental conditions (detector

162 type, beam settings and counting statistics). The standards used during for the

163 WDS analyses included sanidine (Si, K), plagioclase (Ca), rutile (Ti), magnetite

164 (Fe), rhodonite (Mn), fluorite (F), jadeite (Na, Al), apatite (P), biotite (Mg),

165 metallic Nb and Ta (Nb, Ta), uraninite (Th, U, Pb), monazite (La, Ce, Pr, Nd),

166 and synthetic REE phosphates (Y, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb). The

167 measurements were performed at an accelerating voltage of 15 kV and a

168 beam current of 20 nA, with an electron beam ranging 1-5 μm in diameter. For

169 the analysis, Kα analytical lines were used for all elements except La, Ce, Pr,

170 Nd, Nb and Ta (Lα lines for all), and Sm (Lβ line). For REE-bearing minerals,

171 raw WDS data were corrected using empirical interference values for REE and

172 other elements potentially interfering with the REE signals, determined for

173 the well-characterized synthetic glass and phosphate standards. All raw data

174 were corrected with standard ZAF correction procedures. Repeated analysis of

175 the standards showed that precision of the WDS measurements was ±2 % or

176 better for most elements.

177

178 **Synchrotron radiation-induced X-ray diffraction (SR-XRD)**

179 In-situ SR-XRD analysis of Ce-poor, Nd-Y-rich bastnäsite-(La) was

180 performed on polished thin sections at the 4W2 beamline of Beijing

181 Synchrotron Radiation Facility. The wavelength of the monochromatic X-ray

182 beam was 0.6199 Å and the beam size was 20 × 30 μm^2. During the

183 measurement, the silicate minerals surrounding Ce-poor, Nd-Y-rich

184 bastnäsite-(La) were covered with a copper sheet with a hole 150 μm in

185 diameter, which is close to the size of analyzed fluorocarbonate grains. The

186 thin section was continuously rotated from -20° to 20° about the X-ray beam

187 axis at ambient conditions, and the collecting time was 300 s. The X-ray

188 diffraction (XRD) patterns were acquired using an image plate detector

189 (MAR-345), calibrated with a CeO_2 standard, and then integrated to generate

190 conventional one-dimensional profiles using the Fit2D program (Hammersley

191 1997).

192

High-resolution transmission electron microscopy (HRTEM)

194   Electron-transparent foils of representative Ce-poor, Nd-Y-rich

195 bastnäsite-(La) grains for HRTEM analysis were prepared by focused ion

196 beam technique (FIB, Online Material[1] Fig. S3) using a Zeiss Auriga Compact

197 dual beam instrument equipped with an Omniprobe AutoProbe 200

198 micromanipulator at the Institute of Geology and Geophysics, Chinese

199 Academy of Sciences. Final thinning and polishing were done using an ion

200 beam at a voltage of 5-30 kV and beam current of 0.05-2 nA. The FIB section

201 was ~100 nm in thickness. HRTEM images of the foils were obtained with an

202 aberration-corrected scanning transmission electron microscope (FEI Titan

203 Cubed Themis G2 300 at Peking University), which was operated at an

204 accelerating voltage of 300 kV and a beam current of ~2 nA. In addition,

205 high-angle annular dark-field (HAADF) scanning transmission electron

206 microscopy images and energy-dispersive X-ray spectroscopy (EDS) maps

207 were recorded at an accelerating voltage of 300 kV and beam currents of ~50

208 pA and ~100 pA, respectively (Rice et al. 1990). EDS analyses were done in

209 scanning transmission electron microscopy (STEM) mode to avoid mass loss

210 during data acquisition. High-resolution lattice fringe images were used to

211 calculate fast Fourier-transformed (FFT) patterns (Chen et al. 2020). The

212 measurement of *d*-spacings was performed with the Digital Micrograph

213 software.

214

215 **Fluid inclusion analysis**

216   Raman microspectroscopy was used to determine the composition (both

217 fluid and gas phases) of individual fluid inclusions and to identify different

218 mineral phases at ambient conditions. For this purpose, we employed a

219 HORIBA Jobin Yvon LabRAM HR Evolution confocal micro-Raman system

220 equipped with an Olympus microscope and a frequency-doubled Nd:YAG

221 green laser (532 nm) at Peking University (Cui et al. 2020). The micro-Raman

222 system is equipped with a 20× long-working distance objective (NA = 0.25),

223 and a stigmatic 800 mm spectrometer with a 1800 groove/mm diffraction

224 grating. The spectrometer was calibrated using a mirror-polished synthetic Si

225 standard. The laser power at the source was 100 mW. The confocal hole was

226 set at 500 μm and the corresponding spectral resolution was ±0.7 cm^{-1}. The

227 laser beam was focused on fluid inclusions close to the upper surface of thin

228 sections and Raman spectra between 100 and 4000 cm^{-1} were recorded. Data

229 acquisition times for fluid inclusions varied between 30 s and 60 s depending

230 on the morphological and compositional characteristics of each inclusion and

231 its location. For mineral phases, Raman spectra between 100 and 1300 cm^{-1}

232 were recorded for 10 to 15 seconds and were checked against a common

233 standard database.

234   Microthermometric measurements were performed at Peking University

235 using a LINKAM THMS 600 heating-freezing stage operating in a temperature

236 range of -196 °C to +600 °C. Accuracy of the measurements was ensured by

237 calibration at −56.6 °C and 0 °C using synthetic fluid inclusion standards and

238 pure water. The measurement precision ranged from ±0.1 °C between -120

239 and -70 °C, to ±0.2 °C between -70 and 100 °C, and ±1 °C between 100 and

240 600 °C. During each round of measurements, the temperature was first

241 decreased to -120 °C, and then gradually ramped up. The heating rate was

242 reduced to 0.2-0.5 °C min^{-1} close to the phase transitions. Ice-melting

243 temperatures and total homogenization temperatures of fluid inclusions were

244 measured at a heating rate of 0.5 °C min^{-1}. Melting temperatures of solid CO_2

245 and clathrate, and homogenization temperatures of CO_2 phases were

246 observed at a heating rate of 0.2-0.5 °C min^{-1}. Salinities of the NaCl–H_2O

247 inclusions were calculated using the final ice-melting temperatures (Bodnar

248 1993). For tri-phase CO_2-rich inclusions (H_2O-NaCl-CO_2 system), salinities

249 were calculated using the clathrate melting temperatures in combination with

250 liquid-vapor equilibria (Bakker 1997). Program DENSITY and Chueh and

251 Prausnitz's (1967) equation of state were chosen for these calculations.

252

RESULTS

Mineral chemistry

Fresh granite samples comprise abundant K feldspar ($Ab_{2-6}Or_{94-98}$) and plagioclase ($An_{2-10}Ab_{88-97}Or_{\leq1}$) (where Ab, An and Or stand for the albite, anorthite and orthoclase end-members, respectively). Minor albite is also present as exsolution lamellae in K-feldspar. Biotite is a volumetrically significant (up to 10 vol.%) constituent of these rocks, occurring as clusters of platy crystals up to 4 mm across. It contains high FeO and TiO_2 contents (29.8-31.1 and 3.1-3.7 wt.%, respectively) at low MgO levels (3.1-4.0 wt.%, Online Material[1] Table S1). Some biotite crystals contain inclusions of "REE-1" and "REE-2", which correspond to REE-phosphates with high La_2O_3 and Y_2O_3 contents (4-12 and 10-51 wt.%, respectively; Xu et al. 2017). Both these minerals are characterized by low Ce abundances, at or below its detection limit by electron-microprobe analysis. Cerium-poor, Nd-Y-rich bastnäsite-(La) is a fluorocarbonate containing <0.2 wt.% Ce. Its total REE content is high and dominated by La, Nd and Y (up to 30.6, 20.7 and 12.9 wt.% respective oxides, Table 1). To our knowledge, this mineral has not previously been reported in the granites of South China, which generally contain normal bastnäsite-(Ce) and parisite-(Ce) with high Ce but low Y abundances (20-30 wt.% and <4 wt.% respective oxides: Wang et al. 2015; He et al. 2017; Martin et al. 2017). The composition of cerianite could not be determined with accuracy because of its

274   intimate association with hydrous silicates (Online Material[1] Table S1).

275

276   **Ce-poor, Nd-Y-rich bastnäsite-(La) structural analysis**

277   The SR-XRD analysis of representative grains of Ce-poor, Nd-Y-rich

278   bastnäsite-(La) demonstrates that it is composed of randomly oriented crystals

279   (Fig. 3). The collected SR-XRD pattern consists of sharp and narrow diffraction

280   peaks, whose full-width-at-half-maximum values indicate particle sizes of <1

281   μm (Monshi et al. 2012). The measured d-spacings (1.137-4.847 Å) are close

282   to, but slightly smaller than, those of Y-poor bastnäsite-(La) (1.149-4.859 Å,

283   Online Material[1] Table S2), probably due to the relatively large proportion in

284   the La site of such small cations as Y^{3+} and heavy lanthanides.

285   Examination of the Ce-poor, Nd-Y-rich bastnäsite-(La) with high-resolution

286   transmission electron microscopy (HRTEM) reveals that its aggregates contain

287   very small crystallites ranging from 5 to 10 nm across (Fig. 4a). The acquired

288   nanoscale compositional maps (including C, O, F, La, Nd and Y) are uniform

289   and show no compositional variation whatsoever (Fig. 4b-g). The boundaries

290   between nanoparticles and larger grains, imaged by HRTEM (Fig. 5 and

291   Online Material[1] Fig. S4), show gradual transition from crudely aligned

292   nanoparticles to submicrometer-sized grains. The degree of crystallinity within

293   a specific region of the HRTEM foil is directly related to variations between

294   random   and   aligned   aggregation   states   of   the   nanoparticles.   Four

295   representative states have been recognized on the basis of the HRTEM

296   images (Fig. 6), described in further detail below.

297   The first type, represented by randomly aggregated nanoparticles, is

298   characterized by randomly oriented lattice fringes and diffraction rings in fast

299   FFT patterns (Fig. 6a). The aggregation state of Ce-poor, Nd-Y-rich

300   bastnäsite-(La) nanoparticles in this case is similar to that of some synthetic

301   examples produced by rapid crystallization: for example, poorly ordered Cu

302   oxalate (Soare et al. 2006) and akaganeite (Nielsen et al. 2014). The second

303   type of aggregates represents a mixture of randomly oriented and crudely

304   aligned nanoparticles (Fig. 6b). They are characterized by FFT patterns

305   featuring both diffraction spots and rings, indicative of ordered and disordered

306   aggregation, respectively. The third type shows parallelism of most lattice

307   fringes and FFT patterns comprising mostly diffraction spots with some fuzzy

308   diffraction rings (Fig. 6c). These features demonstrate that most of the

309   nanoparticles are aligned, although some misoriented lattice fringes indicate

310   that the process of re-arrangement and recrystallization to eliminate the

311   imperfections of initial aggregation has not finished yet (De Yoreo et al. 2015).

312   In the fourth type of aggregates, nanoparticles are assembled into

313   submicrometer-sized crystallites showing well-defined diffraction patterns (Fig.

314   6d). Notably, adjacent crystals are separated from one another by areas

315   composed of disordered nanoparticles, indicating that oriented aggregation

316   initiated at multiple sites simultaneously (Banfield et al. 2000). The

317   polycrystalline nature of Ce-poor, Nd-Y-rich bastnäsite-(La) suggests that the

318   orientation adopted by one crystal is unrelated to those of adjacent crystals.

319   Atomic plane spacings of about 2.0, 2.9, 3.3, 3.6 and 4.8 Å were observed in

320   lattice fringe images (Fig. 6) and show reasonable agreement with the values

321   measured by SR-XRD (2.0, 2.8, 3.3, 3.5 and 4.8 Å; Online Material[1] Table S2).

322

323   **Fluid inclusions**

324   Two main types of fluid inclusions were recognized in quartz adjacent to

325   the Ce-poor, Nd-Y-rich bastnäsite-(La) (Fig. 7 and Online Material[1] Fig. S1)

326   using Raman microspectroscopy: CO_2-H_2O-dominated and pure H_2O. The

327   CO_2-H_2O inclusions are pervasive and occur both as primary and secondary

328   inclusions forming a compact three-dimensional network and confined to

329   healed fractures. The gas/liquid filling ratio of these inclusions varies widely

330   (Fig. 7a). Two subtypes were distinguished among them. Subtype IA includes

331   three-phase inclusions (Fig. 7b) with an aqueous fluid, liquid CO_2 (20-60 vol.%

332   of the inclusion), and CO_2 gas (10-25 vol.% of the inclusion). The melting

333   temperature of the CO_2 phase in these inclusions ranges from −57.2 to

334   −58.3 °C. Clathrate melting temperatures range from 3.5 to 8.2 °C,

335   corresponding to salinities of 3.2-11.6 wt.% NaCl equivalent (Bakker 1997).

336   These inclusions mostly homogenized to an aqueous phase between 307 and

372 °C, and to a gas phase between 349 and 386 °C (Table 2). Subtype IB is

represented by CO_2-rich two-phase inclusions composed of an aqueous fluid

and a gas bubble, whose volume accounts for 20-70 % of the inclusion. Small

daughter crystals of calcite were also observed in some cases (Fig. 7c). The

pure H_2O inclusions of Type II are interpreted as secondary in origin (Fig. 7d).

The melting temperatures of ice were measured to range between -4.8 and

-7.3 °C, indicating low salinity values from 7.6 to 10.9 wt.% NaCl equivalent

(Bodnar 1993). These inclusions homogenize to a liquid phase between 168

and 347 °C (Table 2).

DISCUSSION

Crystallization by particle attachment under REE supersaturation

The classical nucleation theory, including terrace-ledge-kink and

dislocation growth models, has served as the prevalent conceptual basis for

describing crystal nucleation and growth since the 1950s (Burton et al. 1951;

Kashchiev 2003). However, in the past 30 years, an increasing number of

studies have provided convincing evidence for crystallization by particle

attachment (CPA) (Penn and Banfield 1999; Zhang et al. 2010; Li et al. 2012;

Boneschanscher et al. 2014; De Yoreo et al. 2015). The classical theory works

well for the precipitation of low-solubility phases from dilute solutions, but it is

not applicable at high degrees of supersaturation (Ivanov et al. 2014).

358 Thermodynamically, the nucleation energy barrier and critical nucleus size

359 should decrease with progressive deviation of the system from equilibrium –

360 for example, due to supersaturation (Ivanov et al. 2014). At low degrees of

361 supersaturation, crystals are expected to grow in accord with the classical

362 nucleation theory because the free-energy barrier is still relatively large

363 (Kashchiev 2003; Wallace et al. 2013). At high levels of supersaturation, the

364 free energy barrier is comparable with thermal energy, and nuclei may be

365 generated in sufficiently large numbers at multiple sites so as to counteract

366 supersaturation (Bray 2002; Scheifele et al. 2013). The particle density will

367 reach a level where a high particle collision rate will facilitate crystal growth by

368 CPA (Cölfen and Antonietti 2008).

369   Multiple intermediate states of atom-to-crystal evolution have been

370 recognized, from simple ions to bulk crystals assembling together by CPA, and

371 involving multi-ionic complexes, oligomers and nanoparticles (De Yoreo et al.

372 2015). Recent experiments showed that atoms in nanoscale nuclei (clusters of

373 ordered atoms or ionic groups) may fluctuate reversibly between ordered and

374 disordered states (Jeon et al. 2021). Similarly, fast crystal growth by CPA does

375 not always lead to a well-formed single crystal, but to an aggregate of slightly

376 misaligned domains (Huang et al. 2004; Soare et al. 2006; Nielsen et al. 2014).

377 Such nanoscale misalignment can be eventually eliminated by reaction with a

378 solution to reduce surface energy (Huang et al. 2004; Nielsen et al. 2014).

379   We postulate that crystals of Ce-poor, Nd-Y-rich bastnäsite-(La) in the

380   Zhaibei granites developed from initially disordered nanocrystals that

381   assembled into submicrometer-sized particles through CPA (Fig. 6). The

382   examined grains formed aggregates and were not re-arranged to form discrete,

383   structurally uniform single crystals. This indicates that the Ce-poor, Nd-Y-rich

384   bastnäsite-(La) precipitated rapidly from a supersaturated solution, but did not

385   undergo subsequent recrystallization.

386

387   **REE mineralization under highly oxidized conditions**

388   Supersaturation reported for natural aqueous systems is usually related to

389   microbial activity (Banfield et al. 2000; Penn et al. 2001). However, the

390   temperature of fluids responsible for the REE enrichment in the Zhaibei

391   granites is too high (~170-390 °C) for any microorganism to survive (Brock

392   1985). Notably, CO_2-rich and aqueous fluid inclusions commonly coexist in

393   these rocks. The gas/liquid volume ratio in such inclusions is variable, but their

394   homogenization temperatures are similar, suggesting CO_2-H_2O immiscibility in

395   their parental fluid (Yardley and Bottrell 1988). The loss of a low-salinity,

396   CO_2-rich phase would increase the pH value of the residual fluid, reduce

397   carbonate activity and increase solute concentrations in the H_2O-dominant

398   fraction (Bowers and Helgeson 1983). Thus, CO_2-H_2O immiscibility should

399   lead to REE supersaturation in the aqueous phase, triggering precipitation of

400 such low-solubility phases as cerianite and REE fluorocarbonates (Xiong 2015;

401 Migdisov et al. 2016). The very different Nd isotopic signature of Ce-poor,

402 Nd-Y-rich bastnäsite-(La) [$\varepsilon Nd_{(t)}$ = 0.9 ± 0.8] in comparison with primary

403 monazite and apatite [$\varepsilon Nd_{(t)}$ = -11.5 ± 0.5] in the parental granite (Xu et al.

404 2017) indicates an external fluid contribution. Although its source has not been

405 ascertained yet owing to the lack of isotopic data for other rock types in the

406 study area, the addition of an externally derived fluid would have certainly

407 resulted in rapid cooling of the hydrothermal system (Carrigan 1986). Thus, we

408 hypothesize that a sudden drop in temperature promoted CO_2-H_2O

409 immiscibility and ultimately triggered the precipitation of Ce-poor, Nd-Y-rich

410 bastnäsite-(La) nanoparticles at multiple nucleation sites. The CPA

411 documented in the present work occurred under moderate-temperature

412 hydrothermal conditions, in contrast to the previously reported cases in

413 synthetic, biogenic and low-temperature geological environments (Banfield et

414 al. 2000; Penn et al. 2001; Hochella et al. 2005), or rapidly quenched melt

415 pockets in Martian meteorites (Zhang et al. 2019).

416   The studied Ce-poor, Nd-Y-rich bastnäsite-(La) is characterized by high

417 LREE and HREE levels, but extremely low Ce contents. The presence of

418 cerianite and hematitization of ilmenite (Fig. 2f) indicate a high-fO_2 regime. The

419 oxidation of Ce^{3+} to Ce^{4+} is clearly responsible for the observed fractionation

420 between Ce^{4+} and larger and more mobile REE^{3+} cations; e.g., [8]La^{3+} is 18%

421 larger than $^{[8]}Ce^{4+}$ (Shannon 1976). Owing to the low solubility of CeO_2 in fluids

422 (Xiong 2015), cerianite was precipitated as veinlets associated with the

423 hydrous Al-Fe-rich silicate mineral (Fig. 2e). The logfO_2 values of Jurassic to

424 Early Cretaceous granites in South China range from -0.83 to +4.22 relative to

425 the NNO buffer (Li et al. 2017), which is too low for Ce oxidation (Burnham and

426 Berry 2014). The possible sources of oxidizing components could be incursion

427 of external fluids into granites at the subsolidus stage, derived either from

428 dehydrated lithospheric material, which subducted beneath the amalgamated

429 China continent in the early Jurassic (Liu et al. 2017), or from meteoric sources.

430 The fO_2 levels in arc magmas are estimated to be insufficient for Ce oxidation

431 (Kelley and Cottrell 2012; Burnham and Berry 2014). Incursion of meteoric

432 water into the subsolidus granites could result in high $f(O_2)$ values and

433 oxidation of Ce^{3+} to Ce^{4+} while not affecting the rest of the REE budget. This

434 process could have triggered a rapid temperature drop and the precipitation of

435 nanocrystalline HREE-rich carbonates with strong Ce depletion.

436 The poly-crystalline Ce-poor, HREE-rich minerals with a poorly-ordered

437 structure and numerous defects and dislocations are readily decomposed

438 during weathering (Wilson 2004), resulting in REE removal from the precursor

439 granite. Aqueous complexes can readily fractionate HREE from LREE during

440 intense weathering. In particular, HREE form stronger complexes with

441 carbonate and fluoride ligands than LREE at ambient temperature (Wood

442   1990), thereby increasing the concentration of the former in the fluid and

443   promoting their transport and adsorption onto clay minerals. This mechanism

444   may explain the anomalous HREE enrichment of some South China IAD.

445

446   **IMPLICATIONS**

447   The detailed HRTEM study of Ce-poor, Nd-Y-rich bastnäsite-(La)

448   presented above documented several successive steps in the aggregation of

449   nanoparticles to form submicrometer-sized crystallites. The observed

450   morphological evolution is best explained by CPA under supersaturated

451   conditions, as there is no HRTEM evidence for crystal-growth by terrace or

452   dislocation-constrained mechanisms. Cerium oxidation and its decoupling from

453   trivalent REE, which produced Ce-poor, HREE-rich minerals, and

454   hematitization of ilmenite attest to the high fO_2 values in the fluid. We infer that

455   the interaction of the hydrothermal system with external meteoric fluids led to a

456   sudden drop in temperature and CO_2-H_2O immiscibility, which triggered REE

457   supersaturation and the deposition of nanocrystalline Ce-poor, Nd-Y-rich

458   bastnäsite-(La) and cerianite in the Zhaibei granites. This process has

459   far-reaching implications for the understanding of precursors and prerequisite

460   conditions to the development of HREE-rich IAD. Nanomineralization of the

461   type described in the present contribution could be a "missing link" between

462   magmatic REE hosts, which have low solubility in fluids, and ion-exchangeable

463 phases in the weathering profile. The polycrystalline nano-aggregates of REE

464 minerals are clearly more susceptible to weathering than primary monazite,

465 zircon or apatite (Fu et al. 2019). A detailed mineralogical study of precursor

466 igneous rocks is thus essential for constraining the HREE exploration potential

467 of IAD and for developing a comprehensive REE metallogenic model for these

468 deposits.

469

481

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Endnote:

[1]Deposit item ##, Online Materials. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/##).

FIGURE CAPTIONS

FIGURE 1. Distribution of granites in southeastern China and the location of the Zhaibei granite (modified after Wang et al. 2017).

FIGURE 2. Representative photomicrographs of minerals from the Zhaibei granites. (a) As-yet unidentified phases "REE-1" and "REE-2" formed by alteration of magmatic fluorapatite (Ap). (b) Ce-poor, Nd-Y-rich bastnäsite-(La) [Bast (La)] in fractures cross-cutting K-feldspar (Kfs) and plagioclase (Pl). (c) Encrustations of Ce-poor, Nd-Y-rich bastnäsite-(La) lining a cavity interstitial to quartz (Q). (d) Hydrous Al-Fe-rich silicate at the contact between Ce-poor and Nd-Y-rich bastnäsite-(La), biotite (Bt) and K-feldspar. (e) Veinlet of cerianite intergrown with an unidentified hydrous Al-Fe-rich silicate. (f) Ilmenite (Ilm) partially converted to hematite (Hem).

FIGURE 3. In-situ synchrotron radiation-induced X-ray diffraction analysis of Ce-poor, Nd-Y-rich bastnäsite-(La) [Bast (La)]. (a) Location of the analyzed

736   area within a 75-μm circle; (b) X-ray diffraction pattern and diffraction rings.

737

738   **FIGURE 4.** High-angle annular dark-field scanning transmission electron

739   microscopy (HAADF STEM) image showing nanoparticles of Ce-poor,

740   Nd-Y-rich bastnäsite-(La) (a) and nano-scale compositional maps (b-g)

741   showing a uniform distribution of C, O, F, La, Nd and Y within the

742   nanoparticles.

743

744   **FIGURE 5.** HRTEM image of an irregular boundary between

745   submicrometer-sized particles and nanoparticles of Ce-poor, Nd-Y-rich

746   bastnäsite-(La).

747

748   **FIGURE 6.** HRTEM images of Ce-poor, Nd-Y-rich bastnäsite-(La). (a)

749   Nanoparticles of randomly aggregated Ce-poor, Nd-Y-rich bastnäsite-(La);

750   their FFT pattern shows diffraction rings. (b) Nanoparticles partially aggregated

751   by oriented attachment, with FFT pattern exhibiting diffraction spots and rings.

752   (c) Advanced stage of nanoparticle assembly, with some local misalignment in

753   particle orientation (red circles); note regular diffraction spots in the FFT

754   pattern. (d) Aggregated nanoparticles showing a near-perfect alignment and a

755   well-defined diffraction pattern.

756

757 **FIGURE 7.** Representative photomicrographs of fluid inclusions in quartz. (a)

758 CO_2-H_2O inclusions (Type I) with various gas/liquid filling ratios. (b)

759 Three-phase CO_2-H_2O type inclusions. (c) Calcite daughter crystal (Cal) in a

760 fluid inclusion. (d) CO_2-rich inclusions coexisting with aqueous (Type II) fluid

761 inclusions.
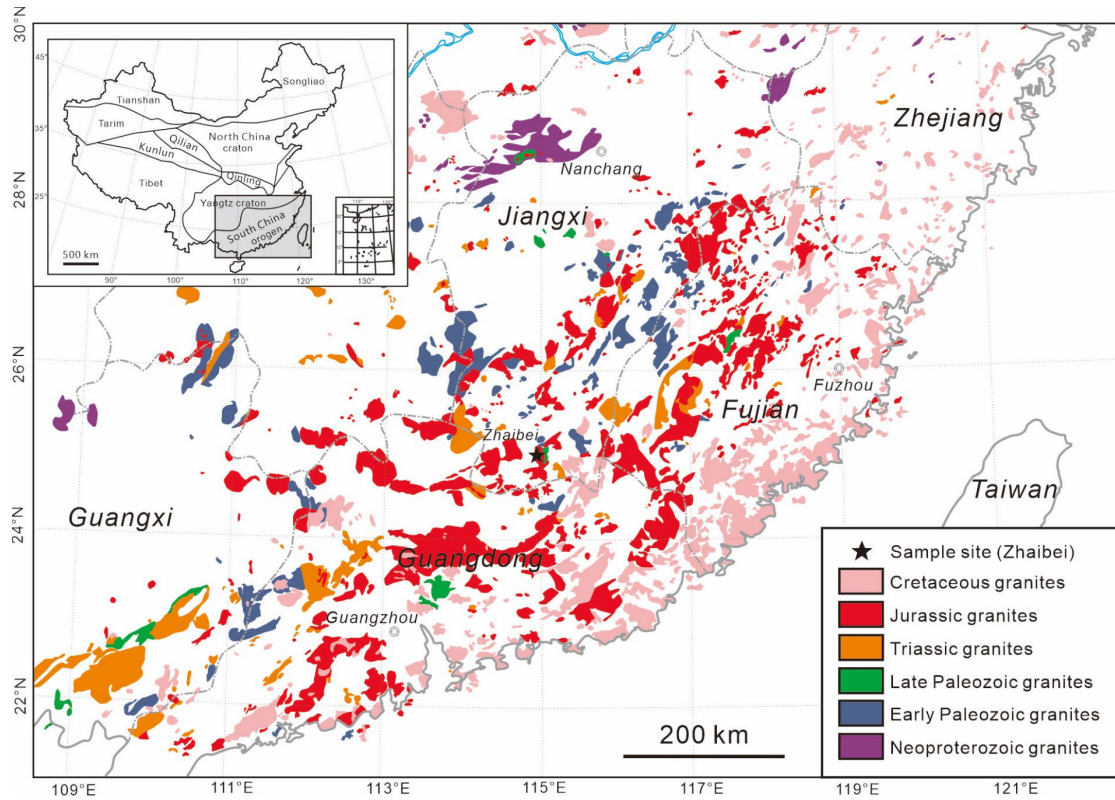
Figure 1. Distribution of granites in Southeast China and the location of Zhaibei granite (modified after Wang et al., 2017).

Figure 2. Representative photomicrographs of minerals from the Zhaibei granites. (**a**) As-yet unidentified phases "REE-1" and "REE-2" formed by alteration of magmatic fluorapatite (Ap). (**b**) Ce-poor, Nd-Y-rich bastnäsite-(La) [Bast (La)] in fractures cross-cutting K-feldspar (Kfs) and plagioclase (Pl). (**c**) Encrustations of Ce-poor, Nd-Y-rich bastnäsite-(La) lining a cavity interstitial to quartz (Q). (**d**) Hydrous Al-Fe-rich silicate at the contact between Ce-poor and Nd-Y-rich bastnäsite-(La), biotite (Bt), and K-feldspar. (**e**) Veinlet of cerianite intergrown with an unidentified hydrous Al-Fe-rich silicate. (**f**) Ilmenite (Ilm) partially converted to hematite (Hem).

Figure 3. In situ synchrotron radiation-induced X-ray diffraction analysis of Ce-poor, Nd-Y-rich bastnäsite-(La) [Bast (La)]. (**a**) Location of the analyzed area within a 75 μm circle. (**b**) X-ray diffraction pattern and diffraction rings.
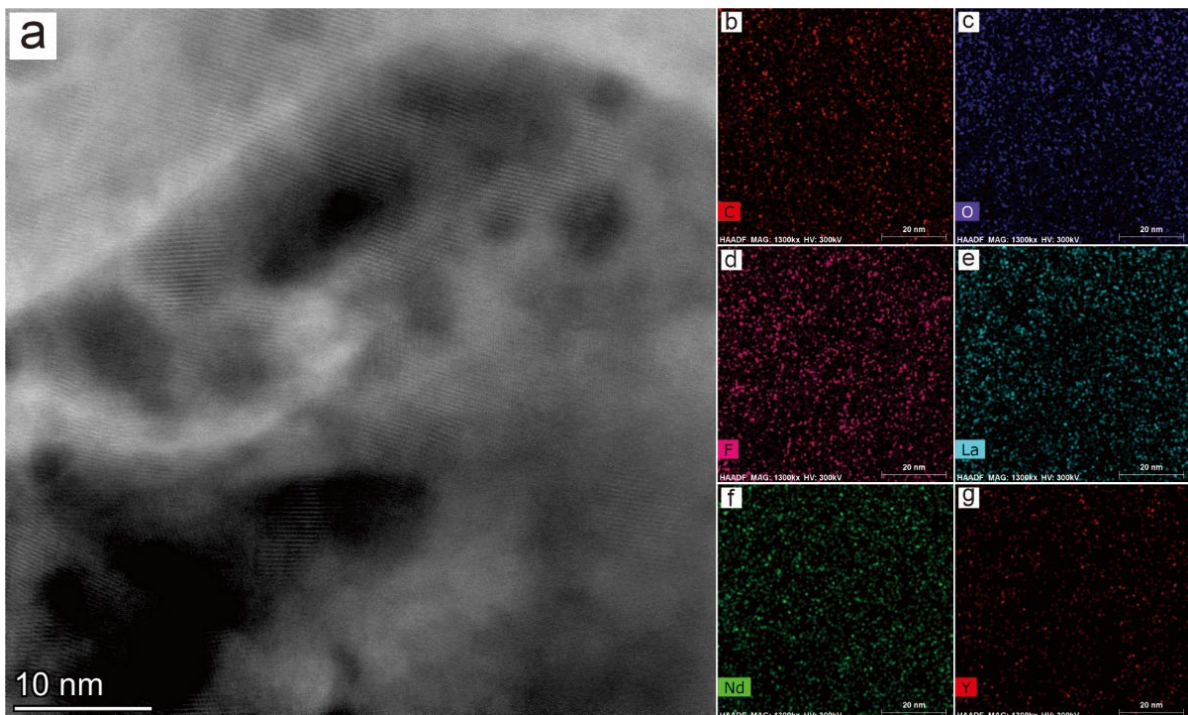
Figure 4. High-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) image showing nanoparticles of Ce-poor, Nd-Y-rich bastnäsite-(La) (**a**) and nanoscale compositional maps (**b-g**) showing a uniform distribution of C, O, F, La, Nd, and Y within the nanoparticles.
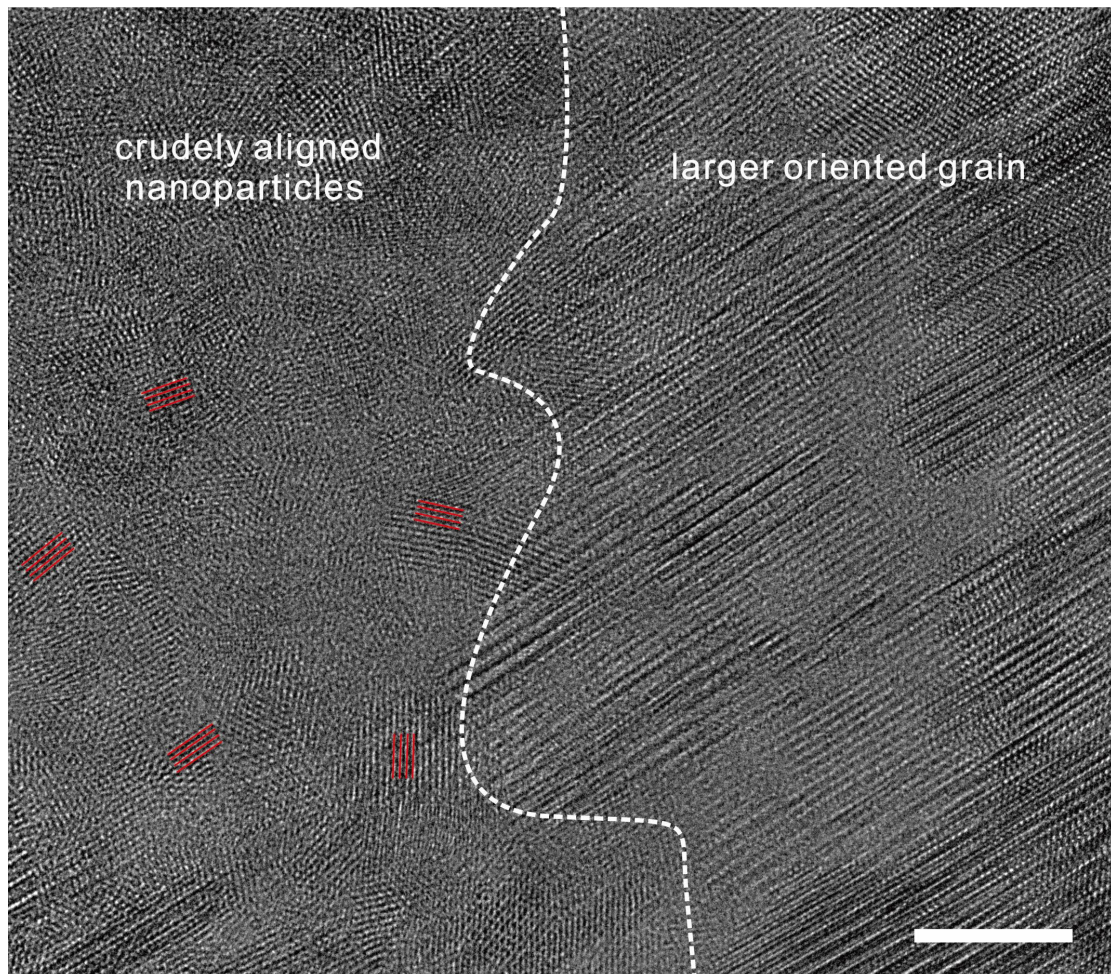
Figure 5. HRTEM image of an irregular boundary between submicrometer-sized particles and nanoparticles of Ce-poor, Nd-Y-rich bastnäsite-(La).
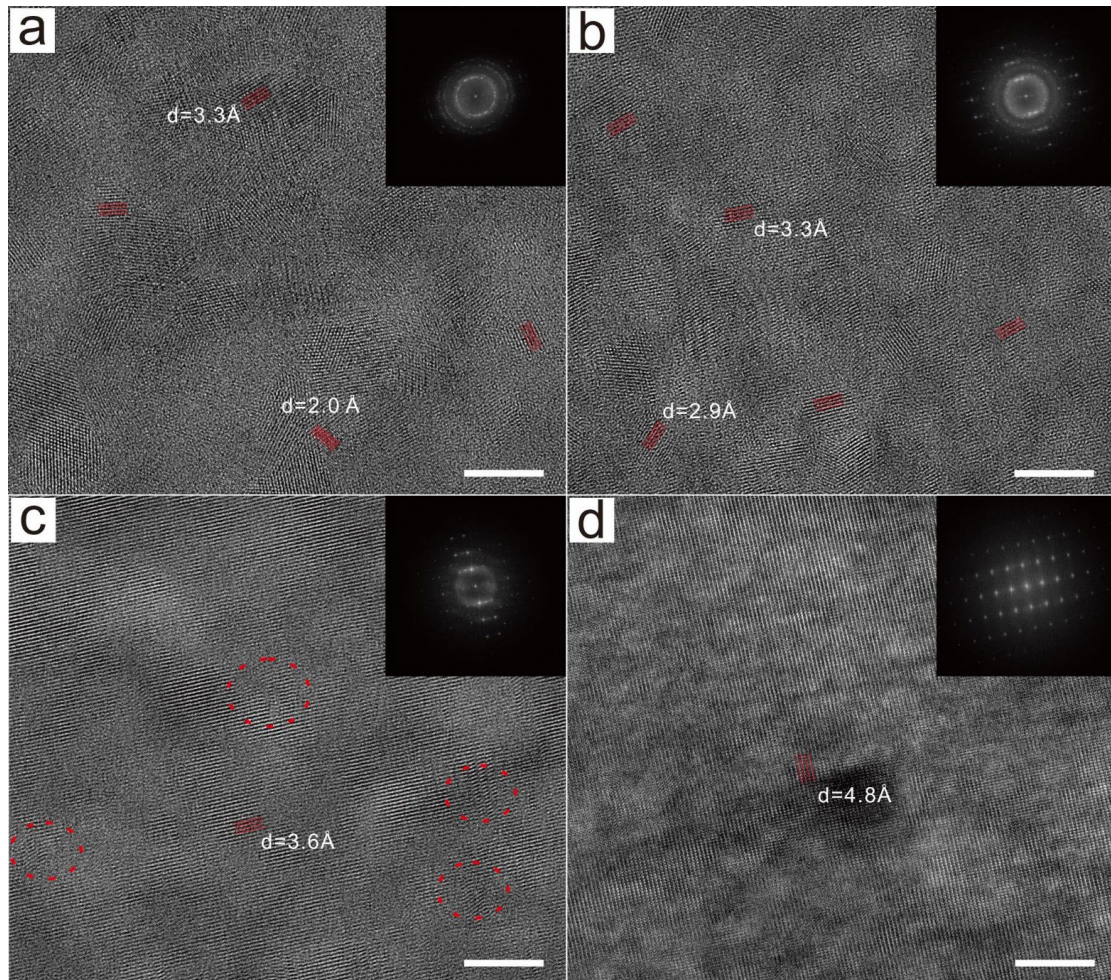
Figure 6. HRTEM images of Ce-poor, Nd-Y-rich bastnäsite-(La). (**a**) Nanoparticles of randomly aggregated Ce-poor, Nd-Y-rich bastnäsite-(La). Their FFT pattern shows diffraction rings. (**b**) Nanoparticles partially aggregated by oriented attachment with FFT pattern exhibiting diffraction spots and rings. (**c**) Advanced stage of nanoparticle assembly with some local misalignment in particle orientation (red circles). Note regular diffraction spots in the FFT pattern. (**d**) Aggregated nanoparticles showing a near-perfect alignment and a well-defined diffraction pattern.

Figure 7. Representative photo-micrographs of fluid inclusions in quartz. (**a**) CO2- H2O inclusions (Type I) with various gas/liquid filling ratios. (**b**) Three-phase CO2- H2O type inclusions. (**c**) Calcite daughter crystal (Cal) in a fluid inclusion. (**d**) CO2- rich inclusions coexisting with aqueous (Type II) fluid inclusions.

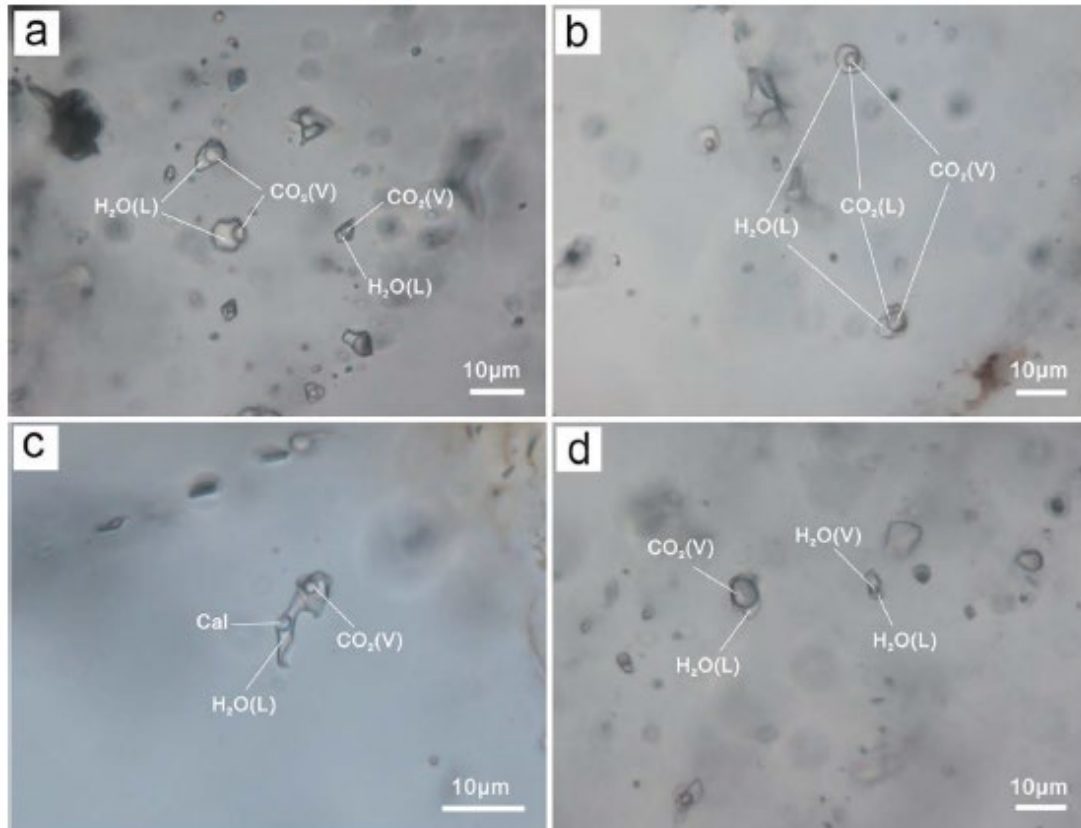| Sample	1	2	3	4	5	6	7	8	9	10
P2O5	0.28	0.37	0.25	0.28	0.23	0.17	0.41	0.12	0.46	0.11
SiO2	0.02	0.03	0.06	0.04	0.02	0.05	0.13	0.08	bdl	0.01
ThO2	bdl	0.01	bdl	bdl	bdl	bdl	0.07	0.03	bdl	bdl
Al2O3	bdl	0.06	bdl	bdl	bdl	0.01	0.09	bdl	0.02	0.03
Y2O3	9.98	6.03	9.36	9.75	11.36	9.88	7.58	10.72	9.36	9.61
La2O3	29.62	29.67	29.45	29.44	30.01	29.29	29.51	29.68	30.06	29.71
Ce2O3	0.11	bdl	0.15	0.01	0.24	bdl	bdl	0.24	0.15	0.05
Pr2O3	5.11	6.24	5.24	5.29	4.71	5.07	5.13	5.11	4.83	5.15
Nd2O3	17.74	20.68	17.97	18.15	17	18.27	19.14	17.35	18.08	18.04
Sm2O3	3.75	4.25	3.88	3.8	3.76	3.99	4.01	3.97	4.03	4.06
Eu2O3	0.36	0.56	0.52	bdl	0.4	0.63	0.51	0.25	0.11	0.23
Gd2O3	2.97	2.46	3.06	2.84	3.41	3.08	2.74	3.1	3.13	3.1
Dy2O3	2.05	1.81	1.84	1.96	2.24	1.97	1.88	2.25	2.01	2.06
Ho2O3	1.48	1.57	1.26	1.09	1.24	1.12	1.48	1.41	1.55	1.57
Er2O3	0.11	0.26	bdl	0.06	0.27	bdl	0.27	0.16	0.37	0.32
Tm2O3	bdl	bdl	0.07	0.18	0.05	bdl	bdl	0.02	bdl	bdl
Yb2O3	0.54	0.44	0.39	bdl	0.02	0.19	0.23	0.23	0.19	0.3
CaO	0.52	0.52	0.54	0.53	0.48	0.55	0.51	0.66	0.47	0.54
FeO	bdl	0.02	0.05	0.08	0.1	0.05	bdl	0.01	bdl	0.01
K2O	bdl	0.02	0.01	0.01	0.01	0.05	0.01	0.03	bdl	0.01
F	5.66	5.56	5.24	6.04	5.13	5.68	8.02	4.98	4.77	5.52
CO2	21.27	20.94	21.12	21.04	21.72	21.31	20.81	21.71	21.22	21.32
H2O	1.67	1.65	1.83	1.44	2.01	1.65	0.47	2.06	2.09	1.73
O=F	−2.38	−2.34	−2.21	−2.54	−2.16	−2.39	−3.38	−2.10	−2.01	−2.32
Total	100.86	100.81	100.08	99.49	102.25	100.62	99.62	102.07	100.89	101.16
Formulas based on 1 cation										
P	0.008	0.011	0.007	0.008	0.007	0.005	0.012	0.003	0.013	0.003
Si	0.001	0.001	0.002	0.001	0.001	0.002	0.005	0.003	0	0
Th	0	0	0	0	0	0	0.001	0	0	0
Al	0	0.002	0	0	0	0	0.004	0	0.001	0.001
Y	0.183	0.112	0.173	0.181	0.204	0.181	0.142	0.193	0.172	0.176
La	0.376	0.383	0.377	0.378	0.374	0.373	0.382	0.371	0.382	0.378
Ce	0.001	0	0.002	0	0.003	0	0	0.003	0.002	0.001
Pr	0.064	0.08	0.066	0.067	0.058	0.064	0.066	0.063	0.061	0.065
Nd	0.218	0.258	0.223	0.226	0.205	0.225	0.24	0.21	0.222	0.222
Sm	0.045	0.051	0.046	0.046	0.044	0.047	0.049	0.046	0.048	0.048
Eu	0.004	0.007	0.006	0	0.005	0.007	0.006	0.003	0.001	0.003
Gd	0.034	0.029	0.035	0.033	0.038	0.035	0.032	0.035	0.036	0.035
Dy	0.023	0.02	0.021	0.022	0.024	0.022	0.021	0.025	0.022	0.023
Ho	0.016	0.017	0.014	0.012	0.013	0.012	0.017	0.015	0.017	0.017
Er	0.001	0.003	0	0.001	0.003	0	0.003	0.002	0.004	0.003
Tm	0	0	0.001	0.002	0.001	0	0	0	0	0
Yb	0.006	0.005	0.004	0	0	0.002	0.002	0.002	0.002	0.003
Ca	0.019	0.019	0.02	0.02	0.017	0.02	0.019	0.024	0.017	0.02
Fe	0	0.001	0.001	0.002	0.003	0.001	0	0	0	0
K	0	0.001	0	0	0	0.002	0	0.001	0	0
F	0.617	0.615	0.576	0.666	0.548	0.62	0.891	0.534	0.52	0.602
C	1.001	1	1.001	1.001	1.002	1.004	0.998	1.004	0.998	1.004
H	0.383	0.385	0.424	0.334	0.452	0.38	0.109	0.466	0.48	0.398

Table 1. Compositions (wt%) of Ce-poor, Nd-Y-rich bastnäsite-(La) in the Zhaibei granites. Bdl-below detection limit. CO_2 in the mineral is calculated using charge balance method. H_2O is calculated assuming a full (F,OH) site. bdl = below determination limits.

Sample	11	12	13	14	15	16	17	18	19	20
P2O5	0.06	0.15	1.38	0.45	0.12	bdl	0.03	0.04	0.06	0.35
SiO2	0.04	0.07	0.08	0.03	0.51	bdl	0.04	0.05	0.03	0.07
ThO2	bdl	0.05	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Al2O3	bdl	0.04	bdl	0.01	0.06	bdl	0.01	bdl	bdl	0.02
Y2O3	10.21	7.45	12.92	9.85	10.73	8.1	8.07	8.55	8.6	8.49
La2O3	29.14	29.16	27.82	30.62	29.5	29.06	29.88	29.2	29.34	30.39
Ce2O3	0.07	0.04	bdl	bdl	bdl	0.01	bdl	bdl	bdl	bdl
Pr2O3	5.06	5.6	4.69	5.05	5.05	5.61	5.51	5.33	5.4	5.65
Nd2O3	17.82	20.02	16.1	18.31	17.48	19.68	20.05	20.25	19.46	19.13
Sm2O3	3.81	4.5	3.19	3.96	3.8	4.23	4.37	4.36	4.27	4.16
Eu2O3	0.25	0.24	0.02	0.56	0.28	0.68	0.52	0.73	0.71	0.49
Gd2O3	3.26	2.92	3.01	3.14	2.76	2.93	2.77	2.65	3.03	2.59
Dy2O3	2.1	1.73	2.36	2.05	2.43	1.89	1.87	1.81	1.95	1.84
Ho2O3	1.59	1.14	1.85	1.07	1.38	1.17	1.48	1.48	1.35	1.07
Er2O3	0.14	0.26	0.37	0.14	0.31	0.25	0.23	0.07	0.14	0.17
Tm2O3	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Yb2O3	0.36	0.19	0.62	0.22	0.14	0.39	0.39	0.02	0.41	0.3
CaO	0.54	0.51	0.49	0.55	0.65	0.57	0.63	0.54	0.6	0.59
FeO	bdl	bdl	0.01	0.03	0.06	0.04	0.01	0.06	bdl	bdl
K2O	0.01	0.03	0.01	0.02	0.17	0.01	0.01	0.01	bdl	0.01
F	5.71	5.87	5.51	5.09	5.32	5.19	5.51	5.85	5.54	6.13
CO2	21.26	20.87	21.74	21.72	22.06	21.07	21.44	21.29	21.32	21.38
H2O	1.63	1.48	1.91	2.04	1.98	1.83	1.75	1.56	1.72	1.47
O=F	−2.41	−2.47	−2.32	−2.14	−2.24	−2.18	−2.32	−2.46	−2.33	−2.58
Total	100.65	99.85	101.76	102.77	102.55	100.53	102.25	101.39	101.6	101.72
Formulas based on 1 cation										
P	0.002	0.004	0.039	0.013	0.003	0	0.001	0.001	0.002	0.01
Si	0.001	0.002	0.003	0.001	0.017	0	0.001	0.002	0.001	0.002
Th	0	0	0	0	0	0	0	0	0	0
Al	0	0.002	0	0	0.002	0	0	0	0	0.001
Y	0.188	0.139	0.228	0.177	0.19	0.151	0.147	0.157	0.158	0.155
La	0.372	0.378	0.34	0.38	0.363	0.375	0.378	0.372	0.373	0.384
Ce	0.001	0.001	0	0	0	0	0	0	0	0
Pr	0.064	0.072	0.057	0.062	0.061	0.071	0.069	0.067	0.068	0.071
Nd	0.22	0.252	0.191	0.22	0.208	0.246	0.246	0.25	0.24	0.234
Sm	0.045	0.055	0.036	0.046	0.044	0.051	0.052	0.052	0.051	0.049
Eu	0.003	0.003	0	0.006	0.003	0.008	0.006	0.009	0.008	0.006
Gd	0.037	0.034	0.033	0.035	0.03	0.034	0.032	0.03	0.035	0.029
Dy	0.023	0.02	0.025	0.022	0.026	0.021	0.021	0.02	0.022	0.02
Ho	0.017	0.013	0.02	0.011	0.015	0.013	0.016	0.016	0.015	0.012
Er	0.002	0.003	0.004	0.001	0.003	0.003	0.002	0.001	0.002	0.002
Tm	0	0	0	0	0	0	0	0	0	0
Yb	0.004	0.002	0.006	0.002	0.001	0.004	0.004	0	0.004	0.003
Ca	0.02	0.019	0.017	0.02	0.023	0.021	0.023	0.02	0.022	0.022
Fe	0	0	0	0.001	0.002	0.001	0	0.002	0	0
K	0	0.001	0	0.001	0.007	0	0	0	0	0
F	0.625	0.653	0.578	0.542	0.561	0.574	0.598	0.639	0.605	0.664
C	1.004	1.003	0.985	0.999	1.004	1.006	1.005	1.005	1.004	1
H	0.375	0.347	0.422	0.458	0.439	0.426	0.402	0.361	0.395	0.336

Table 1. Continued

Table 2. Summary of fluid inclusion data from the Zhaibei granites

inclusion type	size(µm)	Tm CO_2	Tm C	Th CO_2	Tm	salinity (wt.%)	Th
L_1+L_2+V	8	-58.1℃	4.2℃	31.1℃		10.3	307℃-L
L_1+L_2+V	5	-57.6℃	4.1℃	30.89℃		10.4	313℃-L
L_1+L_2+V	7	-57.6℃	5.7℃	30.2℃		8.0	327℃-L
L_1+L_2+V	7	-57.6℃	5.1℃	31.1℃		8.9	339℃-L
L_1+L_2+V	9	-57.7℃	5.8℃	29.8℃		7.8	343℃-L
L_1+L_2+V	8	-58.3℃	8.2℃	28.1℃		3.5	349℃-G
L_1+L_2+V	9	-57.2℃	5.2℃	29.7℃		8.8	356℃-L
L_1+L_{3+V}	8	-57.8℃	4.9℃	30.5℃		9.2	356℃-L
L_1+L_2+V	7	-57.5℃	5.4℃	28.9℃		8.5	361℃-L
L_1+L_2+V	8	-57.4℃	3.5℃	30.67℃		11.3	362℃-G
L_1+L_{4+V}	6	-58.2℃	6.3℃	30.2℃		6.9	362℃-L
L_1+L_2+V	8	-58.2℃	4.9℃	31.1℃		9.2	372℃-L
L_1+L_2+V	9	-58.2℃	7.9℃	28.5℃		4.1	386℃-G
L+V	7				-7.3℃	10.9	168℃
L+V	9				-5.6℃	8.7	174℃
L+V	11				-6.3℃	9.6	182℃
L+V	9				-4.9℃	7.7	210℃
L+V	8				-4.8℃	7.6	211℃
L+V	14				-6.4℃	9.7	218℃
L+V	5				-5.9℃	9.1	220℃
L+V	6				-6.4℃	9.7	253℃
L+V	5				-6.1℃	9.3	276℃
L+V	10				-5.4℃	8.4	313℃
L+V	7				-5.3℃	8.3	326℃
L+V	6				-4.8℃	7.6	345℃
L+V	9				-5.8℃	8.9	347℃

CO_2 melting temperatures (Tm CO_2)
Clathrate melting temperatures (Tm C)
Partial homogenization temperatures (Th CO_2)
Ice-melting temperatures (Tm)
Homogenization temperatures (Th)
The letter behind homogenization temperatures represents the form of homogenization