1   **Hydrothermal upgrading as an important tool for the REE mineralization in the**

2   **Miaoya carbonatite-syenite complex, Central China**

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6   **RONG-LIN MA[1,2], WEI TERRY CHEN[1,2,*], WEI ZHANG[1], AND YOU-WEI**

7   **CHEN[1]**

8

9   1 State key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese

10   Academy of Sciences, Guiyang 550081, China

11   2 University of Chinese Academy of Sciences, Beijing 100049, China

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21   Corresponding author: Wei Terry Chen (chenwei@mail.gyig.ac.cn)

22   **ABSTRACT**

23

24   Secondary hydrothermal reworking of REEs has been widely documented in

25   carbonatites/alkaline rocks, but its potential role in the REE mineralization associated

26   with these rocks is currently poorly understood. This study conducted a combined

27   textural and in-situ chemical investigation on the REE mineralization in the ~430 Ma

28   Miaoya carbonatite-syenite complex, central China. Our study shows that the REE

29   mineralization, dated at ~220 Ma, is characterized by a close association of REE minerals

30   (monazite and/or bastnäsite) with pervasive carbonatization overprinting the carbonatites

31   and syenites. In these carbonatites and syenites, both the apatite and calcite, which are the

32   dominant magmatic REE-bearing minerals, exhibit complicated internal textures that are

33   generally composed of BSE-bright and BSE-dark domains. Under BSE imaging, the

34   former domains are homogeneous and free of pores or mineral inclusions, whereas the

35   latter have a high porosity and inclusions of monazite and/or bastnäsite. In-situ chemical

36   analyses show that the BSE-dark domains of the apatite and calcite have light REE

37   concentrations and $(La/Yb)_N$ values much lower than the BSE-bright areas. These

38   features are similar to those observed in metasomatized apatite from mineral-fluid

39   reaction experiments, thus indicating that the BSE-dark domains formed from primary

40   precursors (i.e. represented by the BSE-bright domains) through a fluid-aid,

41   dissolution-reprecipitation process during which the primary light REEs are

42   hydrothermally remobilized. New, *in-situ* Sr-Nd isotopic results of apatite and various

43   REE minerals, in combination with mass balance calculations, strongly suggest that the

44   remobilized REEs are responsible for the subsequent hydrothermal REE mineralization in

45   the Miaoya complex. Investigations of fluid inclusions show that the fluids responsible

46   for the REE mobilization and mineralization are CO_2-rich, with medium temperatures

47   (227-340 °C) and low salinities (1.42-8.82 wt‰). Such a feature, in combination with

48   C-O isotopic data, indicates that the causative fluids are likely co-genetic with fluids from

49   coeval orogenic Au-Ag deposits (220-200 Ma) in the same tectonic unit. Our new

50   findings provide a strong evidence that the late hydrothermal upgrading of early

51   cumulated REEs under certain conditions could also be an important tool for REE

52   mineralization in carbonatites, particularly for those present in convergent belts where

53   faults (facilitating fluid migration) and hydrothermal fluids are extensively developed.

54

55   **Keywords:** Apatite, Calcite, REE mobilization and mineralization, hydrothermal

56   upgrading, Miaoya carbonatite-syenite complex

57

58   **INTRODUCTION**

59

60   Carbonatites and/or associated alkaline rocks have been important providers of REEs,

61   particular the light REEs (Mariano, 1989; Sheard et al., 2012), thus are important

62   exploration targets. Although there are more than 500 occurrences of carbonatites in the

63   world and most of them contain elevated concentrations of REEs, only a few display

64   economic potential to warrant exploitation (Woolley and Kjarsgaard, 2008; Verplanck et

65   al., 2016). Hence, unveiling key factors or processes leading to economic concentrations

66   of REEs in these rocks have long been an attractive topic for ore genesis studies over the

67   past decades (Xie et al., 2009; Pandur et al., 2014; Hou et al., 2015; Smith et al., 2016;

68   Song et al., 2018). It was commonly accepted that processes responsible for REE

69   enrichment in these rocks include primary magmatic concentration (e.g. the Mountain

70   Pass deposit, California, USA) (Castor, 2008), enrichment in lately exsolved fluids

71   through extreme fractionation of the carbonatitic or alkaline magmas, e.g. the

72   Maoniuping deposit, SW China (Xie et al., 2009; Hou et al., 2015; Liu and Hou, 2017),

73   or a combination of the processes mentioned above (Pandur et al., 2014; Broom-Fendley

74   et al., 2016). There is also increasing evidence showing that hydrothermal redistribution

75   of REEs cumulated in early carbonatites or alkaline rocks, triggered by late autogenetic

76   or external fluids, is also responsible for local REE enrichments, e.g. the Thor Lake and

77   Strange Lake deposits, Canada (Salvi and Wiliams-Jones, 1996; Sheard et al., 2012; Gysi

78   and Williams-Jones, 2013; Cheng et al., 2018; Cangelosi et al., 2020). However, the

79   potential contributions of the hydrothermal reworking to REE mineralization in such

80   kinds of deposits are still far from being clearly understood. Particularly, this unresolved

81   issue likely gives rise to the controversies regarding ore genesis of some

82   carbonatite-related REE deposits that show clear evidence of late hydrothermal overprints.

83   A notable example could be the world largest Bayan Obo REE-Nb-Fe deposit where

84   primary mineralogy and textures were overprinted by multiple hydrothermal events

85   (Smith et al., 2015; and reference therein). In this deposit, late hydrothermal fluids

86   (millions of years younger than the carbonatites) were suggested to be the key for major

87   REE mineralization (Ling et al., 2013; Yang et al., 2017), whereas others proposed that

88   the early carbonatitic magmatism played a key role (Yang et al., 2019).

89   The REE mineralization in the ~430 Ma Miaoya carbonatite-syenite complex, central

90   China is an ideal research target for evaluating the role of late hydrothermal

91   metasomatism on REE mineralization in carbonatites and/or alkaline rocks. Although not

92   mined currently, the potential REE reserve in the Miaoya complex was estimated to be

93   1.21 Mt. REE_2O_3 @ 1.5 wt% (Qian and Li, 1996). The REE mineralization was

94   confirmed to be hydrothermal origin and is spatially restricted to the complex, but direct

95   U-Pb dating of REE minerals obtained much younger ages of 230-210 Ma (Xu et al.,

96   2014; Ying et al., 2017; Zhang et al., 2019a). As such, few studies have suggested that the

97   younger REE minerals could have formed from secondary remobilization of early REE

98   mineralization (Ying et al., 2017, 2020; Zhang et al., 2019a, 2019b) or precipitated from

99   external REE-rich fluids that overprinted the complex (Cimen et al., 2018). However, the

100   reliability of these interpretations cannot be evaluated, as most of the data were obtained

101   by analyses of bulk ore/rocks or minerals separates containing multiple generations of

102   components (Ying et al., 2017, 2020; Cimen et al., 2018; Zhang et al., 2019a, 2019b).

103   Moreover the nature and sources of the causative fluids has not comprehensively been

104   discussed.

105   In this study, we described the styles of the REE mineralization in the Miaoya complex

106   in detail with emphases on the textural relationships of REE minerals with other

107   hydrothermal minerals and the internal features of various rock/ore-forming minerals, in

108   order to re-establish the paragenetic sequence of the complex and associated

109   mineralization/alteration. Moreover, utilizing electron microprobe (EMP) analysis, laser

110   ablation inductively coupled plasma mass spectrometry (LA-ICPMS), and laser ablation

111   multi-collector inductively coupled mass spectrometer (LA-MC-ICP-MS) techniques, we

112   have obtained *in-situ* major-trace elemental and Sr-Nd isotopic compositions of various

113   minerals forming during magmatic (e.g. apatite and calcite) and hydrothermal (e.g.

114   monazite and bastnäsite) stages. The new dataset, together with mass balance calculations

115   based on compositions of altered apatite/calcite and unaltered counterparts, allows us to

116   explore mobilization and mass transfer of REEs during fluids metasomatism, and thus in

117   turn convincingly constrain the sources of REEs and the relative roles of early magmatic

118   and late hydrothermal processes on the REE mineralization. In addition, Raman

119   spectroscopic and microthermometric analyses were conducted to constrain the nature

120   and potential sources of the fluids responsible for the REE mobilization and

121   mineralization.

122

123   **GEOLOGICAL BACKGROUND**

124

125   The Qinling Orogenic Belt, extending east-west nearly 2500 km across Central China,

126   is bounded by the North China Block to the north and the Yangtze Block to the south

127   along the Sanbao and Longmenshan-Dabashan faults, respectively (Meng and Zhang,

128   2000; Ratschbacher, 2003; Dong et al., 2011; Fig. 1a). The belt comprises four units

129   separated by the Luanchuan, Shangdan and Mianlue faults from north southward,

130   including the Southern North China Block, North Qinling unit, South Qinling unit, and

131   Northern South China Block (Fig. 1b). Formation of the orogenic belt involved the

132   collision of North Qinling and South Qinling units during the Carboniferous and the final

133   collision of the North China Craton and South China Craton during the Triassic (230-220

134   Ma) (Meng and Zhang, 2000; Wu and Zheng, 2013; Dong and Santosh, 2016).

135   The South Qinling unit, where the Miaoya carbonatite-syenite complex is located, is

136   comprised of a Precambrian basement covered by a 12 km-thick sedimentary sequence

137   Neoproterozoic to Triassic in age (Dong et al., 2011). The basement rocks are dominated

138   by the Douling and Xiaomoling complexes in the north and the Wudang and Yaolinghe

139   Groups in the south. The Neoproterozoic to Triassic cover sequences include the strongly

140   folded Sinian platform-type carbonate and clastic rocks, Cambrian-Ordovician limestones,

141   Silurian shales, Devonian to Carboniferous clastic rocks with interlayered limestone, and

142   Permian-Triassic sandstones (Mattauer et al., 1985; Ratschbacher et al., 2003; Dong et al.,

143   2011; Wu and Zheng, 2013; Liu et al., 2016). Silurian magmatism is widespread in this

144   region, including ca. 430 Ma mafic-ultramafic dykes, volcanic rocks, and

145   carbonatite-syenite complexes (e.g., Shaxiongdong and Miaoya) (Zhang et al. 2007; Xu

146   et al. 2008). There are also few early Mesozoic granitoids (250 to 190 Ma) randomly

147   distributed in this belt (Xiao et al., 2017; Fig. 1b).

148

REE MINERALIZATION IN THE MIAOYA COMPLEX

150

151   The Miaoya complex is located in the southwestern margin of the Wudang Terrane in

152 the South Qinling unit (Fig. 1b), covering an area of 6.5 km^2. It intruded the meta-quartz

153 keratophyre of the Neoproterozoic Yaolinghe Group and the schist of the Late Silurian

154 Meiziya Group along the Ankang-Desheng-Fangxian fault (Fig. 1c). The complex is

155 composed mainly of syenites (90 %) and carbonatites (7.5 %), with xenoliths of country

156 rocks (2.5 %) mostly present in the margins (Figs. 1c and 2a-2c). The syenites are

157 composed dominantly of K-feldspar (70 vol%) with subordinate but variable amounts of

158 calcite (12 vol%), albite (10 vol%), apatite (1 vol%), zircon, Nb-bearing minerals (e.g.

159 pyrochlore and columbite), and Fe-Ti oxides (e.g. ilmentite, magnetite and rutile) (Fig.

160 2f). The carbonatites are generally present as stocks and/or dykes intruding the syenites

161 (Figs. 1c and 2a), and can be classified as calciocarbonatites (>95%) and

162 ferrocarbonatites (<5%) in terms of different mineral assemblages (Su et al., 2019). The

163 calciocarbonatites are composed mainly of fine- to medium-grained calcite (0.1 to 2 mm)

164 (85 vol%) and subordinate apatite (~9.5 vol%) with trace amounts of monazite, bastnäsite,

165 parasite, allanite, K-feldspar, albite, quartz, biotite, zircon, Nb-bearing minerals (e.g.

166 pyrochlore and columbite), and Fe-Ti oxides (e.g. ilmentite, magnetite and rutile) (Fig.

167 2g). In contrast, the ferrocarbonatites are dominated by fine-grained ankerite (5-20 μm)

168 (>70 vol%) with subordinate calcite (~10 vol%), bastnäsite (~5 vol%), and monazite (~2

169   vol%) and trace amounts of parisite, fluorite, and sulfides (Fig. 3f). Xu et al. (2014) has

170   obtained zircon ages of 766 Ma for the syenites, but such ages were suggested to be

171   unreliable by Zhu et al. (2016) and Ying et al. (2017) who both obtained a similar zircon

172   age of 440 Ma for the syenites. Considering that an age of 766 Ma is comparable to those

173   of the country rocks (i.e. volcanic rocks of the Yaolinghe Group), we speculated that the

174   so-called "syenites" samples in Xu et al. (2014) could be xenoliths of the country rocks

175   (particularly that the Miaoya complex contains 2.5 vol% xenoliths). For the carbonatites,

176   Zhu et al. (2016) and Ying et al. (2017) obtained similar zircon ages of ~430 Ma. This

177   age should be reliable as these zircon grains are characterized by low U and high Th/U

178   ratios, similar to zircons crystallized from carbonatitic magmas (Yuan et al., 2008). These

179   results indicate that both the carbonatite and syenites are broadly coeval and formed at

180   around 440 to 430 Ma.

181   Both the carbonatites and syenites have undergone extensive carbonatization that is

182   characterized by the presence of secondary, fine-grained calcite, ankerite, dolomite,

183   quartz and minor chlorite and Fe-oxides, which replace early carbonatite and syenite

184   assemblages (e.g. calcite, K-feldspar or apatite) (Figs. 2f, 2g, 3a, and 3b). The

185   carbonatization is also associated with the formation of abundant carbonate-rich veinlets

186   composed dominantly of calcite, dolomite, and/or quartz (Figs. 2d, 2e, 2h, and 2i).

187   The REE mineralization in the complex, dated at 230 to 210 Ma, is closely associated

188   with the carbonatization, pervasively overprinting both the carbonatites and syenites as

189   disseminated REE minerals or as REE mineral-rich veinlets or stockworks (Fig. 2e). As

190   such, the REE ores are essentially REE-mineralized syenites and carbonatites (Liu et al.,

191   1984), such that there are no clear boundaries between the REE ores and hosting syenites

192   or carbonatites (Figs. 2a and 2b). REE ore bodies were previously defined by these REE

193   concentrations, and most of the defined ore bodies are lentoid and located mostly in the

194   upper parts of the complex (Fig. 1d).

195   The REE minerals in the ores are dominated by monazite (20-300 μm), bastnäsite

196   (1-35 μm), and/or allanite (1-60 μm) (Fig. 3). Parisite is also locally present, commonly

197   replacing bastnäsite (Fig. 3h). The REE minerals are generally anhedral to subhedral, and

198   are closely intergrown with hydrothermal minerals typically including fine- to

199   medium-grained ankerite, calcite, sulfide, quartz, biotite, and phengite (Fig. 3). It is also

200   noteworthy that some of the monazite grains commonly show an intimate association

201   with relatively large apatite grains in both the syenites and carbonatites (Figs. 3a-3e). For

202   example, they are mostly present as fine inclusions (1-20 μm) enclosed in or as irregular

203   streaks distributed along fissures and margins of the apatite grains. These apatite grains,

204   as will be illustrated below, exhibit complicated internal textures under back scattered

205   electron (BSE) imagings.

206   On the basis of the macro- and micro- textural relationships of the mineral assemblages

207   described above, we establish a paragenetic sequence for the formation of the Miaoya

208   complex and subsequent REE mineralization, consisting of magmatic and hydrothermal

209   stages (Supplemental[1] Fig. 1). The early magmatic stage is characterized by the formation

210   of magmatic minerals in early syenites and slightly later carbonatites. This includes

- 10 -

211   dominantly K-feldspar and calcite, and subordinate apatite, albite, quartz, and biotite with

212   trace amounts of REE minerals such as monazite and allanite (Figs. 2f and 2g) (Zhang et

213   al., 2019a). The late hydrothermal stage is characterized by the formation of abundant

214   REE minerals (monazite, bastnäsite, allanite and parisite) associated with pervasive

215   carbonatization and variable mounts of calcite, K-feldspar, quartz, fluorite, dolomite,

216   chlorite, and phengite (Fig. 3).

217

218   **INTERNAL TEXTURES OF APATITE AND CALCITE**

219

220   Detailed textural relationships between apatite and calcite were further investigated by

221   scanning electron microscopy – cathode luminescence (SEM-CL). Detailed analytical

222   methods are provided in Supplemental[1] Method.

223

224   **Texture of apatite**

225   Apatite grains in the carbonatites and syenites are broadly similar in terms of internal

226   textures (Figs. 3a-3e). Under BSE imaging, these grains are generally composed of

227   several domains with variable BSE intensities (Figs. 3b-3e). In most cases, these textures

228   consist of only two parts consisting of BSE-bright and BSE-dark domains (Figs. 3d and

229   3e), but in rare cases they may consist of three parts named as BSE-bright, BSE-dark-I,

230   and BSE-dark-II domains of which this last domain is darkest under BSE imaging (Fig.

231   3c). The contacts among different domains in each apatite grain are generally irregular

232   and sharp (Figs. 3c-3e). The BSE-bright domains are commonly homogeneous without

233   any cracks, and are present mostly in the centers of the apatite grains (Fig. 3c). In contrast,

234   the BSE-dark domains, including I and II, are mostly present along the margins of the

235   apatite grains, and are irregular, cracks-developed and rich in pores, cracks, and mineral

236   inclusions. Notably, the BSE-dark-II domains, if present, occur as irregular strips and

237   patches embaying both the BSE-bright and BSE-dark-I domains (Fig. 3c).

238   The apatite grains are closely associated with fine-grained REE minerals dominated by

239   monazite with minor bastnäsite (Fig. 3). These REE minerals are either present as fine

240   inclusions enclosed in the BSE-dark domains or as anhedral grains distributed along the

241   apatite grain rim (Figs. 3a-3e) where calcite and sulfide inclusions are also commonly

242   present. In the latter case, the REE minerals are relatively large, subrounded to angular in

243   shape, and are generally homogenous even under high-resolution BSE imagings (Fig.

244   3d).

245

246   **Texture of calcite**

247   Calcite is the predominant mineral of the calciocarbonatites in the Miaoya complex,

248   and is commonly present as subhedral to anhedral grains with grain sizes highly variable

249   (0.1 to 2 mm) (Fig. 2g). Similar to the apatite, the calcite also shows complex internal

250   textures that are composed of BSE-bright and BSE-dark domains under high-contrast

251   BSE imaging (Fig. 3k). The BSE-bright domains are generally homogeneous and free of

252   inclusions or voids, whereas the BSE-dark domains contain abundant voids and mineral

253   inclusions dominated by fine-grained REE minerals, e.g., monazite, bastnäsite, and/or

254   parisite, and minor pyrite, celestite, barite, and strontianite (Fig. 3k).

255

256   **MINERAL CHEMISTRY**

257   Major and trace elemental compositions of different minerals were obtained by EMP

258   analytical and LA-ICPMS techniques, respectively. Analytical methods and results are

259   available in Supplemental[1] Method and Supplemental[1] Table S1-S5, respectively.

260

261   **Apatite chemistry**

262   Apatite grains in the altered carbonatites and syenites, including both the BSE-bright

263   and BSE-dark domains, are all fluorapatite characterized by high F (3.04-4.79 wt%) but

264   low Cl or OH contents (<0.02 wt%) (Fig. 4a; Supplemental[1] Table S1). The BSE-bright

265   domains have CaO (52.40-54.72 wt%) slightly lower than the BSE-dark-I and II domains

266   (53.42-56.52 wt%), whereas the P_2O_5 contents in different domains are broadly similar

267   (Figs. 7a-7c). In terms of trace elements, LA-ICP-MS analyses show that the BSE-bright

268   domains have mean Sr (12647 ppm), Na (2095 ppm), Ga (86 ppm), Ge (40 ppm), Ba (18

269   ppm), and Zr (21 ppm) values remarkably higher than BSE-dark-I and II domains

270   (Supplemental[1] Table S2). Such chemical differences among different domains are also

271   clearly revealed by the EMP mapping (Fig. 7).

272   In terms of REE concentrations, LA-ICP-MS analyses indicate that all the domains are

273   similarly enriched in LREEs relative to HREEs (Fig. 4i), but exhibit dramatically

- 13 -

274   different REE contents and chondrite-normalized REE patterns (Figs. 4 and 5). The

275   BSE-bright domains have the highest REEs (total: 7778-16525 ppm), followed by the

276   BSE-dark-I (5845-10287 ppm) and BSE-dark-II domains (1048-4742 ppm)

277   (Supplemental[1] Table S2). Notably, total contents of REE+Y in all the domains are

278   positively correlated with Na and Sr, but do not exhibit a clear correlation with Si (Figs.

279   4b, 4c and 4e). Moreover, there is a negative correlation between REE+Y+Na and Ca

280   (Fig. 4d). In the chondrite-normalized REE diagrams, both the BSE-bright and

281   BSE-dark-I domains exhibit smoothly, right-dipping REE patterns (Figs. 5a and 5b), even

282   though the BSE-bright domains tend to have relatively high LREE contents, $(La/Yb)_N$

283   and $(La/Nd)_N$ values (Figs. 4g and 4h). In contrast, the BSE-dark-II domains exhibit

284   distinctly inverted "U"-like REE patterns in which the LREE portions are almost flat,

285   corresponding to much lower values of $(La/Yb)_N$ (4.8-74.6) and $(La/Nd)_N$ (0.4-2.3) (Fig.

286   5c; Supplemental[1] Table S2). Instead, the HREE patterns are broadly parallel to those of

287   the BSE-bright and BSE-dark-I domains (Fig. 5). All the domains have undistinguishable

288   Eu anomalies with δEu values varying from 0.87 to 1.22.

289

290   **Calcite chemistry**

291   Both the BSE-bright and BSE-dark domains of the calcite are analysed. The results

292   show that the former has CaO (52.75-55.05 wt%) and REE (240-370 ppm) higher but Na

293   (44.1-64.4 ppm), Mg (910-2346 ppm), Mn (1688-5018 ppm), and Fe (3350-14204 ppm)

294   lower than the latter (Figs. 6a and 6b; Supplemental[1] Table S3 and S4). In total, both

295   domains have comparable Sr contents but in the case of an individual calcite grain, the

296   BSE-bright domain tends to have relatively high Sr. Both domains exhibit similarly

297   LREE-enriched, right-dipping chondrite-normalized REE patterns, but the BSE-dark

298   domains have relatively low LREE contents and $(La/Yb)_N$ ratios (Fig. 6c), which is

299   particularly remarkable for an individual calcite. In contrast, both domains have similar

300   HREE concentrations and exhibit similarly positive Eu anomalies with δEu varying from

301   1.06 to 1.34 (Supplemental[1] Fig. 2).

302

303   **Phengite and chlorite chemisty**

304   Both phengite and chlorite from the late hydrothermal stage were analyzed for major

305   elemental compositions. The phengite grains are F-rich (0.12-1.18 wt%) (Supplemental[1]

306   Table S5), and have limit variations of K_2O (10.34-10.94 wt%), SiO_2 (48.77-51.99 wt%),

307   Al_2O_3 (26.69-31.84 wt%), MgO (1.42-3.33 wt%), and FeO (3.15-4.18 wt%). The chlorite

308   grains have much lower F and Cl (both <0.02 wt%) (Supplemental[1] Table S5), and

309   exhibit relatively large variations in SiO_2 (22.77-25.03 wt%), Al_2O_3 (18.95-23.39 wt%),

310   MgO (5.07-11.46 wt%), and FeO (28.76-38.52 wt%).

311

312   *IN-SITU* SR AND ND ISOTOPES OF MINERALS

313   Detailed methods for *in-situ* Sr-Nd isotopic analyses of apatite, monazite, and

314   bastnäsite are provided in the Supplemental[1] Method, and the results are given in

315   Supplemental[1] table S6-S9.

316

Sr-Nd isotopes of apatite

317

318   All the domains have extremely low $^{87}Rb/^{87}Sr$, consistent with their low Rb but high Sr

319   concentrations (Supplemental[1] Table S2). The $^{87}Sr/^{86}Sr$ ratios of the BSE-bright domains

320   in apatite range from 0.70360 to 0.70389, which are broadly identical to those of the

321   BSE-dark domains (I and II) (Fig. 8; Supplemental[1] Table S6). In addition, the

322   BSE-bright domains have $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios ranging from 0.09064 to

323   0.10809 and 0.51227 to 0.51251, respectively, similar to those of the BSE-dark-I domains,

324   but slightly lower than those of the BSE-dark-II domains with $^{147}Sm/^{144}Nd$ and

325     $^{143}Nd/^{144}Nd$ varying from 0.10600 to 0.25732 and 0.51243 to 0.51263, respectively,

326   (Supplemental[1] Table S7). On the basis of the obtained ages of ~220 Ma for the REE

327   minerals (Xu et al., 2014; Ying et al., 2017, Zhang et al., 2019a), we calculated the $\varepsilon_{Nd}(t)$

328   values, by using the formula of $[(^{143}Nd/^{144}Nd)_{sample}(t) / (^{143}Nd/^{144}Nd)_{CHUR}(t) - 1] \times$

329   10000, for different domains in the apatite grains. The results show that the $\varepsilon_{Nd}(t)$ values

330   of the BSE-bright domains range from -4.58 to 0.03, broadly comparable to those of the

331   BSE-dark-I (-3.66 to 0.19) and BSE-dark-II (-4.63 to 0.36) domains (Fig. 9a).

332

Nd isotopes of monazite and bastnäsite

333

334   Three types of monazite grains, including those associated with apatite, those

335   occurring as a dissemination, and those in veinlets, were selected for *in-situ* Nd isotopic

336   analyses. The monazite grains associated with apatite, including those inside and outside

337 the apatite hosts, have similar $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios ranging from 0.05674

338 to 0.08416 and 0.51240 to 0.51247, respectively. These ratios are broadly identical to

339 those of the monazite grains in the dissemination and veinlets (Supplemental[1] Table S8).

340 Using the age of ~220 Ma, the calculated $\varepsilon_{Nd}(t)$ values for the monazite associated with

341 apatite have a limited variation (-1.18 to 0.30) that are undistinguishable from those of

342 the monazite in disseminations (-2.03 to -0.27) and veinlets (-1.23 to -0.06) (Fig. 9b).

343   Bastnäsite grains, as disseminations and in veinlets, have similarly limited variations of

344 $^{147}Sm/^{144}Nd$ (0.06639-0.09764) and $^{143}Nd/^{144}Nd$ (0.51238-0.51249), corresponding to the

345 calculated $\varepsilon_{Nd}(t)$ values (t=220 Ma) ranging from -0.52 to 0.50 and -1.70 to -0.23,

346 respectively (Supplemental[1] Table S9; Fig. 9c). Such $\varepsilon_{Nd}(t)$ values are also comparable to

347 those of the monazite from the diverse types mentioned above.

348

349 **FLUID INCLUSION MICROTHERMOMETRY AND RAMAN SPECTROSCOPE**

350   Fluid inclusions in the apatite BSE-dark domains were investigated to understand the

351 nature of the late hydrothermal fluids (Fig. 10a). Detailed methods for

352 microthermometric and Raman spectroscopic analyses of the fluid inclusions are

353 provided in Supplemental[1] Method. The fluid inclusions are elliptical or irregular in

354 shape, with sizes ranging from 2 to 8 μm (Figs. 10b and 10c). They are commonly

355 two-phase, liquid-rich inclusions with the vapor bubbles occupying 8-37 vol% (Figs.

356 10-10c). Raman spectroscopic analyses show that there are two peaks around 1284 cm^{-1}

357   and 1387 cm^{-1}, indicating that CO_2 is the major vapor phase (Fig. 10d). Most of the fluid

358   inclusions were observed to contain a clathrate, which decomposed at 5.1 to 9.3 °C,

359   corresponding to salinities of 1.42 to 8.82 wt% NaCl equiv. (Fig. 10f) and

360   homogenization temperatures of 226 to 340 °C (Fig. 10e; Supplemental[1] Table S10).

361

362   **DISCUSSION**

363

364   **Fluid-aided remobilization of early cumulated light REEs in the Miaoya complex**

365   Both apatite and calcite are the dominant primary magmatic, REE-beraing minerals in

366   the early carbonatites and/or syenites. Our textural observations show that the two

367   minerals exhibit similar internal textures that are characterized by the presence of several

368   domains with distinguishable appearances (Figs. 3a-3e). Similar textures, particularly the

369   monazite-bearing apatite, have been replicated in experiments involving mineral-fluid

370   interaction (Harlov et al., 2002b, 2005; Harlov and Föster, 2003). These textures have

371   also commonly been observed in some iron oxides-apatite and iron oxide copper-gold

372   deposits (Harlov et al., 2002a; Chen and Zhou, 2015; Li and Zhou, 2015; Zeng et al.,

373   2016). These textures have been demonstrated to form via a fluid-aided, coupled

374   dissolution-reprecipitation process during which the REEs have been hydrothermally

375   remobilized to form REE minerals such as monazite (Harlov et al., 2002a; Chen and

376   Zhou, 2015; Li and Zhou, 2015). In the case of Miaoya, the BSE-dark domains (including

377   both I and II) in the apatite and calcite host an abundant micro-porosity, fluid inclusions,

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378   and mineral inclusions, compared to the BSE-bright domains that are homogeneous and

379   free of pores and mineral inclusions (Figs. 3b-3e). This feature indicates that the BSE

380   dark domains formed from the birght domains (original apatite) through fluid infiltration

381   and chemical alteration as observed in the experiments (e.g., Harlov et al., 2002a). It is

382   also notable that some of the apatite grains contain both BSE dark I and II domains (Figs.

383   3c-3e), indicating variable degrees of metasomatic alteration possibly related to

384   consecutive infiltration of fluids.

385   Both the BSE dark I and II domains in the apatite and the calcite grains have REE

386   concentrations that are lower than the BSE-bright domains, indicating that the REEs have

387   been extensively mobilized and leached from the original apatite during metasomatic

388   alteration. In particular, the BSE-dark domains are depleted in light REE, indicating that

389   the light REEs were more mobile than the heavy REEs which in many grains are only

390   slightly modified (Fig. 5). In addition to the light REEs, the BSE-dark domains in the

391   apatite are also depleted in Y, Na, and Sr relative to the BSE-bright domains (Fig. 7). It is

392   notable that REE+Y in these domains vary positively with Na and Sr but negatively with

393   Ca (Figs. 4c-4e), indicating that these elements were incorporated in the apatite through

394   the coupled substitution reaction: $Na^+ + (REE + Y)^{3+} = 2Ca^{2+}$ and $Sr^{2+} = Ca^{2+}$ (Fig. 4d;

395   Roeder et al., 1987; Pan and Fleet, 2002; Harlov et al., 2002b, 2005; Harlov and Förster

396   2003). The leached REEs from the apatite and calcite were re-incorporated back into the

397   monazite inclusions and along the apatite grain rim (Fig. 3) (e.g., Harlov et al., 2002a), or

398   were partially transported outwards on scales of meters to be re-deposited as the REE

399   minerals present as disseminations or in veinlets.

400

401   **Remobilized REEs as the major contribution for the REE mineralization in Miaoya**

402   Although monazite or bastnäsite could have formed during the magmatic stage (Castor,

403 2008), our results confirm that the major REE mineralization in Miaoya is hydrothermal

404 in origin. For example, the REE minerals are present as a dissemination or in veinlets

405 where they closely associated with hydrothermal minerals (Fig. 3). The monazite grains

406 are characterized by low ThO_2 concentration (typically < 0.5 wt%, 0.29 wt% on average;

407 Xu et al., 2010), similar to typical hydrothermal monazite (Schandl and Gorton, 2004).

408 Available U-Pb dating of various monazite and bastnäsite have revealed consistent ages

409 of 230 to 210 Ma (Ying et al., 2017; Zhang et al., 2019a). This suggests that REE

410 mobilization and mineralization were coeval and related to a common fluid. However,

411 further evidence is needed to confirm if the major REE mineralization in Miaoya, which

412 occurs either as a dissemination or a veinlet, was also mainly contributed to by mobilized

413 REEs, even though most of the carbonatites and syenites in the Miaoya complex have

414 undergone pervasive carbonatization and extensive REE mineralization. To answer this

415 question, we conducted a comparison of Sr-Nd isotopic data from early apatite and REE

416 minerals in multiple stages and various occurrences. Mass balance calculations were also

417 conducted to confirm if the remobilized REEs are sufficient for the REE mineralization in

418 Miaoya.

419   **In-situ Sr-Nd isotopic constraints**. As the analyzed apatite grains have high Sr

420   (3637-17482 ppm) but extremely low Rb (<3.4 ppm), the measured $^{87}Sr/^{86}Sr$ ratios could

421   be used as initial $^{87}Sr/^{86}Sr$ ratios, without further age calibration. Our new results show

422   that the BSE-dark domains I and II in apatite have $^{87}Sr/^{86}Sr$ ratios and $\varepsilon_{Nd}(t)$ values

423   similar to the primary apatite, i.e. BSE-bright domains (Figs. 8 and 9a), indicating that

424   the causative fluids do not contain enough Sr and Nd to sufficiently modify the initial Sr

425   and Nd isotopic ratios of the primary apatite, or else the fluids have Sr and Nd isotopic

426   compositions similar to the apatite precursors. The latter possibility, however, is unlikely,

427   since the newly obtained $\varepsilon_{Nd}(t)$ values for monazite and bastnäsite in the altered apatite,

428   and as disseminations or veinlets (-2.03 to 0.50) are similar to those of the BSE-bright or

429   BSE-dark domains of the apatite, which ranges from -4.58 to 0.36 (Fig. 9). These features

430   strongly support the idea that REE mineralization in the Miaoya complex was sourced

431   mainly from early cumulated REEs in the magmatic carbonatites and syenites.

432   **Constraint of mass balance calculation**. In order to quantitatively evaluate the

433   overall mass transfer of REEs during remobilization, we also conducted mass balance

434   calculations for the altered apatite and calcite. Following the procedures of Li and Zhou

435   (2017), the calculations were made by assuming that Tm in apatite and Lu in calcite are

436   hydrothermally immobile. At the very beginning, the concentrations of Tm or Lu in the

437   altered domains of the apatite or calcite were normalized to those of the primary ones. On

438   this basis, other elements could be also normalized accordingly, and an enrichment factor

439   for a certain element could be calculated following the formula: $Xm = C_b / (\rho * C_a)$ (Li and

440   Zhou, 2017), in which Xm represents the enrichment factor of a certain element, while C_a

441   and C_b are the concentrations of certain element in the primary and altered domains,

442   respectively. The ρ values are the relative ratios of concentrations of immobile elements

443   (i.e. Tm and Lu) in the altered and primary domains, and were calculated to be 1.1 and

444   0.99 for Tm in apatite and Lu in calcite, respectively. The calculated enrichment factors

445   are provided in Supplemental[1] Table S11 and illustrated in Figure 11. In Figure 11, the

446   solid line for the enrichment factor as 1 defines no gain or loss. Departure from the line

447   defines gain (above the line) or loss (below the line) for a certain element. The calculated

448   results for apatite show that components lost include light REEs (La, Ce, Pr, Nd; 89.8%

449   lost), Na, Sr, Ba, Ga and Ge, whereas Mg, Al, Si, Zr, Nb, Th, U, Fe, and Mn were

450   variably enriched (Fig. 11a). On the other hand, components lost in calcite include

451   LREEs (La, Ce, Pr, Nd; 28.3% lost), P, Si, U, Ga, and Ge, whereas Na, K, Nb, Th, Sc,

452   and V are variably enriched (Fig. 11b).

453   On the basis of the calculated proportions of the LREE losses, we are able to estimate

454   the total amounts of remobilized LREEs from the primary apatite and calcite in the

455   Miaoya complex in order to confirm if it matches the reported REE reserve in Miaoya.

456   Detailed steps for the calculation are provided in Table 1. Firstly, we know that the

457   carbonatites stocks, which are mostly altered, cover a total area of about 0.49 km^2

458   whereas the altered syenites cover a total area of about 5.85 km^2. Both rock types extend

459   to a depth of ~640 m below the current surface (Liu et al., 1984). As such, the total

460   volume of the carbonatites and the syenites are calculated to be 3.15×10^8 m^3 and $3.76 \times$

461   10^9 m^3, respectively (Table 1). Secondly, the total volumes of apatite and calcite in the

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462   complex can be estimated on the basis of their contents in the carbonatites and syenites

463   (Table 1). On this basis, using a density (~3.19 ton/m^3) and the average LREE contents

464   (13660 ppm) for the primary apatite, along with the estimated proportions of LREE

465   losses (89.8%), the remobilized amounts of LREEs from the apatite in the carbonatites

466   and syenites were calculated to be 1.173 and 1.476 Mt, respectively (Table 1). On the

467   other hand, using the density (~2.71 ton/m^3) and average LREE contents (155 ppm) of

468   calcite, and the estimated proportions of LREE losses (28.3%), the remobilized amounts

469   of LREEs from calcite in the carbonatites and syenites were calculated to be 0.032 and

470   0.054 Mt, respectively (Table 1). As such, the total amount of remobilized LREEs can be

471   calculated to be 2.735 Mt (Table 1). Such a value is much higher than the reported

472   REE_2O_3 reserve of 1.21 Mt, which is only for those areas > 1.2 wt% REE_2O_3 (Fig. 1d)

473   (Qian and Li, 1996). However, if those ores with grades ranging from 0.3 to 1.2 wt%

474   REE_2O_3 are incorporated (Fig. 1d), the total reserve, i.e. REE_2O_3 > 0.3 wt%, would be

475   much larger and could broadly match the estimated value of the mobilized LREEs (e.g.

476   Fig. 1d). Therefore, our mass balance calculation confirms that early cumulated LREEs,

477   which were mostly in the magmatic apatite and calcite from the complex, were sufficient

478   for the REE mineralization related to late hydrothermal reworking.

479

480   **Nature and potential sources of the causative fluids**

481   Results from the fluid inclusion study show that the causative fluids responsible for

482   REE remobilization and mineralization are CO_2-rich, with medium temperatures

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483   (226-340 °C), and low salinities (1.42-8.82 wt‰) (Fig. 10). The local presence of fluorite

484   and F-rich phengite in the mineralized veinlets imply that the fluids were also rich in F

485   (Supplemental[1] Table S5). All these ligands were well confirmed to be important

486   mediums aiding the mobility of REEs, particularly light REEs (Harlov et al., 2005;

487   Williams-Jones et al., 2012; Williams-Jones and Migdisov, 2014; Li et al., 2015; Perry

488   and Gysi, 2018). It is thus concluded that such low-salinity, CO_2-, F-, and Cl-rich fluids,

489   presumably unsaturated with REEs, should be responsible for REE mobilization and

490   subsequent mineralization in the Miaoya complex.

491   The potential sources of the causative fluids have not been addressed previously but

492   can be speculated about due to coeval, 230-210 Ma hydrothermal/mineralization events

493   in the same region. Available studies have revealed that numerous orogenic, 220 to 200

494   Ma Au-Ag deposits, e.g. Yindonggou, Xujiapo, Shejiayuan, Putang and Xunyang

495   deposits, are distributed along the South Qinling unit (Chen and Santosh, 2014). The

496   ore-forming fluids for these deposits were constrained to be CO_2-rich, with low to

497   medium temperatures and salinities (Feng et al., 1997; Cai et al., 1999; Pang et al., 2001;

498   Xu et al., 2012, 2018; Yue et al., 2013), which are broadly similar to the causative fluids

499   documented in Miaoya (Fig. 10). Moreover, a summary of previous C-O isotopic results

500   from the altered rocks/ores in the Miaoya complex shows that these data plot the field in

501   between the primary carbonatites and the Au-Ag deposits (Fig. 12) (Xu et al., 2014;

502   Cimen et al., 2018; Su et al., 2019; Zhang et al., 2019b). Such an isotopic feature strongly

503   indicates that the causative fluids are likely coeval and co-genetic with those of the

504   Au-Ag deposits in the same region.

505

A genetic model for the REE mineralization in the Miaoya complex

507   This study confirms that the formation of the Miaoya complex and associated REE

508   mineralization involved two separated stages. Both the syenites and carbonatites formed

509   from partial melting of the upper mantle under a rift setting at ~430 Ma (Xu et al., 2014;

510   Zhu et al., 2016; Su et al., 2019; Zhang et al., 2019a), likely followed by a combined

511   fractionation-immiscibility process (Fig. 13a; Su et al., 2019). It is noteworthy that

512   although both the carbonatites and syenites have elevated REE concentrations, our work

513   reveals that the REE-rich minerals formed in this stage were dominantly apatite with

514   minor monazite and/or bastnäsite (<1 vol%). Subsequent infiltration and overprinting by

515   external fluids during 230-210 Ma (Ying et al., 2017; Zhang et al., 2019a), possibly

516   co-genetic with the coeval orogenic Au-Ag mineralization in the same belt, pervasively

517   metasomatized the early carbonatites and syenites (Fig. 13b). Triggered by metasomatism,

518   the early cumulated REEs were extensively mobilized and transported on scales of meters

519   or even possibly tens of meters to be re-deposited as monazite and/or bastnäsite in the

520   form of disseminations or veinlets (Fig. 13c).

521

522   **IMPLICATIONS**

523

524   Numerous carbonatites and/or alkaline rocks are enriched in light REEs, but only few

525   contain sufficient amounts of REE minerals, here monazite and bastnäsite, for economic

526   exploitation. In most cases, the REEs in carbonatites are distributed in diverse minerals

527   (e.g. carbonates or apatite) that are generally not exploited. Our study provides a strong

528   evidence that secondary hydrothermal upgrading of early cumulated REEs under certain

529   conditions is the key for the REE mineralization, i.e. re-precipitation of economic REE

530   minerals, in the Miaoya complex. It could also be an also alternative important tool for

531   REE mineralization in other carbonatite-related deposits, such as the Bayan Obo. In

532   particular, our findings that the causative fluids for REE mineralization are co-genetically

533   related to the orogenic Au-Ag deposits formed during the final collision between the

534   North China and South China Cratons allow us to further speculate that hydrothermal

535   mobilization of REEs could be more widespread than previously documented,

536   particularly for REE deposits present in convergent belts where faults (facilitating fluid

537   migration) and hydrothermal fluids are generally more extensively developed. This

538   suggests that carbonatites and alkaline rocks (or even other REE-rich rocks) distributed in

539   the convergent belts could be potential targets for REE exploration.

540

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551

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770

771

FIGURE CAPTIONS

773   **Fig. 1** (a) Simplified tectonic map of China. (b) Geological sketch of the Qinling

774   Orogenic Belt and the location of the Miaoya and Shaxiongdong deposits (modified from

775   Zhang et al. 2019a). (c) Simplified geological map of the Miaoya complex (modified

776   from Liu et al., 1984). (d) Simplified geological map showing the distributions of various

777   REE ore bodies in the Miaoya complex (modified from Liu et al., 1984). Abbreviations:

778   S-NCB–Southern North China Block, NQL–North Qinling, SQL–South Qinling,

779   N-SCB–Northern South China Block.

780

781   **Fig. 2** Field photos and BSE images of various rocks/ores in the Miaoya complex. (a)

782   Carbonatites intruding syenites. (b) The boundaries between the carbonatites and syenites

783   are sharp/straight. Note that the syenites have been carbonatized. (c) Xenoliths of wall

784   rocks locally present in the carbonatites. (d) Veins of quartz + dolomite crosscutting

785   carbonatites. (e) Veins of ankerite + quartz in the carbonatite crosscut by stockworks

786   consisting of bastnäsite, pyrite and graphite. (f) Fine-grained syenite composed

787   dominantly of K-feldspar and albite with minor apatite. Note that the rock was

788   extensively altered. (g) Carbonatite is composed of calcite and apatite with minor

789   ilmenite and chlorite. (h) Veinlet of fluorite + bastnäsite crosscutting carbonatites. (i)

790   Veinlet of K-feldspar + albite + quartz + ankerite crosscutting carbonatites. Abbreviations:

791   Ab – albite, Ank – ankerite, Ap – apatite, Bas – bastnäsite, Cal – calcite, Chl – chlorite, Fl

792   – fluorite, Ilm – ilmenite, Kfs – K-feldspar, Ph – phengite, Py – pyrite, Qz – quartz, Sd –

793   siderite.

794

795   **Fig. 3** BSE images of diverse apatite grains in carbonatite and syenites and various REE

796   ores. (a) Euhedral to subhedral apatite grains in carbonatites are intergrown with calcite

797   and/or pyrite, eroded or replaced by phengite, K-feldspar, monazite, and quartz. (b) The

798 apatite in carbonatites is extensively embayed by dolomite, phengite, biotite, pyrite and

799 K-feldspar. Note that the apatite contains abundant monazite and bastnäsite inclusions. b1

800 is a CL image of this grain. (c) Apatite in the carbonatite is extensively modified and

801 contains three domains with irregular and sharp contacts. Note that BSE-dark-II domain

802 occurs as strips which embay both the BSE-bright and BSE-dark-I domains. (d) A

803 number of monazite grains distributed along the margins of modified apatite in the

804 carbonatites. (e) Relatively large monazite inclusions hosted in an extensively modified

805 apatite grain in the carbonatites. (f) Disseminated monazites in ferrocarbonatite are

806 irregular in shape, and homogenous under high-contrast BSE imagings (f1). (g)

807 Disseminated bastnäsite in carbonatite. Note that the bastnäsite is mainly associated with

808 the BSE-dark domains of the calcite. (h) Veinlet of bastnäsite + parisite + quartz in

809 carbonatites. (i) Veinlet of monazite + ankerite + graphite in syenite. (j) Veinlets of

810 batnäsite + allanite in carbonatite. (k) Abundant strontianite, barite, celestite and

811 bastnäsite grains mainly distributed in the BSE-dark areas in the calcite. (l) Veinlets of

812 barite + albite + apatite in syenite. Abbreviations: Brt – barite, Clt – celestite, Dol –

813 dolomite, Mnz – monazite, Par – parisite，Str – strontianite. Other abbreviations are the

814 same as those in Fig. 2.

815

816 **Fig. 4** Bimodal plots of F vs. $LREE_2O_3$ (a), REE+Y vs. Si (b), REE+Y vs. Na (c), Ca vs.

817 REE+Y+Na (d), REE+Y vs. Sr (e), Th+U vs. Pb (f), $(La/Yb)_N$ vs. REE+Y (g), $(La/Nd)_N$

818 vs. REE+Y (h), and LREE vs. HREE+Y (i) for different areas in the apatite.

819

820   **Fig. 5** Chondrite-normalized REE patterns from the BSE-bright (a), BSE-dark-I (b), and

821   BSE-dark-II (c) areas in the apatite.

822

823   **Fig. 6** Bimodal plots of Na vs. LREE (a), Fe+Mn+Mg vs. LREE (b), and $(La/Yb)_N$ vs.

824   LREE (c) from different areas in the calcite.

825

826   **Fig. 7** Elemental mapping of an apatite grain from the carbonatites, showing the

827   distribution patterns of Ca, P, La, Sr, and F in the grain.

828

829   **Fig. 8** Plots of in-situ $^{87}Sr/^{86}Sr$ vs. ^{88}Sr (v) values from the the BSE-bright and BSE-dark I

830   and II areas in the apatite. Note that $^{88}Sr(v)$ represents the Sr signal intensities during

831   analyses.

832

833   **Fig. 9** Histograms showing $\varepsilon_{Nd}(t=220$ Ma) values for different areas in the apatite (a),

834   various monazites (b), and bastnäsite (c). Note: $\varepsilon_{Nd}(t)$ values are calculated based on the

835   age of 220 Ma; $\varepsilon_{Nd}(t)= [(^{143}Nd/^{144}Nd)_S(t) / (^{143}Nd/^{144}Nd)_{CHUR}(t) - 1] \times 10000$; where S =

836   sample, $(^{143}Nd/^{144}Nd)_{CHUR} = 0.512638$, $(^{147}Sm/^{144}Nd)_{CHUR} = 0.1967$.

837

838   **Fig. 10** Fluid inclusions in the altered apatite. (a) BSE image and (b) transmit-light image

839   of an altered apatite grain containing abundant fluid inclusions. Also note that small voids

840 are randomly distributed in the grain, possibly representing relics of fluid inclusions. (c)

841 Typical fluid inclusions composed of a liquid phase and vapor bubble. (d) Laser Raman

842 spectra collected at room temperature for the vapor bubble of the fluid inclusion, showing

843 that the bubbles are rich in CO_2. (e) Homogenization temperatures of the fluid inclusions.

844 Also shown are those in quartz from the 220-200 Ma orogenic Au-Ag deposits in the

845 South Qinling unit (data from Feng et al., 1997; Pang et al., 2001; Xu et al., 2012, 2018;

846 Yue et al., 2013). (f) Fluid inclusion salinities. Also shown are fluid inclusion salinities

847 from the orogenic Au-Ag deposits (data from Xu et al., 2012; Yue et al., 2013).

848 Abbreviations are the same as those in Fig. 2.

849

850 **Fig. 11** Calculated enrichment factors relative to Tm and Lu for various elements during

851 alteration of apatite (a) and calcite (b).

852

853 **Fig. 12** Summary of previous C-O isotopic compositions of carbonate grains from the

854 Miaoya complex (Xu et al., 2014; Cimen et al., 2018; Zhang et al., 2019b; Su et al.,

855 2019). The data for the orogenic Au-Ag deposits in South Qinling unit are cited from

856 Pang et al. (2001), Zhang et al. (2010), and Yue et al. (2019), whereas the field of primary,

857 mantle-derived carbonates is cited from Taylor et al. (1967). Arrows indicate

858 schematically the major processes responsible for changes in C-O isotopic compositions

859 (Demény et al., 1998).

860

861 **Fig. 13** Cartoons illustrating the formation process of the REE mineralization in the

862 Miaoya deposit. (a) The carbonatites and syenites in the Miaoya complex formed initially

863 at ca. 440-430 Ma, during which magmatic calcite, apatite, and minor allanite and

864 monazite formed. (b) Significant remobilization of early cumulated REEs in apatite and

865 calcite were triggered by the infiltration of external fluids at ca. 220 Ma, responsible for

866 the formation of abundant monazite and bastnäsite. (c) At the hydrothermal stage, the

867 early cumulated REEs were remobilized and transported on scales of meters or even

868 possibly tens of meters to be re-deposited as monazite and/or bastnäsite. Further details

869 are available in the text.

Fig. 1
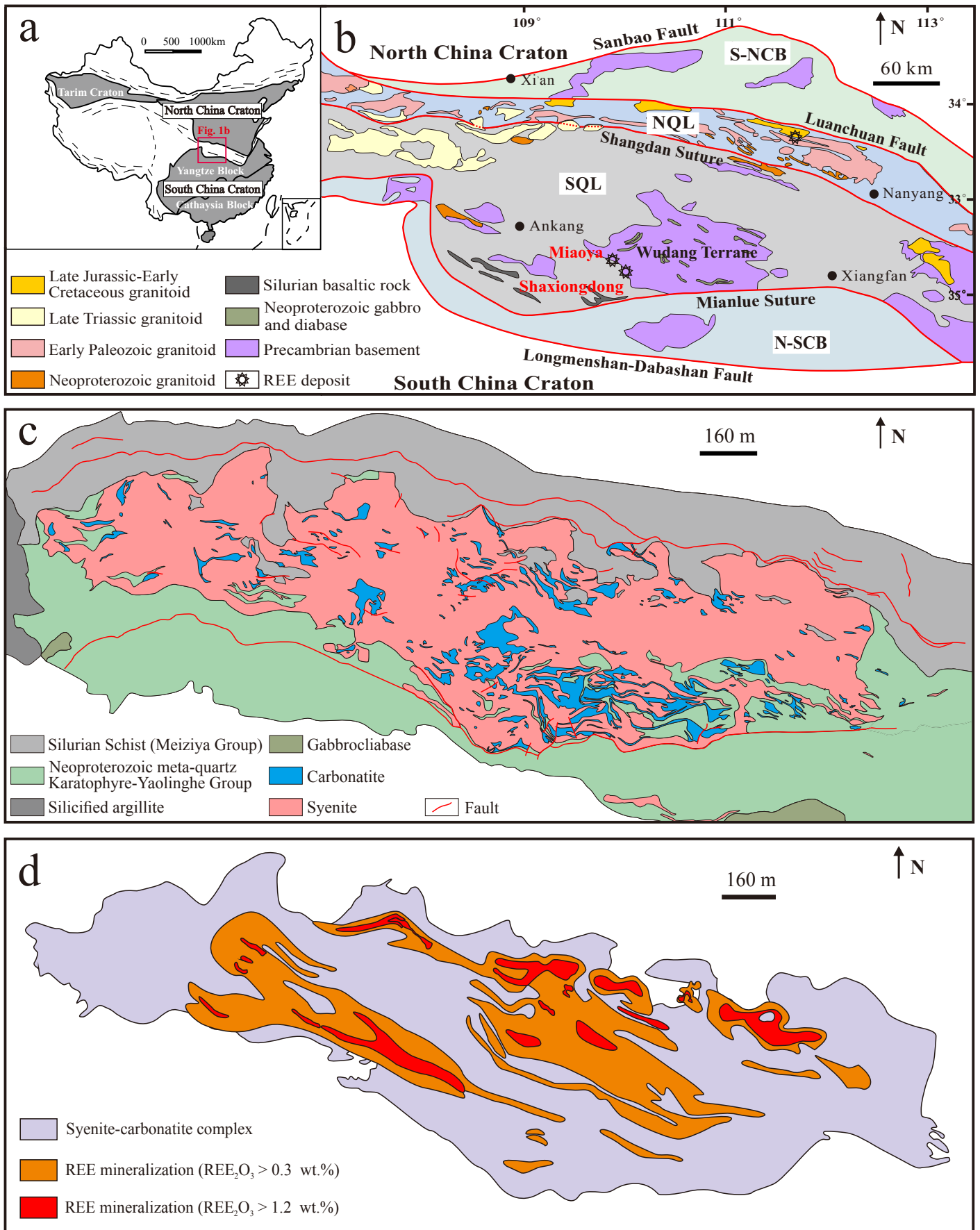
Fig. 2
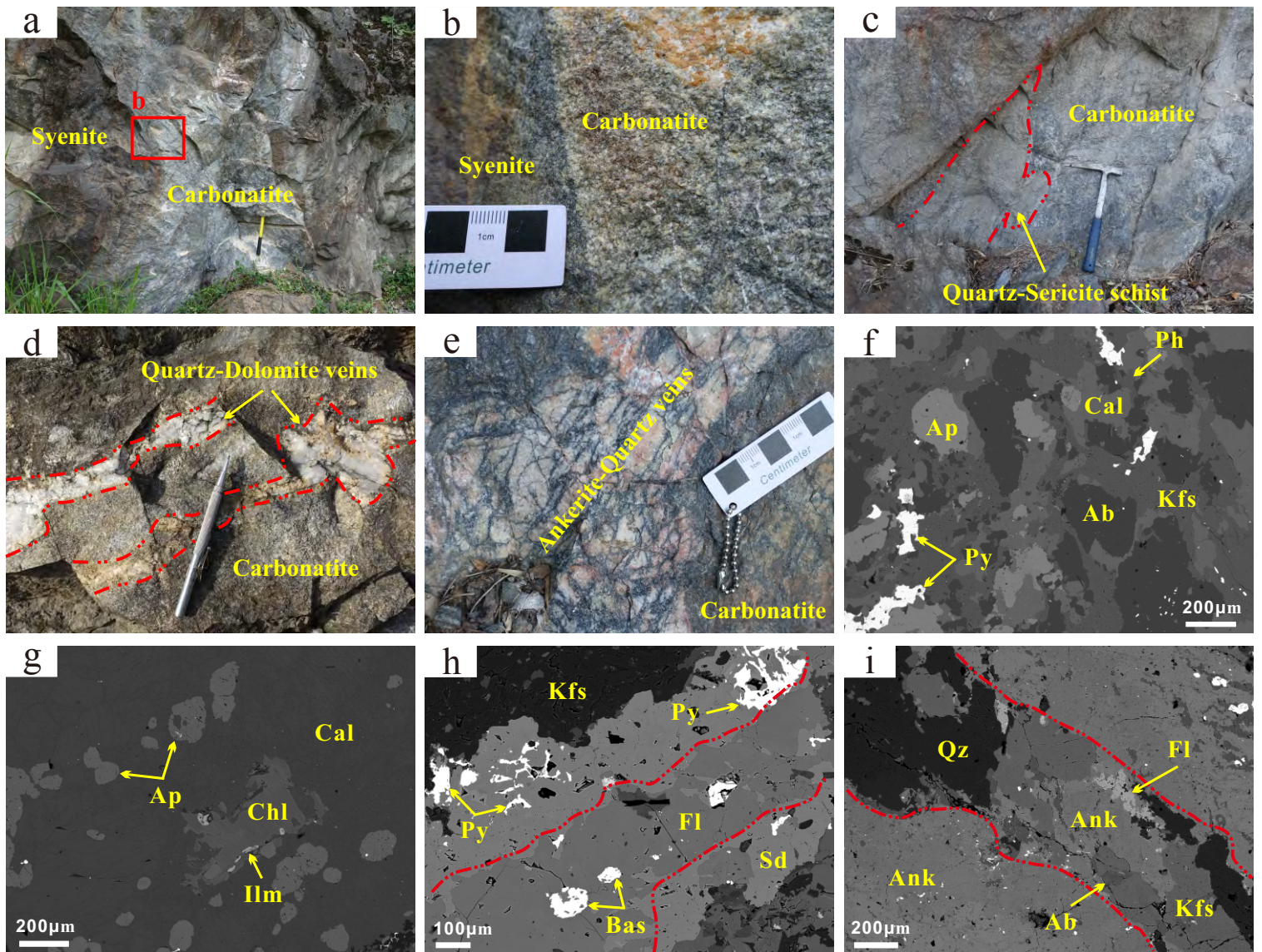
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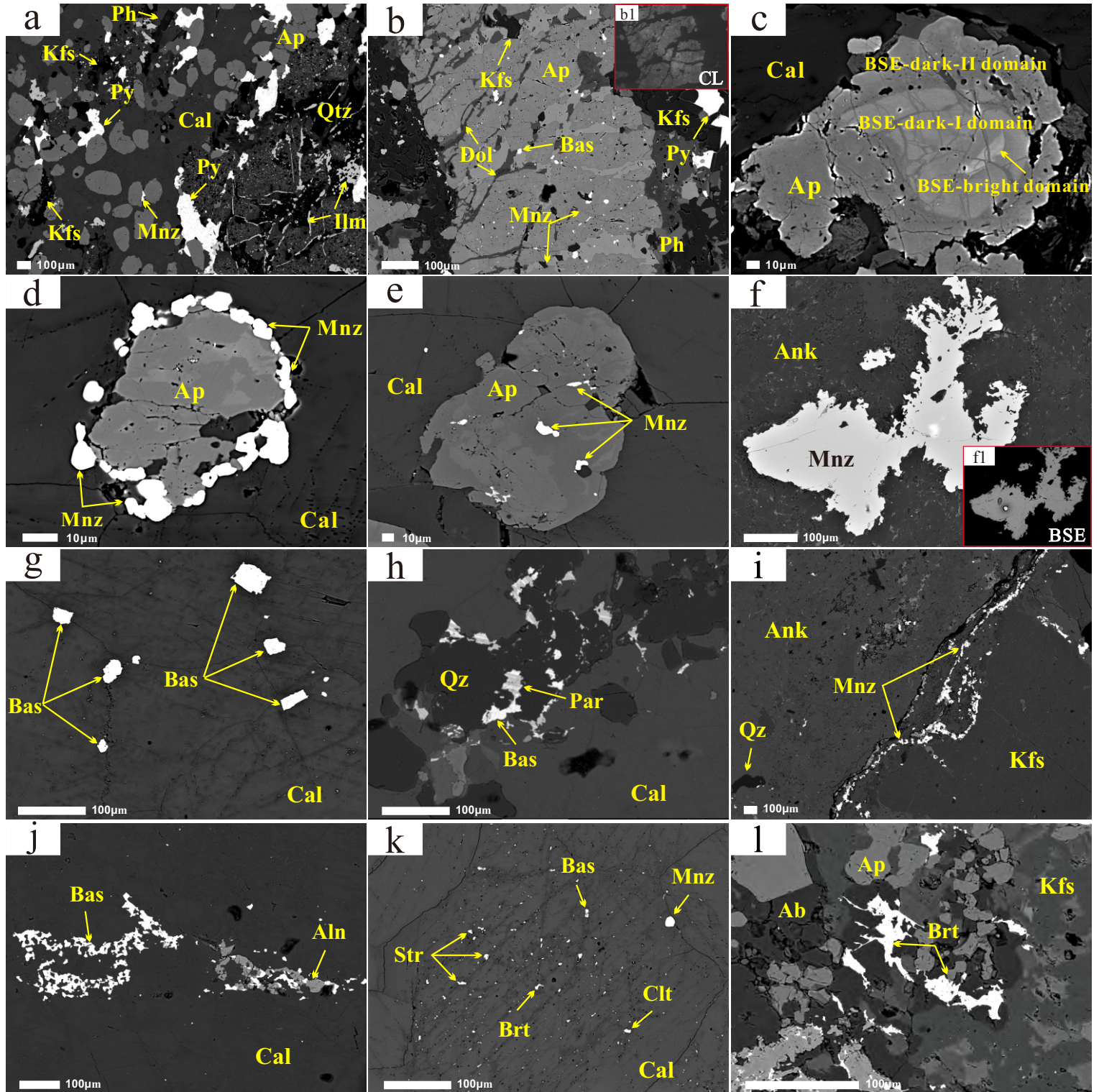
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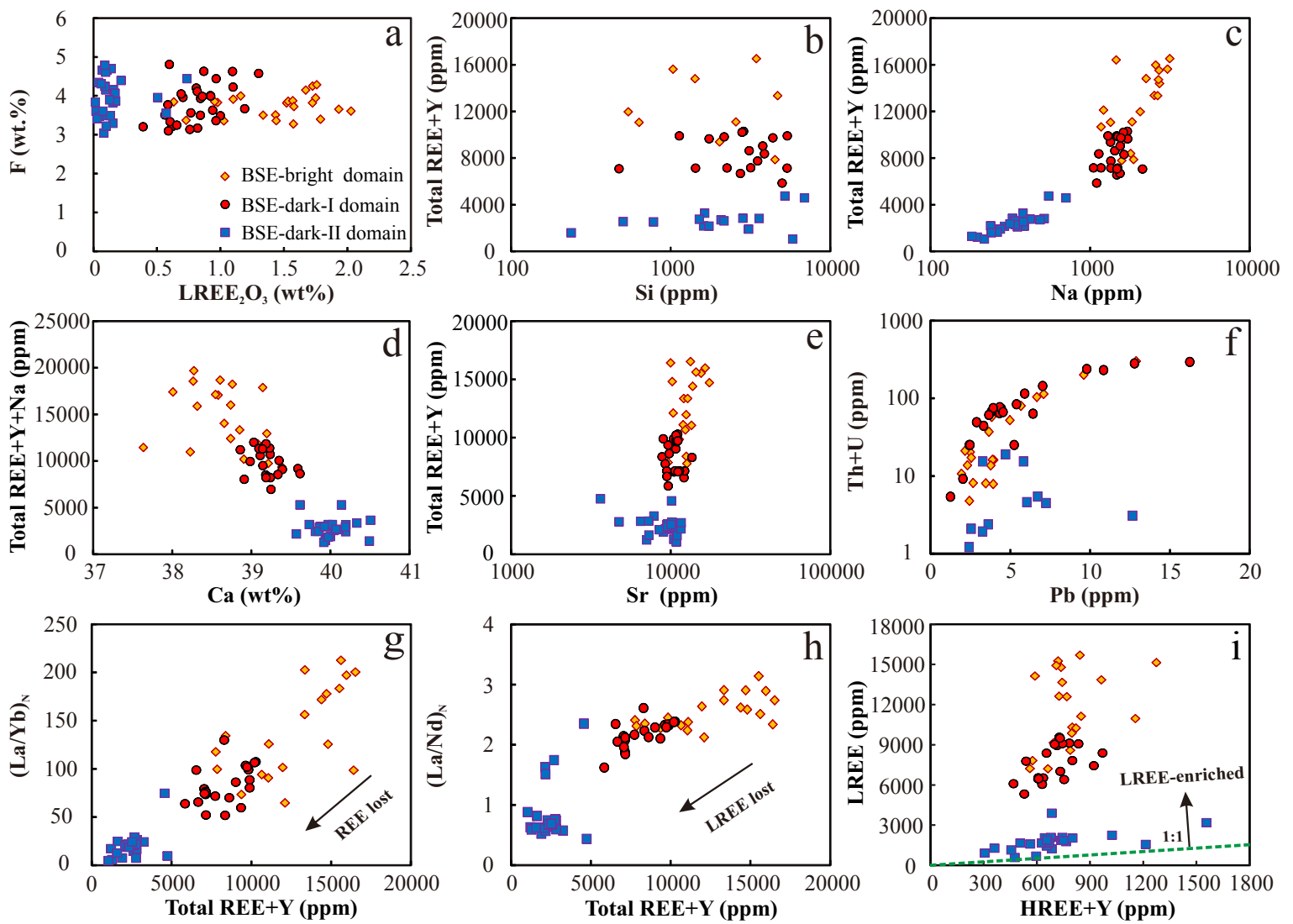
Fig. 5
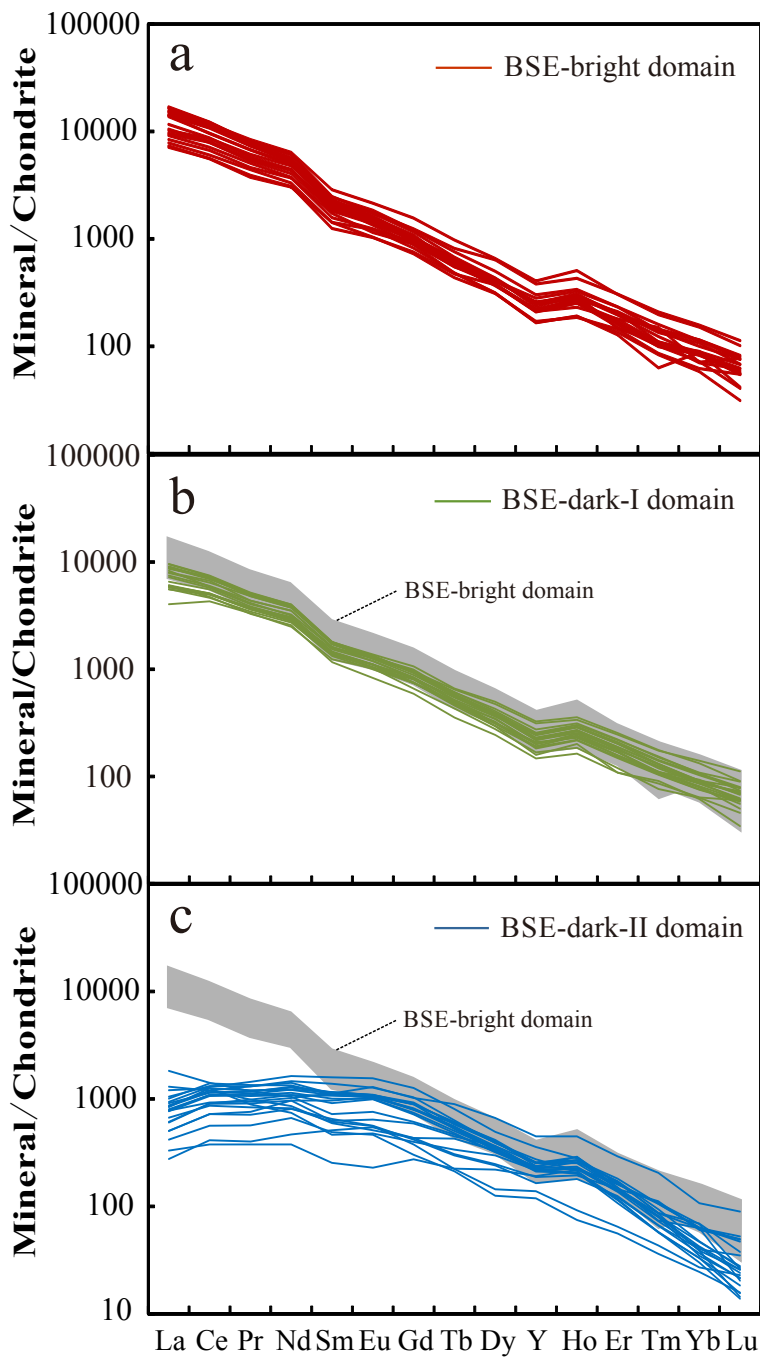
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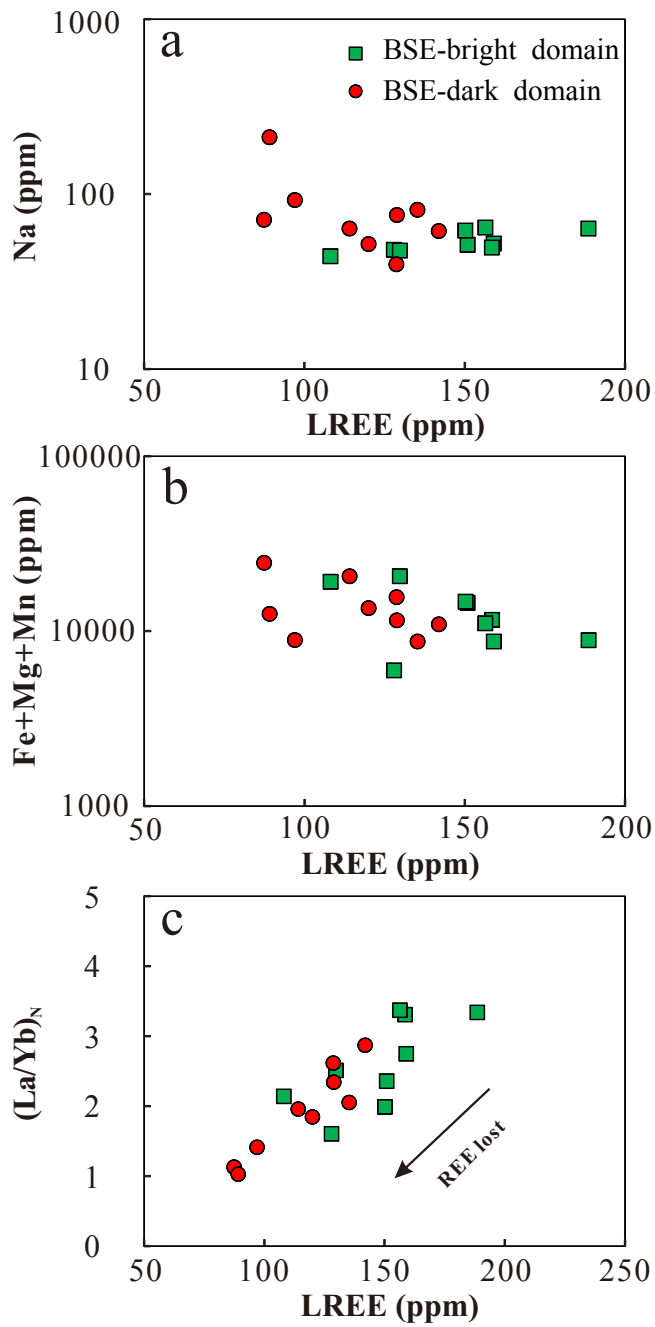
Fig. 7
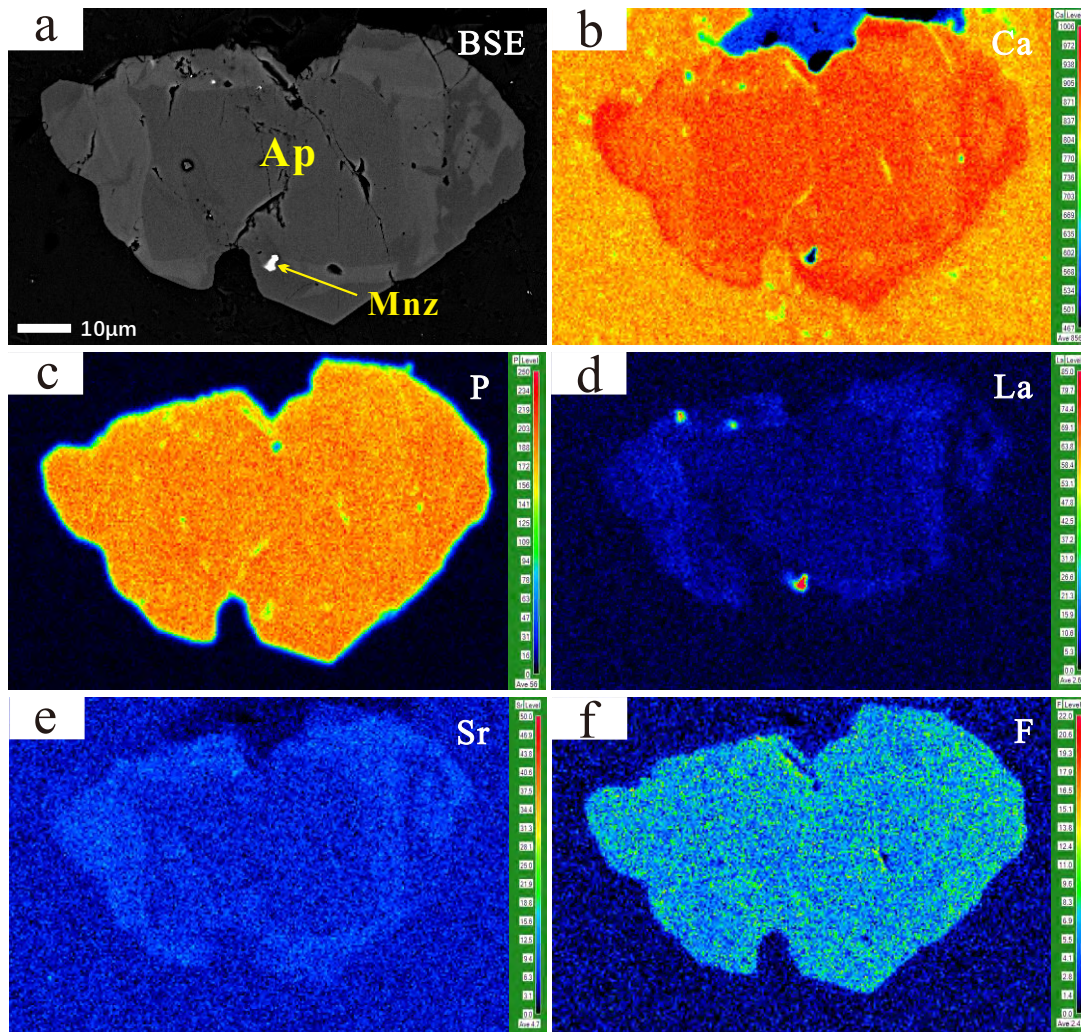
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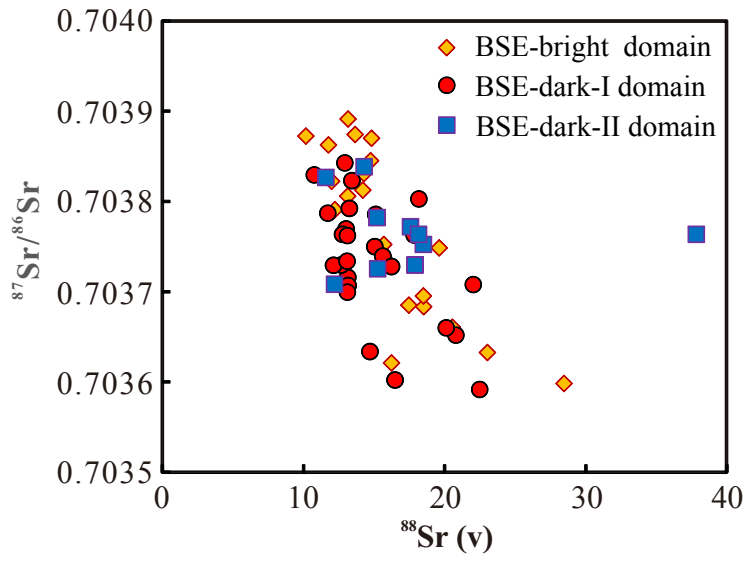
Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

a 440-430 Ma (Early magmatic stage)

b 230-210 Ma (Late hydrothermal stage)

c 230-210 Ma

Calcite
Representative altered calcite
BSE-bright (unaltered) Fluorapatite
BSE-dark I (altered) fluorapatite
BSE-dark II (altered) fluorapatite
Monazite
Pyrite
Bastnasite
Allanite
Barite
Celetite
Biotite
K-feldspar
REE mobilization
Hydrothermal fluids

Yaolinghe Group
Meiziya Group
Syenite
Carbonatite
Ore body
Fault

hydrothermal fluids

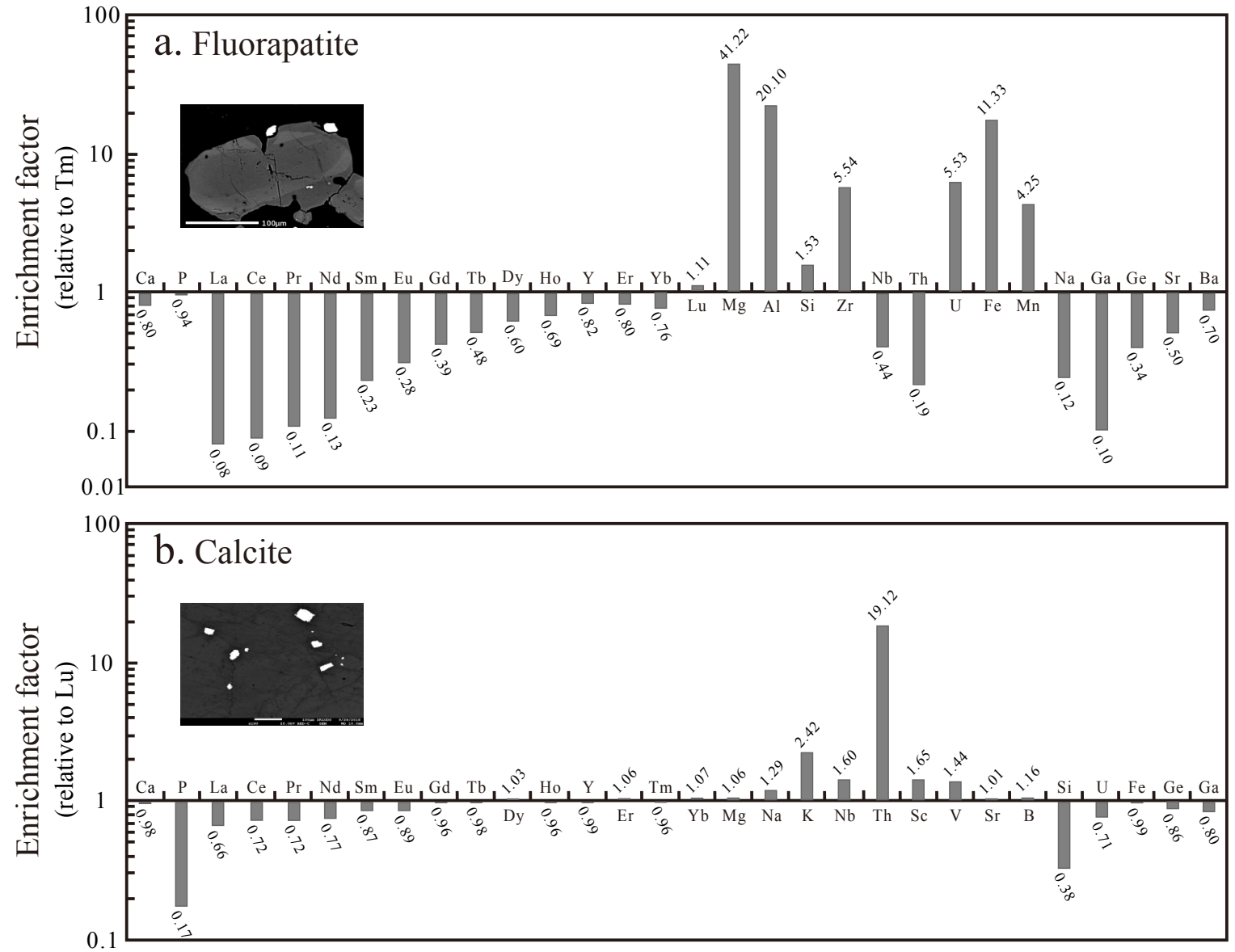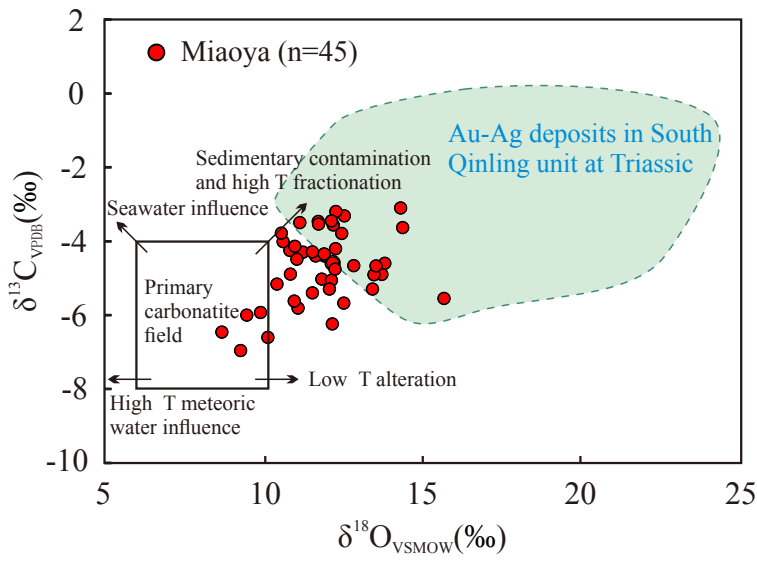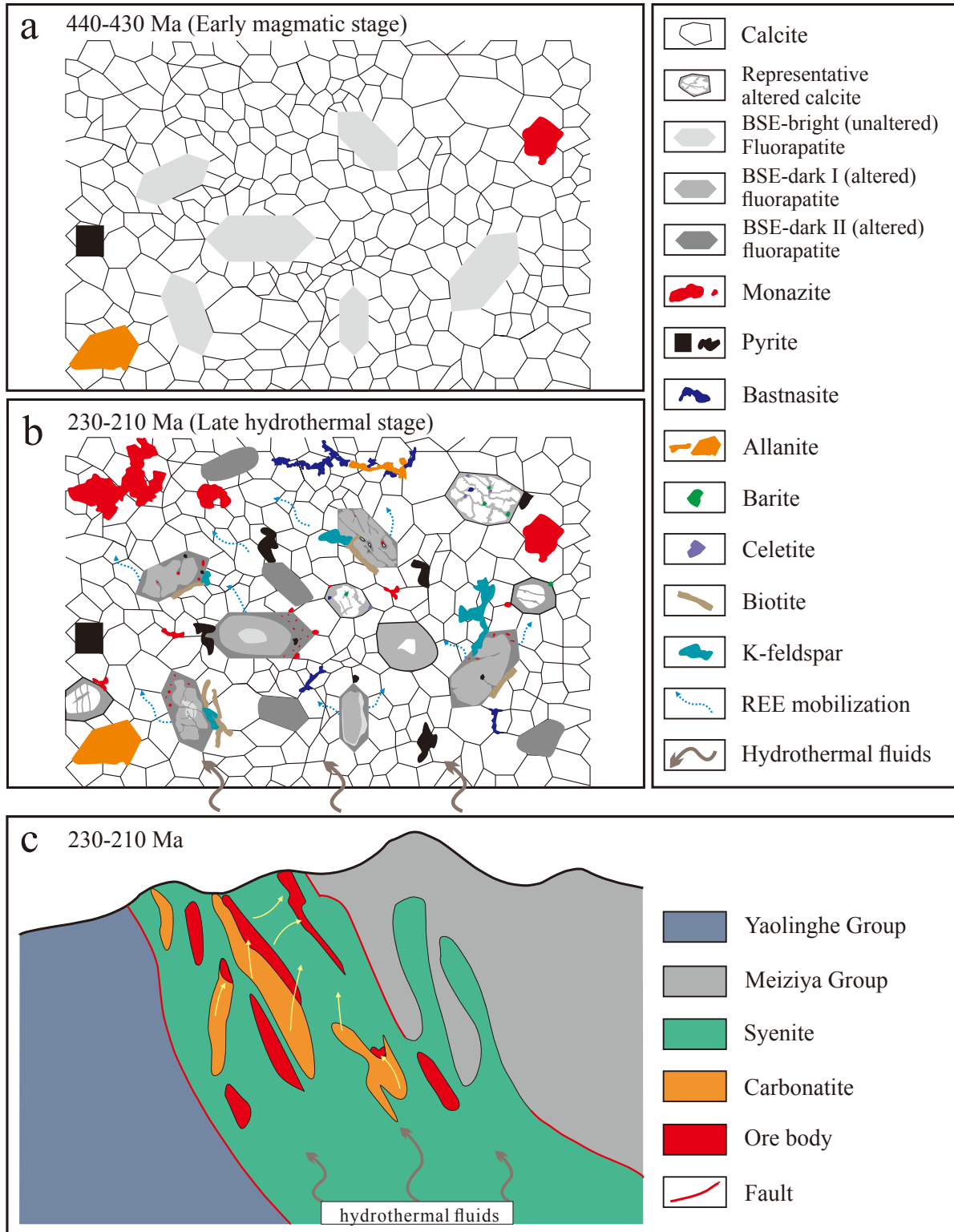**TABLE 1** Steps of the calculation related the total mobilized REEs from carbonatites and syenites

	Carbonatites	Syenites
Covering Area (m^2)	4.9×10^5	5.85×10^6
Maximum depth (m)	640	
Maximum volume (m^3)	3.15×10^8	3.76×10^9
Average proportion of apatite	9.5%	1%
Average proportion of calcite	85%	12%
Maximum volume of apatite (m^3)	2.99×10^7	3.76×10^7
Maximum volume of calcite (m^3)	2.68×10^8	4.51×10^8
Remobilized amounts of LREE from apatite (Mt)	1.173	1.476
Remobilized amounts of LREE from calcite (Mt)	0.032	0.054
Remobilized amounts of LREE (Mt)	1.205	1.53
Total amount of remobilized LREE (Mt)	2.735	

Note: The densities of fluorapatite and calcite are 3.19 ton/m^3 and 2.71 ton/m^3, respectively. Average LREE contents of fluorapatite and calcite are 13660 and 155 ppm, respectively. We have calculated that about 89.8% and 28.3% of LREEs (La, Ce, Pr, Nd) lost from the primary fluorapatite and calcite, respectively. Firstly, we need to calculate the maximum volume of carbonatites and syenites. Secondly, Maximum volume of apatite and calcite can be calculated based on the average proportion of apatite and calcite, and the maximum volume of carbonatites and syenites. Thirdly, remobilized amounts of LREEs from apatite and calcite can be calculated based on the densities, average LREE contents, estimated proportion of LREE losses and the maximum volume of apatite and calcite. Finally, the sum of the LREE remobilized from apatite and calcite in carbonatites and syenites represents total amount of remobilized LREEs.