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2   # Reconstructing volatile exsolution in a porphyry ore-

3   # forming magma chamber: Perspectives from apatite

4   # inclusions

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16   **Abstract**

17   Porphyry-type deposits in the shallow crust (3-5 km) are formed from metal-rich

18   fluids exsolved from underlying magma chambers (5-15 km). However, a direct

19   volatile record of the fluid exsolution in the magma chamber is commonly lacking.

20   Here, we analyse the compositions of apatite inclusions (in biotite and plagioclase

21   phenocrysts, and fully-/partly-included in zircon microphenocrysts) and the apatite in

22   groundmass from the largest Cretaceous Luoboling porphyry Cu–Mo deposit in South

23   China. In combination with thermodynamic models, we reconstructed the volatile

24   behaviour in the ore-forming magma. The analysed apatites are magmatic in origin,

25   without hydrothermal overprint, as indicated by their homogeneous

26   cathodoluminescence (CL) and higher Cl and REE contents than typical hydrothermal

27   apatite. Apatite inclusions fully enclosed in zircon show decreasing X_{Cl}^{Ap}/X_{OH}^{Ap} (1.5-

28   0.1) with increasing X_{F}^{Ap}/X_{OH}^{Ap} (0.4-3.3) and X_{F}^{Ap}/X_{Cl}^{Ap} (0.5-21), and display a steep

29   drop in X_{Cl}^{Ap} at approximately constant X_{OH}^{Ap} in the ternary F–Cl–OH plot. These trends

30   follow the modelled compositional trajectories of isobaric H$_2$O-saturated

31   crystallisation, indicating volatile exsolution during or before zircon crystallisation in

32   the magma chamber. Groundmass apatite crystals, phenocryst-hosted apatite

33   inclusions and apatite inclusions, which are partially enclosed by zircon

34   microphenocrysts, have comparable volatile compositions, with much higher

35   X_{F}^{Ap}/X_{OH}^{Ap} (1.7-78.8) and X_{F}^{Ap}/X_{Cl}^{Ap} (2.3-37.5) but lower X_{OH}^{Ap} and X_{Cl}^{Ap} than those fully

36   enclosed in zircon. Compositional similarities between these crystals in different

37   textural associations indicate that the phenocryst-hosted apatite inclusions do not

38   preserve their original volatile records at the time of entrapment, and the volatile

39   compositions were overprinted by later re-equilibration with the residual melt and the

40   exsolved magmatic fluids. Given the porphyry magma is highly oxidized, and the

41   sulfides phases would be unstable in such circumstance, we suggest that volatile

42   exsolution in the magma chamber is essential for the Cl and Cu-Mo extraction from

43   the melts and therefore the porphyry mineralization. In this study, only zircon-hosted

44   apatite inclusions appear to best record the magmatic volatile compositions in a

45   porphyry system faithfully. Therefore, using apatite hosted in other minerals or

46   groundmass compositions to unravel magma volatile contents in porphyry Cu system

47   should be conducted with caution.

48   **Keywords:** porphyry deposit, apatite inclusions, volatile exsolution, diffusional re-

49   equilibration

50   **1. Introduction**

51   Porphyry-type deposits contribute >75% and 25% of the global Cu and Au

52   reserves, respectively (Sillitoe, 2010). They are usually associated with small shallow-

53   emplaced (1-5 km) intermediate–felsic porphyries, mineralised by the fluids exsolved

54   from underlying magma chambers (5-15 km) (Chiaradia, 2021; Hedenquist and

55   Lowenstern, 1994; Richards, 2011; Sillitoe, 2010). Since Cu, Mo, Au, Cl, and S are

56   strongly partitioned into buoyant magmatic fluids (Audetat and Simon, 2012;

57   Lowenstern, 1994; Williams-Jones and Migdisov, 2014), the volatile exsolution in the

58   magma chamber was suggested to play an essential role in metal extraction and

59   mineralisation (Candela and Holland, 1986; Cooke et al., 2005; Halter et al., 2002;

60   Huber et al., 2012; Nadeau et al., 2010). However, a direct continuous volatile record

61   of the fluid exsolution in the magma chamber is still lacking, as the melt inclusions,

62   the conventional medium for tracing magmatic volatiles, is often compromised by

63   post-entrapment crystallisation and volatile diffusion in the plutonic (porphyry)

64   systems (Bucholz et al., 2013; Gaetani et al., 2012).

65   Apatite [$Ca_5(PO_4)_3$(F, Cl, OH)] incorporates F^-, Cl^-, and OH^- directly into its

66   crystal structure within a dedicated volatile site (Z). Apatite volatile analysis has

67   recently received increasing attention as a new effective way to constrain the

68   magmatic volatile concentration and behaviour in terrestrial (e.g., Boyce and Hervig,

69   2008; Humphreys et al., 2021; Stock et al., 2018) and extraterrestrial (e.g., Boyce et

70   al., 2014; McCubbin and Jones, 2015) systems. Apatite inclusions in volcanic rocks

71   can preserve the record of volatiles at the time of entrapment, even where melt

72   inclusion H_2O concentrations have been modified by post-entrapment processes

73   (Stock et al., 2018; Stock et al., 2016). Notably, zircon-hosted apatite inclusions have

74   been proven resistant to re-equilibration and hydrothermal alteration in granitic and

75   porphyry systems (Bell et al., 2018; Bell et al., 2015; Kendall-Langley et al., 2021; Li

76   et al., 2021; Meng et al., 2022). Thus, apatite inclusions in minerals can potentially

77   record the volatile evolution in porphyry ore-forming magmas.

78   The Luoboling Cu–Mo porphyry deposit was selected for study. The deposit is

79   genetically associated with the largest Zijinshan epithermal-porphyry Cu-Au-Mo ore

80   field in Asia (Fig. 1, Huang et al., 2018; Jiang et al., 2013). We present analysis of the

81   volatile compositions of unaltered apatite inclusions in plagioclase and biotite

82   phenocrysts, in the groundmass, and the tiny apatite inclusions in zircon

83   microphenocrysts from the syn-mineralisation granodiorite porphyry. The apatite

84   inclusions with various textures (phenocryst-, groundmass-hosted, fully included by

85   zircon/partly included by zircon) place constraints on the time when apatite inclusions

86   were isolated from their host melt and may reflect the volatile compositions across the

87   porphyry ore-forming magma evolution. Compared with the apatite thermodynamic

88   model of Stock *et al.* (2018), we unravelled the behaviour of volatile species and

89   delineated a continuous volatile evolution trend for the causative magma of the

90   Luoboling porphyry deposit. This provides insights into the behaviours of both

91   volatile components (Cl and H_2O) and ore metals (Cu and Mo) they carried.

92   **2. Geological Background and Ore Geology**

93   The Zijinshan in southeastern China (Fig. 1a) is the largest epithermal-porphyry

94   orefield in Asia, which contains many epithermal and porphyry deposits associated

95   with the Cretaceous Paleo-Pacific subduction (Fig. 1b) (Huang et al., 2018; Jiang et

96   al., 2013; So et al., 1998; Zhong et al., 2014). These deposits contain 399 metric

97   tonnes (t) Au, 6400 kt Ag, 4.137 Mt Cu, and 110 kt Mo (Zhang, 2013; Zhong et al.,

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98   2014). In particular, the Luoboling porphyry Cu–Mo deposit in northeastern Zijinshan

99   contains 1.4 Mt Cu @ 0.3% and 110 kt Mo @ 0.036% (Zhong et al., 2014).

100   The Neoproterozoic Louziba Group is the oldest stratum in the Zijinshan ore

101   field, which comprises meta-clastic rocks (Fig. 1b). These rocks are unconformably

102   overlain by Upper Devonian and Carboniferous sedimentary rocks. The Lower

103   Cretaceous Shimaoshan Group volcanic rocks are exposed across the Zijinshan

104   orefield (Fig. 1b), which yielded zircon U–Pb ages of 113–93 Ma (Jiang et al., 2013).

105   Intrusions in the Zijinshan ore field were emplaced in the Mesozoic, including

106   the Zijinshan granite complex (zircon U–Pb age: 154–165 Ma; Li et al., 2015), Caixi

107   monzogranite (zircon U–Pb age: 157–150 Ma; Jiang et al., 2013), Sifang granodiorite

108   (zircon U–Pb age: 112 ± 1 Ma; Jiang *et al*., 2013), Luoboling granodiorite porphyry

109   (zircon U–Pb age: 97–103 Ma; Huang et al., 2013), and the Zhongliao porphyritic

110   granodiorite (zircon U-Pb ages of 95.9 ± 0.6 Ma; Li and Jiang, 2014). The Luoboling

111   granodiorite porphyry intrudes the Sifang granodiorite and Caixi monzogranite (Fig.

112   1b). The Zhongliao porphyritic granodiorite was revealed by drilling to underly the

113   Luoboling granodiorite porphyry (Fig. 2).

114   Porphyry mineralisation occurred mainly in the Luoboling granodiorite

115   porphyry. There are three main hydrothermal alteration stages (I to III) at Luoboling:

116   (I) potassic–silicic (K-Q) alteration; (II) phyllic (Phy) alteration; and (III) alunite-

117   dickite (Alu-Di) alteration, which are spatially associated with pyrite, bornite, and

118   digenite mineralization (So et al., 1998, Zhong et al., 2014). This alteration is

119   generally located in the exocontact of the Zhongliao porphyritic granodiorite (Fig. 2).

120   The porphyry Cu–Mo mineralisation generally occurred (as veinlet or disseminated

121   sulfides) where the K-Q alteration was overprinted by Phy alteration (K-Q+Phy). Ore

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122   minerals at the Luoboling deposit include mainly pyrite, chalcopyrite, and

123   molybdenite.

124   **3. Sample Description**

125   Luoboling granodiorite porphyry samples (LBL-82 and LBL-77) were collected

126   from drill holes ZK405 at 680 m and 682 m depth, respectively. The granodiorite

127   porphyry includes phenocrysts (>0.5 mm) of plagioclase (~25 vol.%), biotite (~5

128   vol.%), and quartz (~5 vol.%) within a groundmass of quartz (~25 vol.%), K-feldspar

129   (~25 vol.%), biotite (~10 vol.%), plagioclase (~5 vol.%), and anhydrite (<5 vol.%)

130   (Fig. 3a). Accessory minerals (<5 vol.%) mainly consist of apatite, zircon, and

131   magnetite. The samples are weakly altered, yet most minerals appear fresh (Fig. 3a).

132   Zircon occurs in the groundmass (Fig. 3b) or as inclusions within other

133   phenocryst phases (Fig. 3c). Zircons in the groundmass are more elongate than those

134   hosted in the phenocrysts, and their length-width ratios are >3 for the former (Fig. 3b)

135   and 2-3 for the latter (Fig. 3c). Tiny apatite inclusions widely occur within the zircon

136   grains (Fig. 4). Apatite crystals occur mainly as inclusions within plagioclase (Fig. 3c)

137   and biotite phenocrysts (Fig. 3d) or in the groundmass (Fig. 3e-f). The groundmass-

138   hosted apatites are either enclosed by other phases (i.e., quartz and K-feldspar) or as

139   interstitials among other minerals (Fig. 3e). Most apatite crystals are euhedral and

140   clear without fluid or mineral inclusions (Fig. 3c-e). Some apatite grains, especially

141   the apatite micro-phenocrysts (> 200 μm) in the groundmass, were altered and contain

142   abundant fluid inclusions and monazite inclusions (Fig. 3f).

143   In this study, we divided the primary apatite inclusions into three types based on

144   their occurrences, namely those (1) included in zircon; (2) included in phenocrysts;

145   (3) in the groundmass.

146   **4. Sample Preparation and Methods**

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4.1 Sample preparation

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148   Polished thin sections were made from each sample. About 1 kg of the

149   granodiorite porphyry was crushed and sieved to extract zircon microphenocrysts

150   from the 300–350 μm size fraction using conventional density and magnetic

151   separation techniques. Euhedral, clear zircon crystals (> 200μm) were handpicked

152   under a binocular microscope, which were then mounted in epoxy and polished before

153   the analysis. Cathodoluminescence (CL) imaging was performed (with 10 kV

154   acceleration voltage) to reveal zircon zoning textures and zircon-hosted apatite

155   inclusions.

156   **4.2 Apatite minerology**

157   CL imaging and *in situ* element mapping were carried out at the iCRAG Lab in

158   Trinity College Dublin, Ireland. Samples were first coated with 12 nm of carbon

159   before being introduced to a TESCAN S8000 field emission scanning electron

160   microscope (FE-SEM) operating with TESCAN Essence software platform (2018).

161   The SEM was used for imaging and performing a fully quantitative energy dispersive

162   x-ray spectroscopy (EDX) chemical analysis of the apatites. The instrument is

163   equipped with Bright Beam SEM column technology, backscatter electron (BSE)

164   imaging, colour CL detectors, and four Oxford Instruments X-Max 170 mm^2

165   detectors, with AZtec software version 5.1 used to interpret the EDX results. The CL

166   imaging was conducted on carbon-coated thin sections using a colour

167   cathodoluminescence detector at an acceleration voltage of 15 kV, a beam current of

168   3nA, a working distance of 15 mm, and an image scanning speed of 320 μs per pixel.

169   The EDX analysis was carried out with an acceleration voltage of 20 kV, a beam

170   current of 3 nA, and a working distance of 15 mm.

171   **4.3 Electron probe microanalysis**

172   ***Apatite inclusions***

173   Before the geochemical analysis, we observed the sample and crystal texture

174   using an optical microscope and BSE imaging. The BSE imaging was conducted on

175   carbon-coated thin sections, using an accelerating voltage of 15 kV. Only the

176   inclusion-free, euhedral plagioclase-/biotite-hosted apatite inclusions and

177   groundmass-hosted apatite grains with homogeneous or zoned texture under BSE

178   imaging were selected for further study. Cathodoluminescence was conducted on the

179   apatite-host zircon to reveal the zircon internal texture. The zircon grains were briefly

180   polished before analysing the apatite inclusions to mitigate any potential beam

181   damage.

182   Major element compositions of the apatite inclusions were determined on a

183   JEOL JXA-8100 electron probe microanalyser (EPMA) at the State Key Laboratory

184   for Mineral Deposits Research, Nanjing University (China). Analysis was conducted

185   under 15 kV, 20 nA, and 2 μm beam size to generate sufficient counts to quantify the

186   low Cl content in the tiny apatite inclusions. Although these analytical conditions risk

187   minor electron-beam-induced sample damage (Goldoff et al., 2012; Stock et al., 2015;

188   Stormer et al., 1993), F and Cl were analysed first using shorter analysis times to

189   minimise this effect. The peak/background elemental counting times were

190   10/5 s for P, Ca, Cl and F, 20/10 s for Si. The standards used for the analysis included

191   the Durango apatite for Ca, P, and F, almandine for Si, barite for S, and tugtupite for

192   Cl. Previous studies have revealed the time-dependent variation in apatite halogen X-

193   ray counts during EPMA analysis (Goldoff et al., 2012; Stock et al., 2015). The effect

194   is most pronounced when the electron beam is oriented parallel to the crystallographic

195   c-axis, whereas it is minimal when the beam is parallel to the a- or b-axis (Goldoff et

196   al., 2012; Stock et al., 2015). The grains whose c-axis is parallel to the beam were

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197   discarded to minimise the problem induced by the apatite anisotropy. We discarded

198   the apatite grains with a hexagonal symmetry (whose c-axis is likely beam-parallel;

199   crystals marked with white circles in Fig. 4b) and selected only the elongated apatite

200   grains (whose c-axis is likely beam-perpendicular; crystals marked with yellow, red,

201   and green circles in Fig. 4b). Analytical accuracy is <1% for P, <2% for Ca and F, and

202   <5% for Cl. Relative precision, quantified through repeated analyses of the

203   Wilberforce apatite, is ±2% for Ca, P, and F and ± 4% for Cl (Table DR 1). The mole

204   fractions of fluorapatite and chlorapatite are calculated directly from the concentration

205   of F and Cl, with the mole fraction of hydroxyl-apatite (apatite OH content) estimated

206   using the approach in Ketcham (2015).

207   ***Biotite and plagioclase phenocrysts***

208   Major element compositions of the apatite-hosting biotite and plagioclase were

209   analysed on a JXA-8230 EMPA at the Key Laboratory of Mineralogy and

210   Metallogeny (KLMM), Guangzhou Institute of Geochemistry, Chinese Academy of

211   Science (GIG CAS). The analysis was carried out using a 15 kV accelerating

212   voltage, 20 nA probe current, and 1 μm beam diameter. Peak/background counting

213   times are 20/10 s for Si, Al, Mg, Fe, and Ti,10/5 s for K, Na, F, and Cl, 40 s for Mn,

214   and 20 s for Ca. The calibration standards include biotite for Si, magnetite for Fe,

215   olivine for Mg, almandine for Al, rutile for Ti, rhodonite for Mn, orthoclase for

216   K, albite for Na, Cr-diopside for Ca, BaF_2 for F, and tugtupite for

217   Cl. ZAF (Z: atomic number; A: absorption; F: fluorescence) calibration procedures we

218   re used to reduce the matrix effect.

219   **4.4 Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)**

220   **analysis**

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221   Trace element contents of zircon were analysed on an ELEMENT XR (Thermo

222   Fisher Scientific) ICP-SF-MS coupled with a 193-nm (ArF) Resonetics RESOlution

223   M-50 laser ablation system at GIG CAS. The analysis consisted of a 33 μm laser spot

224   size with a repetition rate of 5 Hz and an energy fluence of 4 J/cm^{-2}. NIST SRM 610

225   glass (Jochum et al., 2011; Pearce et al., 1997) and Temora zircon (Black et al., 2003)

226   standards were used for external calibration. A detailed analytical procedure is

227   described by Zhang et al.(2019).

228   We used LA-ICP-MS to analyse the apatite trace element contents at the School

229   of Resources and Environmental Engineering, Hefei University of Technology, using

230   an Agilent 7900 ICP-MS coupled with a 193-nm (ArF) Analyte HE laser-ablation

231   system. The analysis used a 30 μm beam with a repetition rate of 8 Hz and an energy

232   fluence of 4 J/cm^2. NIST SRM 610, NIST SRM 612, and BCR-2G were used for

233   external standards. The Ca concentration determined by EMPA was used as the

234   internal standard. The offline data processing, time-drift correction, and quantitative

235   calibration of both the zircon and apatite data were carried out with the

236   ICPMSDataCal program (Liu et al., 2008).

237   **5. Results**

238   **5.1 Host mineral compositions and saturation temperature**

239   Biotite phenocrysts are euhedral and un-zoned (Fig. 3d) and have near-

240   homogeneous interagrain compositions (Fig. DR2). They have high Mg# (molar

241   Mg/(Mg+Fe): 0.69–0.72; Table DR3) and TiO_2 content (3.65–4.82 wt.%), indicating

242   a magmatic origin (Rasmussen and Mortensen, 2013) despite weak alteration.

243   Following Henry et al. (2005), we calculated the Ti-in-biotite saturation temperature

244   to be 759–789 °C (mean= 777 ± 8 °C, n=25; Table DR3). The Al-in-biotite barometer

245   for granites was used to estimate the crystallisation pressure (Uchida et al., 2007). The

246   pressures at the time of biotite crystallisation are 167–249 MPa (mean 205 ± 24 MPa).

247   The water solubility at this pressure was estimated with the equation by Tattitch et al.

248   (2021), which yielded 6.14 ± 0.49 wt.% (n = 25; Table DR3).

249   Plagioclase phenocrysts are euhedral and concentric oscillatory-zoned (Fig. 3a,

250   3c). They are andesine in composition, with An values (100 × molars CaO/(CaO +

251     $Na_2O + K_2O$) of 37–46 (Table DR4), and display a progressive decrease from core

252   ($An_{41–46}$) to rim ($An_{37–43}$). The An in plagioclase is sensitive to the magmatic water

253   content and temperature, but less sensitive to pressure (Water and Lange, 2015). The

254   plagioclase hygrometer is used to estimate the magmatic water content at the time of

255   plagioclase crystallisation (Water and Lange, 2015). Since the plagioclase and the

256   biotite phenocrysts should have both crystallised in the magma chamber, the biotite

257   thermobarometer (205 MPa) and the Ti-in-biotite saturation temperature (777 °C)

258   were used to estimate the water content. The average magmatic water content for the

259   sample was estimated to be 6.62 ± 0.07 wt.% (n = 16), similar to the results from

260   biotite.

261   Our zircon samples show oscillatory zoning in CL images (Fig. 4b). They have

262   ∑REE and Y concentrations of 727 to 1339 ppm (Table DR2) with strong LREE

263   depletion and positive Ce anomalies typical of igneous zircons (Fig. DR1), indicating

264   a lack of hydrothermal alteration (Fu et al., 2009; Hoskin, 2005). Following Loucks et

265   al. (2020), we calculated the Ti-in-zircon saturation temperature with pressure

266   correction. As quartz is a matrix constituent in the granodiorite porphyry, this

267   suggests that $\alpha SiO_2 = 1$. The presence of titanite indicates that αTiO_2 should be ~0.7

268   (Chelle-Michou et al., 2014). In our calculation, we used 1.0 and 0.7 for αSiO_2 and

269   αTiO_2, respectively.The estimated pressure for correction is 205 MPa (Table DR3,

270   Uchida et al., 2007). The analysis yielded apparent temperatures of 722–818 °C

271 (mean $766 \pm 29°C$, n = 13; Table DR2), broadly consistent with the Ti-in-zircon

272 saturation temperatures reported from other porphyry deposits (e.g., 750-650 °C at

273 Bajo da la Alumbrera (Argentina); Buret et al., 2016; 850-700°C at Yanacocha

274 (Puru), and Yerington (Nevada); Dilles et al., 2015). The zircon oxybarometer in

275 Loucks et al. (2020) was used to calculate the oxygen fugacity of the magma, which

276 yielded $\Delta FMQ + 0.9$ to $\Delta FMQ + 1.6$ (mean $= \Delta FMQ + 1.2$, n = 13).

277 **5.2 Cathodoluminescence features and Cl distribution**

278 The magmatic apatite grains in groundmass (Fig. 5a-c), biotite phenocryst (Fig.

279 5d-f), and plagioclase phenocryst (Fig. 5g-i) are texturally homogeneous under BSE

280 imaging and display pink to purple luminescence under CL imaging. Some grains

281 contain brown luminescence patches (Fig. 5b). The unaltered magmatic apatite grains

282 consistently show a homogeneous intragrain Cl concentration (Fig. 5c, f, and i),

283 regardless of their luminescence.

284 The altered apatite grains are characterized by containing fluid inclusions or

285 monazite inclusions and voids in BSE images (Fig. 5j), and complex textures under

286 the CL imaging (Fig. 5k). They consist of the remnants of magmatic apatite with

287 brown or pink luminescence, and the hydrothermal apatite with blue-grey

288 luminescence (Fig. 5k). The hydrothermal apatite form euhedral rims with light-blue

289 luminescence, overgrown on a grey-dark luminescence core (Fig. 5k). Monazite

290 inclusions in the grey-dark luminescence core indicate a fluid-coupled dissolution-

291 reprecipitation process within apatite during the alteration (Harlov et al., 2002; Harlov

292 and Förster, 2003). Element distribution in the altered apatite shows a sharp

293 compositional boundary, with the hydrothermal replaced/altered parts having a much

294 lower Cl content than the magmatic apatite remnants (Fig. 5l). This reflects the

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295   interaction with hydrothermal fluids where Cl partitions into the fluid phase (Webster

296   et al., 2009).

297   **5.3 Apatite trace element composition**

298   Trace element composition of 17 unaltered magmatic apatite grains (7 phenocryst-

299   host and 10 in groundmass) and 4 altered apatites measured by LA-ICP-MS are

300   shown in Fig. 6 and listed in Table DR5.

301   The 17 unaltered apatite in phenocrysts phases yield REE+Y contents of 3433-

302   5412 ppm (mean 4289 ppm, n = 7) and slight LREE-enriched patterns ($(La/Yb)_N$ =

303   2.41-3.04) (Fig. 6). The apatite in the groundmass has REE+Y contents of 3017-6024

304   ppm, (mean 4422 ppm, n = 10) and $(La/Yb)_N$ = 2.43-3.08, comparable to those of the

305   apatite in phenocrysts.

306   The altered apatite has much lower REE+Y contents (449-1482 ppm) with higher

307    $(La/Yb)_N$ (5.04-16.1) than those of the unaltered apatite (Fig. 6). This composition is

308   consistent with the altered apatite in other porphyry systems (Bouzari et al., 2016),

309   indicating REE dissolution and remobilisation by the hydrothermal fluids.

310   **5.4 Apatite volatile compositions**

311   The EPMA volatile element compositions of the apatite inclusions in zircon

312   microphenocrysts, apatite inclusions in phenocryst phases, and apatite in the

313   groundmass are summarised in Table 1, shown in Fig. 7, and detailed in Table DR6-

314   DR8.

315   *Apatite inclusions in zircon microphenocrysts*

316   We further divided the zircon-hosted apatite inclusions into three textural sub-

317   groups (Fig. 4b): (1) apatite fully enclosed in the zircon core; (2) apatite fully

318   enclosed in the zircon rim; (3) apatite partially enclosed in zircon. In total, we

319   analysed 93 apatite inclusions in 25 zircons, and the results are listed in Table DR6.

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320   Zircon-hosted apatite inclusions display significant intragrain variation in their

321   halogen contents (Fig. 7; Table 1).

322   Apatite from the zircon core has 0.78–1.51 wt.% (mean 1.05 wt.%, n = 15) F,

323   1.40–2.72 wt.% (mean 1.96 wt.%) Cl, and 1.12–1.79 wt.% (mean 1.38 wt.%) OH.

324   This equates to X_F^{Ap}/X_{OH}^{Ap}, X_{Cl}^{Ap}/X_{OH}^{Ap}, and X_F^{Ap}/X_{Cl}^{Ap} ratios of 0.4–1.2, 0.4–1.0, and

325   0.5–1.8, respectively (where X_F^{Ap}, X_{Cl}^{Ap}, and X_{OH}^{Ap} are mole fractions of F, Cl, and OH

326   in apatite, respectively).

327   Apatite from the zircon rim has slightly higher F (0.67–2.61 wt.%, mean 1.20

328   wt.%, n = 58), similar Cl (0.20–2.97 wt.%, mean 1.98 wt.%), and lower OH (0.69–

329   1.65 wt.%, mean 1.20 wt.%) contents than apatite from the zircon core. Their

330   X_F^{Ap}/X_{OH}^{Ap}, X_{Cl}^{Ap}/X_{OH}^{Ap}, and X_F^{Ap}/X_{Cl}^{Ap} ratios are of 0.4–3.3, 0.1–1.5, and 0.5–21,

331   respectively.

332   Apatite partly enclosed by zircon has higher F content (1.44–2.65 wt.%, mean

333   1.94 wt.%, n = 17), lower Cl (0.41–1.93 wt.% mean 1.21 wt%), and lower OH

334   contents (0.72–1.44 wt.%, mean 0.97 wt%) than apatite fully enclosed by zircon.

335   Their X_F^{Ap}/X_{OH}^{Ap}, X_{Cl}^{Ap}/X_{OH}^{Ap}, and X_F^{Ap}/X_{Cl}^{Ap} ratios are 0.9–3.2, 0.2–1.0, and 1.5–12.1,

336   respectively.

337   ***Apatite inclusions in phenocryst phases***

338   We analysed 41 apatite inclusions from 13 biotite phenocrysts and 18 apatite

339   inclusions from 8 plagioclase phenocrysts (Fig. 7 and Table DR7). These apatite

340   inclusions are all fully enclosed in their host phenocrysts. Apatite from the biotite

341   phenocrysts exhibits a more restricted compositional range than the zircon-hosted

342   inclusions, with 1.85–3.45 wt.% (mean 2.26 wt.%) F, 0.20–1.45 wt.% (mean 1.22

343   wt.%) Cl, and 0.07–1.01 wt.% (mean 0.67 wt.%) OH. This equates to X_F^{Ap}/X_{OH}^{Ap},

14

344   X_{Cl}^{Ap}/X_{OH}^{Ap}, and X_{F}^{Ap}/X_{Cl}^{Ap} ratios of 1.7–38, 0.4–9.2, and 2.5–32, respectively. Apatite

345   from the plagioclase phenocrysts has a volatile composition similar to those for

346   apatite hosted by biotite, with 2.13–3.35 wt.% (mean 2.64 wt.%) F, 0.18–1.47 wt.%

347   (mean 0.87 wt.%) Cl, and 0.06–0.84 wt.% (mean 0.49 wt.%) OH contents. This

348   equates to X_{F}^{Ap}/X_{OH}^{Ap}, X_{Cl}^{Ap}/X_{OH}^{Ap}, and X_{F}^{Ap}/X_{Cl}^{Ap} ratios of 2.4–49.0, 0.15–5.4, and 3.1–

349   35, respectively.

350   ***Apatite crystals in groundmass***

351   We analysed 49 apatite grains in the groundmass (Table DR8). They have 1.92–

352   3.39 wt.% (mean 2.59 wt.%) F, 0.15–1.55 wt.% (mean 1.07 wt.%) Cl, and 0.04–0.87

353   wt.% (mean 0.44 wt.%) OH. This equates to X_{F}^{Ap}/X_{OH}^{Ap}, X_{Cl}^{Ap}/X_{OH}^{Ap}, and X_{F}^{Ap}/X_{Cl}^{Ap}

354   ratios of 2.1– 78.8, 0.1–18.4, and 2.3–37.5, respectively.

355   **6. Discussion**

356   **6.1 Apatite origin and textural constraints on the timing of apatite entrapment**

357   Porphyry mineralization accompanies hydrothermal alteration, which may alter

358   the magmatic apatite and modify its geochemical composition (Bouzari et al., 2016;

359   Xing et al., 2020). Therefore, only the primary apatite free from alteration would

360   preserve the magmatic volatile record. Altered apatite is usually depleted in Mn, REE,

361   and Y, and forms new REE phosphates (incl. monazite inclusions; Xing et al., 2019;

362   Bouzari et al., 2016), due to the coupled dissolution-reprecipitation mechanism

363   (Harlov et al., 2002; Harlov and Förster, 2003; Harlov et al., 2005). Since Mn and

364   REEs are the most common CL activators in apatite (Barbarand and Pagel, 2001;

365   Roeder et al., 1987), altered apatite usually shows replacement texture in CL images.

366   Moreover, altered apatite in the porphyry systems is characterised by extremely low

367 Cl contents regardless of alteration types (Bouzari et al., 2016) because Cl partitions

368 more strongly into fluids than apatite (Webster et al., 2009).

369   In our study, the textures and geochemical compositions of zircon, biotite, and

370 plagioclase phenocrysts indicate that these minerals are magmatic in origin and free of

371 or weakly affected by hydrothermal alteration (section 5.1). Thus, the apatite

372 inclusions in these minerals should be magmatic in origin and be isolated from

373 hydrothermal alteration. The magmatic apatite grains analysed are free of fluid

374 inclusions with homogeneous or zoned texture under BSE (Fig. 5a, d, g) and CL

375 imaging (Fig. 5b, e, h). Compositionally, the apatite grains analysed yielded Mn/Fe

376 >1 and much higher REE+Y contents (>3000 ppm) than those of the altered apatite

377 (<1000 ppm), further indicating that they are unaltered (Bouzari et al., 2016). Besides,

378 the apatite in our study yielded Cl contents > 0.1 wt.% and plot on a continuous

379 composition trend in the ternary F–Cl–OH plot (Fig. 7g). Such a compositional trend

380 is inconsistent with the low Cl content for the apatite altered by hydrothermal fluids

381 (Bouzari et al., 2016), which should have recorded the magmatic volatile evolution.

382   Since our apatite grains should record magmatic volatile compositions (either the

383 timing of entrapment or re-equilibration), compositional comparison of apatite with

384 different textures could provide relative temporal constraints on the magmatic volatile

385 evolution. Phenocrysts are crystallised in the magma chamber, whereas the

386 groundmass phases are formed by rapid crystallisation during the magma ascent or

387 degassing in the roof of the magma chamber (Burnham, 1967). Thus, unless their host

388 phenocrysts did not provide an effective barrier from re-equilibration, apatite

389 inclusions that are fully enclosed by phenocrysts should have recorded the volatile

390 composition of melt at an earlier stage compared with apatite in the groundmass,

391 which can re-equilibrate with their host magma (and the exsolved fluid) until a late

392 stage.

393 Some zircon microphenocrysts contain more than one apatite inclusion, which

394 may be fully or partially enclosed by the host zircon. The former may preserve a

395 record of melt volatile evolution, whereas the latter may record the volatile

396 equilibration with the ambient magma. For these zircons, we assume that apatite fully

397 enclosed in the zircon core was entrapped before those in the zircon rim, and that both

398 inclusion types would preserve the volatile record at the time of entrapment. In

399 contrast, apatite partly enclosed by a zircon microphenocryst was likely in contact

400 with the ambient melt until solidification and could re-equilibrate with volatiles from

401 a later-stage melt, similar to the case of groundmass apatite.

402 **6.2 Apatite compositional evolution in an H$_2$O-saturated porphyry magma**

403 **chamber**

404 As F, Cl, and OH are stoichiometric constituents in the crystal structure of

405 apatite, their crystal-melt partitioning is non-Nernstian and can be described by a

406 series of exchange reactions in the form:

407 $$X_{Cl}^{Ap} + X_{OH}^{M} \leftrightarrows X_{Cl}^{M} + X_{OH}^{Ap} \tag{1}$$

408 where the superscripts denote apatite (Ap) and melt (M).

409 The equilibrium relationship between the volatile composition of apatite crystals

410 and their host melt can be expressed by K$_D$ exchange equations of the form:

411 $$K_{D\,(Cl-OH)}^{Ap-M}(P,T) = \frac{X_{Cl}^{AP}}{X_{OH}^{Ap}} \times \frac{X_{OH}^{M}}{X_{Cl}^{M}} \tag{2}$$

412 where the exchange coefficients (K$_D$) are constant at a given pressure and

413 temperature (Piccoli and Candela, 1994). Equation 2 assumes that F–Cl–OH exchange

414 in apatite behaves as an ideal solid solution; although this may not be strictly true, it is

415   consistent with the available experimental data (see the discussion in Stock *et al.*

416   2018). A comparison of ideal vs non-ideal apatite thermodynamic models suggests

417   that any non-ideality must be small (Humphreys et al., 2021).

418   Stock et al. (2016, 2018) proposed a thermodynamic model to calculate the

419   apatite compositional evolution during H_2O-undersaturated and H_2O-saturated

420   magmatic crystallisation by varying the modelling parameters (incl. crystal–melt and

421   fluid–melt volatile partition coefficients, initial melt volatile content, and melt H_2O

422   solubility). The modelling compositional trends can be compared with datasets of

423   natural apatite to determine whether the magma, the apatite crystallised from, was

424   H_2O-saturated.

425   Regarding our textural constraints, X_{Cl}^{Ap}/X_{OH}^{Ap} appears to decrease while X_F^{Ap}/X_{OH}^{Ap}

426   and X_F^{Ap}/X_{Cl}^{Ap} appears to increase during magma evolution, from apatite fully

427   enclosed by zircon (esp. apatite in the zircon core, which was isolated from the earlier

428   melt) to apatite partly enclosed by zircon (which re-equilibrated with the later melt)

429   (Fig. 7c, f). The compositional trajectory recorded by zircon-hosted apatite is

430   inconsistent with cooling at a constant melt composition, which would generate

431   apositive X_{Cl}^{Ap}/X_{OH}^{Ap} vs. X_F^{Ap}/X_{OH}^{Ap} correlation (Piccoli and Candela, 1994; Stock et al.,

432   2018). The compositional trajectory is also inconsistent with volatile-undersaturated

433   crystallisation models, which are characterised by decreasing X_F^{Ap}/X_{Cl}^{Ap} and away

434   from the F apex in the ternary F–Cl–OH plot during magma evolution (Stock et al.,

435   2018). This is because F partitions more strongly into common hydrous minerals (e.g.,

436   apatite, biotite, and amphibole) than Cl, while Cl partitions more strongly than OH

437   (i.e., $\overline{D}_F^{C/M} > \overline{D}_{Cl}^{C/M} > \overline{D}_{OH}^{C/M}$; Benard et al., 2017; Li and Hermann, 2015; Mathez and

438   Webster, 2005; Van den Bleeken and Koga, 2015). This is especially true, if the Cl

18

439   partition coefficient between the mineral and the melt ($\overline{D}_{Cl}^{C/M}$) is extremely low, the

440   water under-saturated evolution would produce increasing X_{Cl}^{Ap}/X_{OH}^{Ap} with decreasing

441   X_{F}^{Ap}/X_{OH}^{Ap} and X_{F}^{Ap}/X_{Cl}^{Ap}, similar to the negative correlation trends observed in our

442   zircon-hosted apatite inclusions (Fig. 7c and 7f; Stock et al., 2018). However, this is

443   inconsistent with that of a porphyry magma, which should have a relatively high

444     $\overline{D}_{Cl}^{C/M}$ due to the crystallisation of abundant Cl-bearing biotite and amphibole

445   (Richards et al., 2012). Besides, the decreasing F and increasing Cl content of the

446   melts during water-undersaturated evolution with low $\overline{D}_{Cl}^{C/M}$ would drive apatite

447   compositionally away from the F apex and towards the Cl apex in F-Cl-OH space

448   (Stock et al., 2018), which is opposite to the trend shown by our samples (Fig. 7g).

449   Instead, the compositional trend of our apatite inclusions closely matches those of the

450   H_2O-saturated crystallisation models (Fig. 7g), where Cl is partitioned from the melt

451   into an exsolving vapour phase while F is retained in the felsic melt (Candela, 1986;

452   Cassidy et al., 2022; Doherty et al., 2014; Stock et al., 2018; Webster et al., 2009). As

453   the solubility of H_2O in a magmatic system is mainly pressure-dependent, the

454   trajectory of apatite volatile evolution should be different during isobaric and

455   polybaric (decompressed) H_2O-saturated crystallisation. After H_2O saturation in the

456   isobaric scenario (i.e., second boiling), the melt water concentration remains constant,

457   water is exsolved due to continuous crystallisation, and changes in apatite volatile

458   concentration are driven primarily by partitioning of Cl into the vapour phase. In the

459   F-Cl-OH ternary space (Fig. 7g), following H_2O-saturation under isobaric conditions,

460   apatite compositions would move directly towards the F–OH binary, as Cl is strongly

461   partitioned into the vapour, before moving towards the F apex (Stock et al., 2018).

462   After H_2O saturation in the polybaric scenario (i.e., first boiling), the melt H_2O

463   concentration drops due to its decreasing solubility during decompression. The Cl

464   partition coefficients for fluid-melt are pressure dependent (Tattitch et al., 2021) but

465   always larger than 1 in felsic melts (Aiuppa et al., 2009; Webster et al., 2009), thus

466   the melt Cl still partitions into the vapour phase. The apatite compositions are

467   influenced by the decrease of both H_2O and Cl in the melt. In the ternary F-Cl-OH

468   plot, following H_2O-saturation under polybaric conditions, the apatite compositions

469   would move closer to the F apex than the trends created by the isobaric scenario, as

470   the H_2O is extracted from the melt alongside Cl (Fig. 7g; Stock et al., 2018). The

471   pressure dependence of apatite–melt K_D values would be superimposed on these

472   compositional changes, but the variation caused by this dependence is expected to be

473   small over the normal crustal pressure range (Riker et al., 2018).

474   The apatite fully enclosed by zircon displays a steep drop in X_{Cl}^{Ap} at

475   approximately X_{OH}^{Ap} in the ternary F–Cl–OH plot (Fig. 7g), consistent with the

476   trajectories modelled by isobaric H_2O-saturated (the continuous lines in Fig. 7g) and

477   the slowly-decompressed H_2O-saturated crystallisation (red dashed line in Fig. 7g,

478   Stock et al., 2018). This indicates that the apatites were entrapped by zircons at

479   relatively constant magmatic H_2O content/solubility, which likely took place in the

480   magma chamber. Therefore, we suggest that the apatite grains fully enclosed by

481   zircons recorded the volatile exsolution in the magma chamber. The fertile Zijinsan

482   porphyry magma likely reached water saturation during/before zircon crystallisation

483   in the magma chamber.

484   An alternative explanation is that the compositional trends of apatite in zircons

485   are controlled by the assimilation of Cl-depleted or F-enriched material, which would

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486 increase the apatite X_F^{Ap} and drive crystals towards higher X_F^{Ap}/X_{OH}^{Ap} and X_F^{Ap}/X_{Cl}^{Ap}

487 ratios. However, a large amount of Cl-depleted or F-enriched material would be

488 required to decrease the apatite X_{Cl}^{Ap} by 80% (according to our data) within the time

489 frame of zircon growth. Furthermore, the most probable Cl-depleted and F-enriched

490 endmember in the Zijinshan district is the Proterozoic sedimentary rocks. Zircon Hf

491 isotopic analysis of the Luoboling granodiorite porphyry indicated that their

492 assimilation was insignificant (Huang et al., 2018; Jiang et al., 2013; Li and Jiang,

493 2014). This further suggests that assimilation of Cl-depleted or F-rich materials is

494 unlikely the cause of decreasing X_{Cl}^{Ap} and X_{Cl}^{Ap}/X_{OH}^{Ap}, and increasing X_F^{Ap}/X_{OH}^{Ap} and

495 X_F^{Ap}/X_{Cl}^{Ap} in zircon hosted apatite.

496   The thermobarometer for the biotite (Uchida et al., 2007) indicates that the

497 pressure of the Zijinshan fertile magma chamber was ~205 MPa (eqv. ~6.8 km depth)

498 and comparable to those of most porphyry magma chambers around the world

499 (5~15km, Sillitoe, 2010). Since our fertile porphyry magma has achieved water

500 saturation in the chamber, the water solubility estimated by the pressure should

501 represent the water content (~6.14 wt.%). The result is close to the water content

502 estimated by the plagioclase phenocryst compositions (~ 6.62 wt.%). Both results

503 suggest that the fertile porphyry magma was characterized by a significantly higher

504 water content than the common arc magmas (~ 4 wt.%; Plank et al., 2013). The high-

505 water content should therefore be the key factor contributing to the water saturation in

506 the magma chamber at the time of the zircon-apatite crystallisation. Meanwhile, a

507 high magmatic water content is not unique for fertile porphyry systems. Similar

508 magmatic water contents (> 6 wt.%) have been reported in many subduction-related

509 porphyry ore systems, such as the Rio Blanco in Peru (Chen et al, 2022), and the

510 Santo Tomas II, Black Mountain, Clifton, and Bumolo in the Philippines (Huang et al,

511 2023a).

6.3. Volatile re-equilibrium between non-zircon hosted apatite and the melt after

magma chamber exsolution

514 Given that the Ti-in-biotite saturation temperatures (mean 777 ± 7 °C) are

515 similar with the Ti-in-zircon saturation temperatures (mean 766 ± 29 °C), and that

516 plagioclase likely reaches the liquidus substantially earlier than zircon, we would

517 expect the biotite and plagioclase phenocrysts hosted apatite inclusions to record a

518 period during magmatic volatile evolution that was simultaneous with or earlier than

519 that of the fully enclosed zircon-hosted apatite inclusions (i.e., equal or higher X_{OH}^{Ap}

520 and X_{Cl}^{Ap}, and lower X_F^{Ap}/X_{OH}^{Ap} and X_F^{Ap}/X_{Cl}^{Ap}). In fact, despite having some

521 compositional overlap with fully enclosed zircon-hosted inclusions, apatite inclusions

522 in the biotite and plagioclase phenocrysts extend to markedly higher X_F^{Ap}/X_{OH}^{Ap} (Fig.

523 8b) and X_F^{Ap}/X_{Cl}^{Ap} (Fig. 8e), and lower X_{Cl}^{Ap} and X_{OH}^{Ap} (Fig. 7g), similar to the apatite

524 partly enclosed by zircon or that in the groundmass (Fig. 7).

525 While groundmass apatite crystals may have grown from a late-stage melt,

526 after significant degassing and shortly before emplacement, we might expect

527 inclusions within phenocrysts and zircon microphenocrysts to preserve a volatile

528 record earlier in magmatic evolution, at or before their entrapment. Their

529 compositional correlation with groundmass crystals can be explained by diffusional

530 re-equilibration with the late-stage melt and exsolved fluid, which can occur within

531 days to months under magmatic conditions (Stock et al. 2016; Li et al, 2020). In the

532 case of zircon-hosted inclusions which were not fully enclosed by their host crystals,

533 diffusive re-equilibration is possible because crystals had not been isolated from their

22

534   host magma. In terms of inclusions within plagioclase and biotite phenocrysts, these

535   phases are weakly altered in our porphyry samples (Fig. 3), likely due to interaction

536   with exsolved Cl-rich magmatic fluids. This might have compromised them as an

537   inclusion host and permitted re-equilibration of apatite inclusions (Krause et al.,

538   2013).

539   The complexity of apatite volatile compositions in porphyry system might also

540   be explained by the slower cooling and the longer lifespan (100,000 to several million

541   years; Sillitoe, 2010) of the porphyry systems, which is long enough for volatile

542   diffusion to achieve re-equilibrium under high (magmatic) temperatures (Brenan,

543   1994; Costa et al., 2008; Costa et al., 2020). This is in contrast to previous analyses of

544   non-porphyry volcanic apatite inclusions, where common phenocrysts appear to be

545   reliable host phases, permitting apatite inclusions to retain a volatile record at their

546   time of entrapment (Stock et al., 2018). Nevertheless, our data indicate that zircon

547   could robustly shield the fully enclosed apatite inclusions from diffusive re-

548   equilibration in porphyry systems, allowing them to preserve their primary volatile

549   composition at the time of entrapment. This is consistent with the recent experimental

550   study, which indicates that zircon can resist alteration by Cl-rich fluids at magmatic

551   conditions (900ºC and 1000 MPa; Harlov et al., 2023).

552   The steep decreases in X_{Cl}^{Ap} and X_{OH}^{Ap} between apatite inclusions which are

553   fully enclosed by zircon host crystals and those in other textural associations (i.e. all

554   of our crystals which are not fully enclosed within zircon; Fig. 7g) indicates a

555   substantial depletion of Cl in the melt by the exsolving H_2O-rich fluids. This is

556   consistent with the volatile compositions of the melt calculated to be in equilibrium

557   with the apatite crystals using the model Li and Costa (2020) (Fig. 8). Melt

558   equilibrium with zircon-hosted apatite has higher $\frac{X_{OH}^M}{X_F^M}$, $\frac{X_{Cl}^M}{X_F^M}$, and $\frac{X_{OH}^M}{X_{Cl}^M}$ than those in

559   equilibrium with apatite crystals in other textural associations, suggesting that the

560   zircon hosted crystals record an earlier stage in magmatic evolution, where the melt

561   had undergone less volatile degassing. Apatite inclusions within biotite and

562   plagioclase phenocrysts, apatite inclusions which are only partly enclosed by zircon,

563   and groundmass apatite crystals preserve a later-stage volatile record compared to

564   apatite inclusions which are fully enclosed in zircon (Fig. 9a), after significantly more

565   volatile exsolution in the magma chamber (Fig. 9b).

566   Previous experimental studies indicated that Cu in the melt partitions strongly

567   into the sulphide (Li and Audetat, 2012) and fluid phases (Zajacz et al., 2008). Our

568   porphyry magma is highly oxidized ($\sim \Delta FMQ+1.2$), where sulphate (S^{6+}) should be

569   the dominating sulphur phase (Jugo et al., 2009), and the fractionation of sulphides

570   should be depressed (e.g., Lynton et al., 1993; Ballard et al., 2002; Sun et al., 2014).

571   In such an oxidized environment, Cu and Mo readily form Cl-complexes and partition

572   into H_2O-rich fluids (Audétat, 2019; Audetat and Simon, 2012; Candela and Holland,

573   1986; Williams-Jones and Migdisov, 2014). Therefore, we suggest that, along with

574   the Cl, most of the Cu and Mo in the magma should have been extracted by the fluids

575   during the volatile exsolution in the magma chamber.

576   **7. Implications**

577   Previous research has suggested that volatile exsolution in magma chambers

578   controls the metal budgets of porphyry ores, based on the observation that fluid

579   inclusions, bulk ore, and volcanic gases have metal ratios comparable to those in the

580   sulfide melts (Halter et al., 2002; Nadeau et al., 2010; Rottier et al., 2019; Stavast et

581   al., 2006). Moreover, modeling studies indicated that volatile exsolution in magma

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582   chambers would benefit the fluid-melt chemical equilibrium, thereby enhancing

583   extraction of the ore-forming materials (Cu, Mo, Cl, and S) from the melts (Candela,

584   1986, Huber et al., 2012).

585   Our results indicate the zircon-hosted apatite inclusions can provide a direct record

586   of the volatile evolution and exsolution in a porphyry magma chamber, and that their

587   water-saturated compositional patterns indicate that Cl and H_2O (and associated Cu and

588   Mo) were extracted from the melt by isobaric degassing (Fig. 9a). Besides, recent

589   research indicates that some other porphyry systems have achieved water saturation in

590   their magma chamber(s) at the time of zircon-apatite crystallisation, such as at the

591   Quellaveco porphyry deposit, Peru (Nathwani et al., 2023) and the Yulong porphyry

592   deposit, Tibet (Huang et al., 2023b). Since volatile exsolution in the magma chamber

593   is an essential prerequisite for porphyry ore magma fertility, zircon-hosted apatite with

594   water-saturated compositional patterns could be a novel mineral-geochemical indicator

595   for potential porphyry mineralization.

596   Our study also indicated that some resilient minerals, such as zircon, can shield

597   apatite inclusions from hydrothermal alteration and post-entrapment diffusion in the

598   porphyry system, whereas other minerals (e.g., plagioclase and biotite phenocrysts)

599   may not shield the apatite inclusions from the diffusive volatile re-equilibrium after

600   apatite entrapment due to the propensity for hydrothermal alteration, or volatile

601   diffusion at a magmatic temperature during an up to millions years' time window of

602   cooling in the porphyry system (Brenan, 1994). This contrasts with phenocryst-hosted

603   apatite inclusions in rapid cooling volcanic systems, which can retain the volatile

604   composition at the time of entrapment even when the melt inclusion record has been

605   reset by post-entrapment diffusive re-equilibration (Stock et al., 2016, 2018). Hence,

606   reconstruction of magmatic volatile compositions using apatite inclusions from

607   porphyry systems should be performed with caution, and post-entrapment re-

608   equilibrium with the melt or the exsolved magmatic fluids must be considered.

609   Finally, although the zircon can resist the Cl-rich fluid metasomatism in

610   porphyry systems, it can be altered, or replaced by another mineral in alkali- and F-

611   rich fluids at crustal temperature-pressure conditions (i.e. Harlov et al., 2023; Huang

612   et al., 2020). Therefore, the application of zircon-host apatite inclusions in other

613   magmatic-hydrothermal systems (such as the pegmatites and highly evolved granites)

614   should be performed with caution, and systemic mineralogical and geochemical

615   studies are necessary before interpretating data from these mineral inclusions.

616   **Acknowledgements**

629   **Figure Captions**

630   **Figure 1** Geological map of the Zijinshan orefield (modified after Huang et al., 2018).

631

632   **Figure 2** Geological cross section of the Luoboling porphyry Cu-Mo deposit

633   (modified after Li and Jiang, 2017).

634

635   **Figure 3** BSE images showing (a) mineral assemblage of the Luoboling granodiorite

636   porphyry, (b) zircon in the groundmass, (c) zircon inclusion in plagioclase phenocryst,

637   (d) apatite inclusion enclosed by biotite phenocryst, (e) primary apatite in the

638   groundmass, and (f) altered apatite in the groundmass. Abbreviation: Anh =

639   anhydrite; Ap = apatite; Bi = biotite; Mon = monazite; Pla = plagioclase; Qtz =

640   quartz; Pl= plagioclase; Zr = zircon.

641

642   **Figure 4** Transmitted-light (a) and cathodoluminescence (b) microphotographs of

643   apatite inclusions enclosed by zircon. Abbreviations: AFIZC = apatite inclusions fully

644   enclosed by a zircon core; AFIZR= apatite fully enclosed by a zircon rim; APIZ =

645   apatite partially enclosed by zircon.

646

647   **Figure 5.** Apatite textural association under BSE imaging (left) and CL imaging

648   (middle) and EDS Cl distribution (right) in the Luoboling granodiorite porphyry.

649   Primary apatite in the groundmass (a-c), biotite phenocryst (d-f), and plagioclase

650   phenocryst (g-i) show homogeneous texture under BSE and CL imaging, with even Cl

651   distribution. Hydrothermally altered apatite from the groundmass in which monazite

652   inclusions formed (j). Complex replacement texture in CL (k). The altered part shows

653   a lower Cl content than the primary apatite (l). Abbreviation: Ap = apatite; Anh =

                                            27

654 anhydrite; Bi = biotite; Cal= calcite; Kfs = K-feldspar; Nfs = Na-feldspar; Mon =

655 monazite; Pla = plagioclase.

656

657 **Figure 6** Chondrite-normalised rare earth elements (REEs) patterns for the apatite

658 inclusions in the Luoboling granodiorite porphyry. The normalising values are from

659 Sun and McDonough (1989).

660

661 **Figure 7** Scatter plots of apatite compositions in (a, b, and c) X_{Cl}^{Ap}/X_{OH}^{Ap} vs. X_{F}^{Ap}/X_{OH}^{Ap} ,

662 (d, e, and f) X_{Cl}^{Ap}/X_{OH}^{Ap} vs. X_{F}^{Ap}/X_{Cl}^{Ap}, and (g) ternary F–Cl–OH space. The insets in (c,

663 f, g) show modelled apatite compositional trajectories from Stock et al. (2018). Black

664 solid line shows one potential trajectory of apatite compositional evolution during

665 volatile-undersaturated crystallisation. Colored lines distinguish the volatile-saturated

666 models with $D_{F}^{f/m} = 0.7$, and $D_{Cl}^{f/m} = 50$ (dark blue), $D_{Cl}^{f/m} = 20$ (red), $D_{Cl}^{f/m} = 10$

667 (green), and $D_{Cl}^{f/m} = 4$ (orange). The line types illustrate the difference between

668 isobaric and polybaric conditions. Continuous lines show the trajectories modelled by

669 the isobaric volatile-saturated crystallization (with 0% water loss per unit

670 crystallisation); Dashed lines denote the trajectory of apatite compositional evolution

671 during decompression with 0.1 wt.% water loss per unit crystallization; Dotted line

672 shows a higher H_2O loss rate at 0.25 wt.% per unit crystallisation. Note that the fluids

673 and melts partition coefficients of F and Cl applied in the green lines (D_{Cl} [fluid/melt] = 10

674 and D_F [fluid/melt] = 0.7) are similar to the experimental results of the dacite melts at

675 similar pressure and temperature to our granodioritic porphyry (D_{Cl} [fluid/melt] = 11.1 ±

676 3.5; D_F [fluid/melt] = 0.8 ± 0.8 at 50-150 MPa and 800-1000 °C; Cassidy et al., 2022).

677

28

678   **Figure 8** Scatter plots of calculated volatile ratios equilibrated with apatites following

679   Li and Costa (2020). (a) X_{OH}^M/X_F^M vs. X_{Cl}^M/X_F^M, and (b) X_{OH}^M/X_{Cl}^M vs. X_{Cl}^M/X_F^M.

680   Symbol legend is the same as for Figure 7.

681

682   **Figure 9** Schematic diagram summarising the volatile evolution during porphyry Cu

683   ore formation, based on the apatite composition (modified after Richards, 2016). The

684   F–Cl–OH ternary diagram illustrates apatite composition changes during different

685   magmatic processes in the porphyry ore system. (a) Magma achieved volatile

686   saturation and began to generate separated fluid phases that extracted S, Cu, Mo, and

687   Cl from the magma chamber at a relatively steady pressure. The apatite grains

688   captured by plagioclase, biotite phenocrysts, and zircon at this stage should have

689   plotted on the compositional trends consistent with isobaric H_2O-saturated

690   crystallization; (b) The magma exsolved large amounts of fluids during its ascent and

691   emplacement, and caused the steep drop in the magma H_2O-Cl contents. The zircon

692   resisted the fluid metasomatism and the apatite grains fully enclosed by zircon cores

693   and rims preserved the primary volatile record of isobaric H_2O-saturated

694   crystallization. The reset of apatite inclusions (partly enclosed by zircon, in the

695   groundmass, and fully enclosed by the plagioclase and biotite phenocrysts) achieved

696   re-equilibrium with the post-exsolution melts, thereby falling on a compositional

697   trend toward the F apex in the F–Cl–OH ternary diagram.

698   Abbreviations: AFIZC = apatite inclusions fully enclosed by a zircon core; AFIZR=

699   apatite fully enclosed by a zircon rim; APIZ = apatite partially enclosed by zircon;

700   AFIB = apatite inclusions in biotite phenocryst; AFIP = apatite inclusions in

701   plagioclase phenocryst; AMG = apatite in the groundmass. Ap = apatite; Bio =

702   biotite; Pla = plagioclase; Kfs = K-feldspar; Qtz = quartz; Zr = zircon.

29

703

Tables

Table 1 Summarization of the volatile composition of apatite from the Luoboling granodiorite porphyry

Type	In zircon						In phenocryst phases				In groudmass					
	Zircon core		Zircon rim		Partly included		Biotite		Plagioclase		In Quartz		In K-feldspar		Intergranular	
Amount	15		58		17		41		18		21		14		14	
	range	avg.	range	avg.	range	avg.	range	avg.	range	avg.	range	avg.	range	avg.	range	ave.
F (wt.%)	0.78-1.51	1.05	0.67-2.61	1.2	1.44-2.65	1.94	1.85-3.45	2.26	2.13-3.35	2.64	1.95-2.97	2.53	2.03-3.39	2.63	1.92-3.03	2.58
Cl (wt.%)	1.40-2.72	1.96	0.20-2.97	1.98	0.41-1.93	1.21	0.20-1.45	1.22	0.18-1.47	0.87	0.43-1.47	1.16	0.18-1.40	1.1	0.15-1.55	1.09
OH(wt.%)*	1.12-1.79	1.38	0.69-1.65	1.21	0.72-1.44	0.97	0.07-1.01	0.67	0.06-0.84	0.49	0.11-0.83	0.45	0.04-0.87	0.44	0.03-0.83	0.45
X_F/X_{OH}	0.4-1.2		0.4-3.3		0.9-3.2		1.7-38		2.4-49.0		2.1-23.9		2.2-66.4		2.2-78.8	
X_{Cl}/X_{OH}	0.4-1.0		0.1-1.5		0.2-1.0		0.4-9.2		0.15-5.4		0.5-6.1		0.5-14.0		0.1-18.4	
X_F/X_{Cl}	0.5-1.8		0.5-21		1.5-12.1		2.5-32		3.1-35		2.7-13.0		2.7-34.9		2.3-37.5	

704

30

705 **Supplementary Materials**

706 **Figure DR1** Chondrite-normalized REE patterns of the zircon-hosted apatite

707 inclusions.

708 **Figure DR2** Chemical compositional diagrams of biotite phenocryst (after

709 Rieder *et al.*, 1998).

710 **Table DR1** Composition of the Wilberforce secondary apatite standard.

711 **Table DR2** Trace element composition and Ti-in-zircon temperature of zircon in

712 Luoboling granodiorite porphyry

713 **Table DR3** Major element composition of biotite phenocrysts from the

714 Luoboling porphyry Cu-Mo deposit

715 **Table DR4** Major element composition of plagioclase phenocrysts from the

716 Luoboling porphyry Cu-Mo deposit

717 **Table DR5** Trace element composition of primary and altered apatite grains in

718 the Luoboling granodiorite porphyry

719 **Table DR6** Composition of apatite inclusions in zircon from the Luoboling

720 porphyry Cu-Mo deposit

721 **Table DR7** Composition of primary apatite in the biotite and plagioclase

722 phenocrysts from the Luoboling porphyry Cu-Mo deposit

723 **Table DR8** Composition of primary apatite in the groundmass from the

724 Luoboling porphyry Cu-Mo deposit

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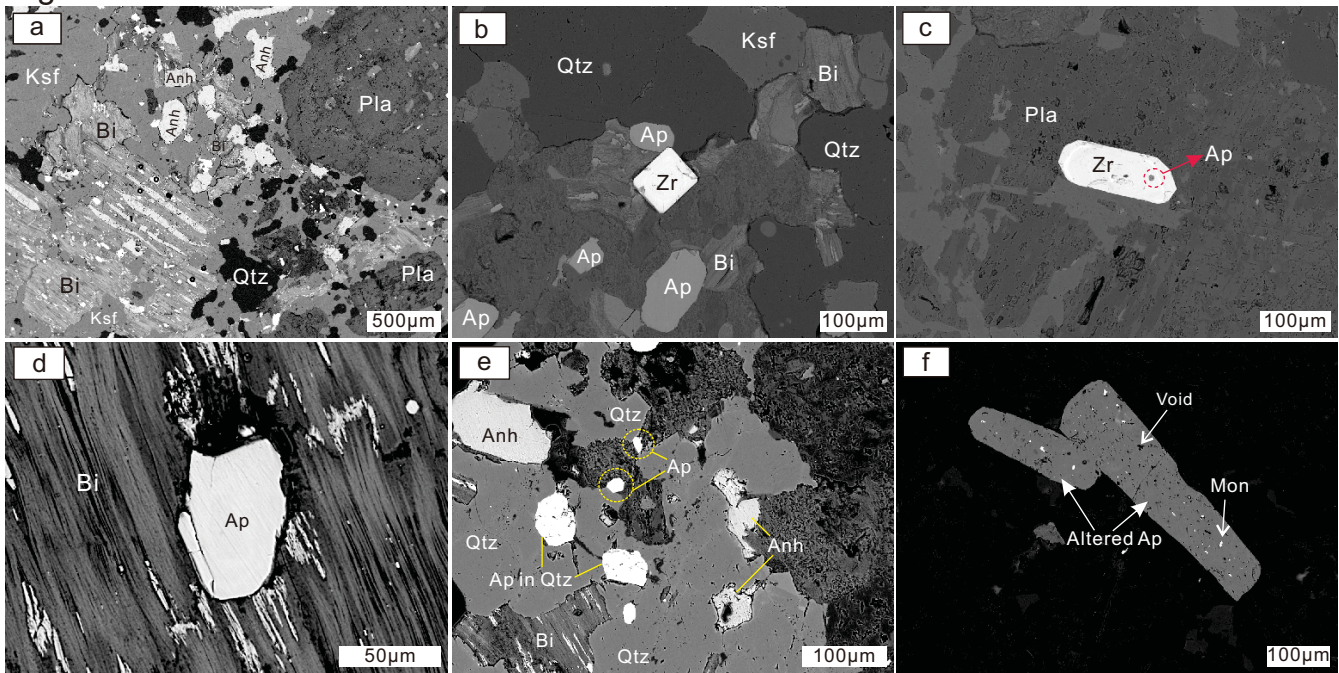
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Figure 1

Neoproterozoic metamorphosed clastic sediments

Late Devonian clastic sediments

Carboniferous clastic sediments

Quaternary sediments

Middle Jurassic Zijinshan granites complex

Late Jurassic Caixi monzogranite

Early Cretaceous Sifang granodiorite

Early Cretaceous Luoboling granodiorite porphyry

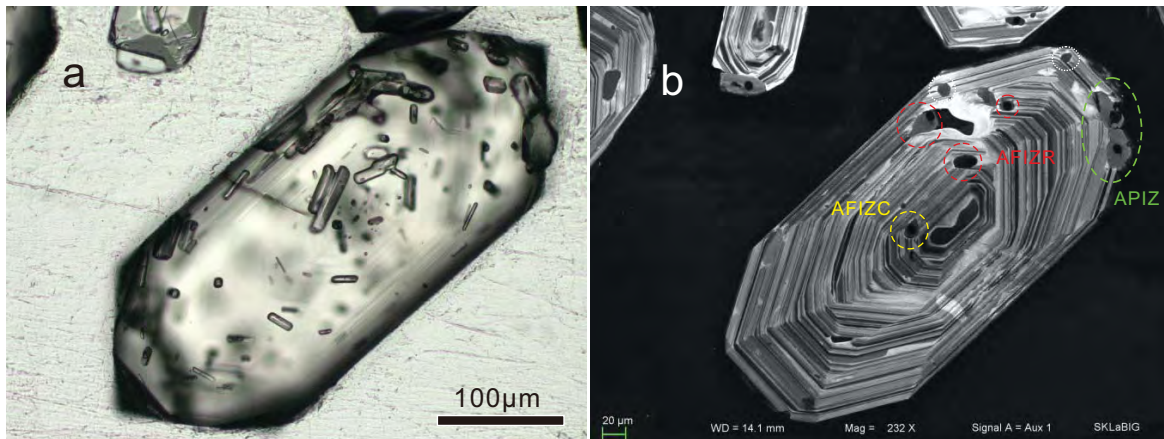Early Cretaceous volcanic rocks

Cryptoexplosive breccia
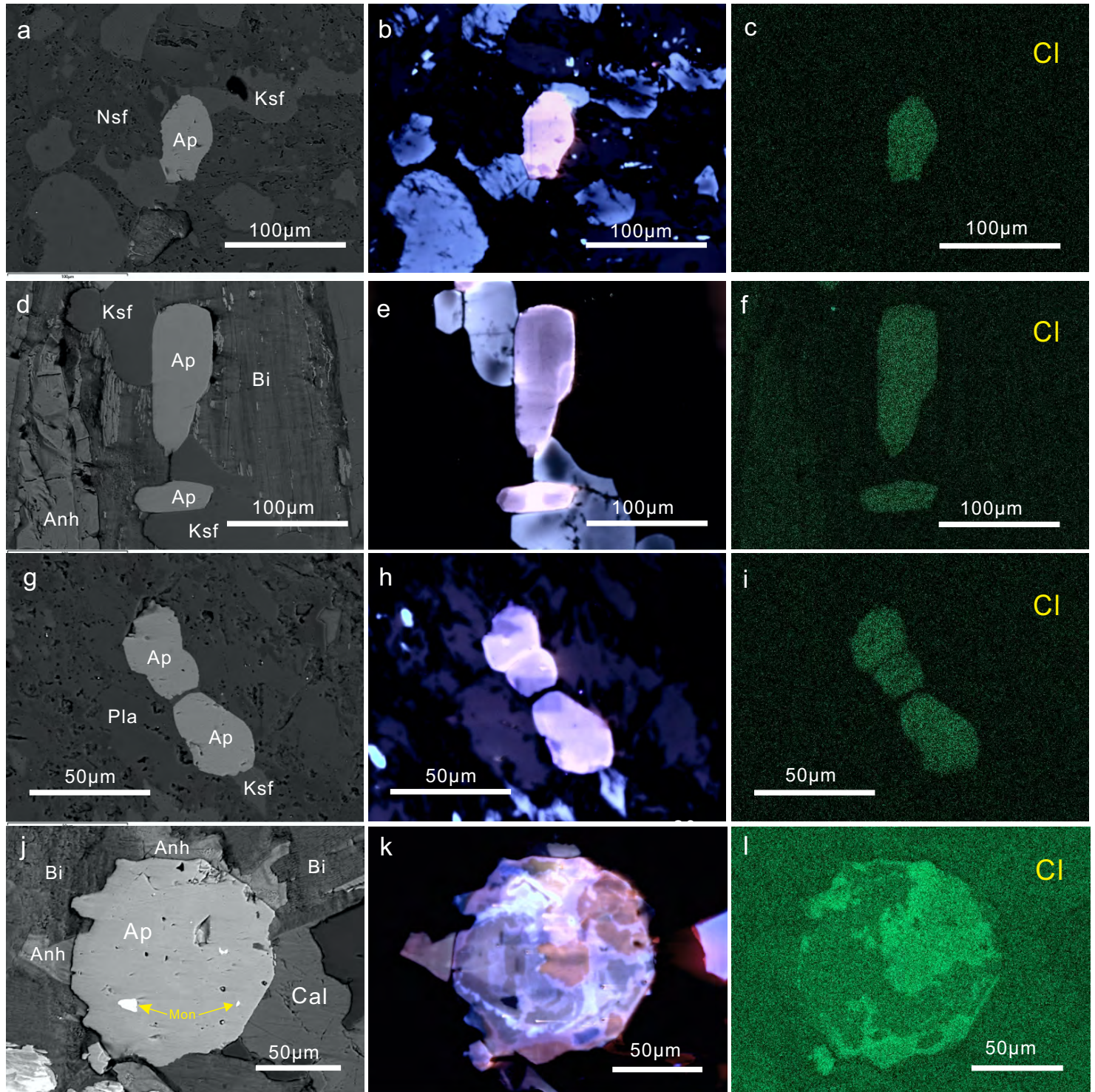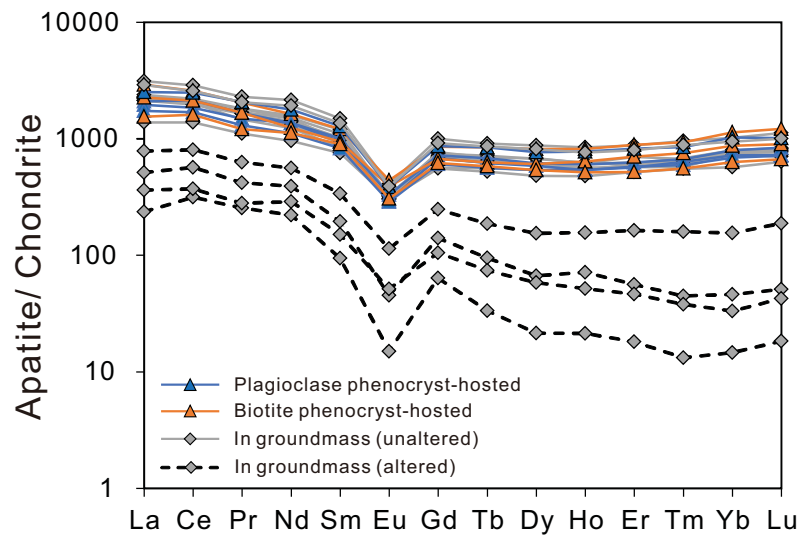
Dacite porphyry

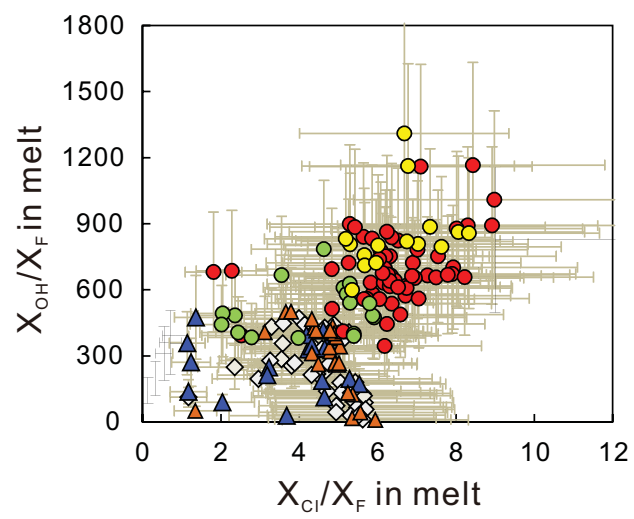Deposits   Faults

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9