Reconstructing volatile exsolution in a porphyry ore-forming magma chamber: Perspectives from apatite inclusions

Wenting Huang\textsuperscript{1,2,3}, Michael J. Stock\textsuperscript{2}, Paul C. Guyett\textsuperscript{2,4}, Xiao-Ping Xia\textsuperscript{1,3,*}, Huaying Liang\textsuperscript{1,3*,} Weidong Sun\textsuperscript{5}, and Chun-kit Lai\textsuperscript{6}

\textsuperscript{1} Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
\textsuperscript{2} Department of Geology, Trinity College Dublin, Dublin, Ireland
\textsuperscript{3} CAS Center for Excellence in Deep Earth Science, Guangzhou, 510640, China
\textsuperscript{4} iCRAG, SFI Research Centre for Applied Geosciences, Ireland
\textsuperscript{5} Center of Deep Sea Research, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China.
\textsuperscript{6} Global Project Generation and Targeting, Fortescue Metals Group Ltd., East Perth WA 6004, Australia

Abstract

Porphyry-type deposits in the shallow crust (3-5 km) are formed from metal-rich fluids exsolved from underlying magma chambers (5-15 km). However, a direct volatile record of the fluid exsolution in the magma chamber is commonly lacking. Here, we analyse the compositions of apatite inclusions (in biotite and plagioclase phenocrysts, and fully-/partly-included in zircon microphenocrysts) and the apatite in groundmass from the largest Cretaceous Luoboling porphyry Cu–Mo deposit in South China. In combination with thermodynamic models, we reconstructed the volatile
behaviour in the ore-forming magma. The analysed apatites are magmatic in origin, without hydrothermal overprint, as indicated by their homogeneous cathodoluminescence (CL) and higher Cl and REE contents than typical hydrothermal apatite. Apatite inclusions fully enclosed in zircon show decreasing $X_{Cl}^{Ap}/X_{OH}^{Ap}$ (1.5-0.1) 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 drop in $X_{Cl}^{Ap}$ at approximately constant $X_{OH}^{Ap}$ in the ternary F–Cl–OH plot. These trends follow the modelled compositional trajectories of isobaric H$_2$O-saturated crystallisation, indicating volatile exsolution during or before zircon crystallisation in the magma chamber. Groundmass apatite crystals, phenocryst-hosted apatite inclusions and apatite inclusions, which are partially enclosed by zircon microphenocrysts, have comparable volatile compositions, with much higher $X_{F}^{Ap}/X_{OH}^{Ap}$ (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 enclosed in zircon. Compositional similarities between these crystals in different textural associations indicate that the phenocryst-hosted apatite inclusions do not preserve their original volatile records at the time of entrapment, and the volatile compositions were overprinted by later re-equilibration with the residual melt and the exsolved magmatic fluids. Given the porphyry magma is highly oxidized, and the sulfides phases would be unstable in such circumstance, we suggest that volatile exsolution in the magma chamber is essential for the Cl and Cu-Mo extraction from the melts and therefore the porphyry mineralization. In this study, only zircon-hosted apatite inclusions appear to best record the magmatic volatile compositions in a porphyry system faithfully. Therefore, using apatite hosted in other minerals or groundmass compositions to unravel magma volatile contents in porphyry Cu system should be conducted with caution.
1. Introduction

Porphyry-type deposits contribute >75% and 25% of the global Cu and Au reserves, respectively (Sillitoe, 2010). They are usually associated with small shallow-emplaced (1-5 km) intermediate–felsic porphyries, mineralised by the fluids exsolved from underlying magma chambers (5-15 km) (Chiaradia, 2021; Hedenquist and Lowenstern, 1994; Richards, 2011; Sillitoe, 2010). Since Cu, Mo, Au, Cl, and S are strongly partitioned into buoyant magmatic fluids (Audetat and Simon, 2012; Lowenstern, 1994; Williams-Jones and Migdisov, 2014), the volatile exsolution in the magma chamber was suggested to play an essential role in metal extraction and mineralisation (Candela and Holland, 1986; Cooke et al., 2005; Halter et al., 2002; Huber et al., 2012; Nadeau et al., 2010). However, a direct continuous volatile record of the fluid exsolution in the magma chamber is still lacking, as the melt inclusions, the conventional medium for tracing magmatic volatiles, is often compromised by post-entrapment crystallisation and volatile diffusion in the plutonic (porphyry) systems (Buchholz et al., 2013; Gaetani et al., 2012).

Apatite \([\text{Ca}_5(\text{PO}_4)_3(F, \text{Cl}, \text{OH})]\) incorporates F\(^-\), Cl\(^-\), and OH\(^-\) directly into its crystal structure within a dedicated volatile site (Z). Apatite volatile analysis has recently received increasing attention as a new effective way to constrain the magmatic volatile concentration and behaviour in terrestrial (e.g., Boyce and Hervig, 2008; Humphreys et al., 2021; Stock et al., 2018) and extraterrestrial (e.g., Boyce et al., 2014; McCubbin and Jones, 2015) systems. Apatite inclusions in volcanic rocks can preserve the record of volatiles at the time of entrapment, even where melt inclusion H\(_2\)O concentrations have been modified by post-entrapment processes.
Notably, zircon-hosted apatite inclusions have been proven resistant to re-equilibration and hydrothermal alteration in granitic and porphyry systems (Bell et al., 2018; Bell et al., 2015; Kendall-Langley et al., 2021; Li et al., 2021; Meng et al., 2022). Thus, apatite inclusions in minerals can potentially record the volatile evolution in porphyry ore-forming magmas.

The Luoboling Cu–Mo porphyry deposit was selected for study. The deposit is genetically associated with the largest Zijinshan epithermal-porphyry Cu-Au-Mo ore field in Asia (Fig. 1, Huang et al., 2018; Jiang et al., 2013). We present analysis of the volatile compositions of unaltered apatite inclusions in plagioclase and biotite phenocrysts, in the groundmass, and the tiny apatite inclusions in zircon microphenocrysts from the syn-mineralisation granodiorite porphyry. The apatite inclusions with various textures (phenocryst-, groundmass-hosted, fully included by zircon/partly included by zircon) place constraints on the time when apatite inclusions were isolated from their host melt and may reflect the volatile compositions across the porphyry ore-forming magma evolution. Compared with the apatite thermodynamic model of Stock et al. (2018), we unravelled the behaviour of volatile species and delineated a continuous volatile evolution trend for the causative magma of the Luoboling porphyry deposit. This provides insights into the behaviours of both volatile components (Cl and H$_2$O) and ore metals (Cu and Mo) they carried.

2. Geological Background and Ore Geology

The Zijinshan in southeastern China (Fig. 1a) is the largest epithermal-porphyry orefield in Asia, which contains many epithermal and porphyry deposits associated with the Cretaceous Paleo-Pacific subduction (Fig. 1b) (Huang et al., 2018; Jiang et al., 2013; So et al., 1998; Zhong et al., 2014). These deposits contain 399 metric tonnes (t) Au, 6400 kt Ag, 4.137 Mt Cu, and 110 kt Mo (Zhang, 2013; Zhong et al., 2014).
In particular, the Luoboling porphyry Cu–Mo deposit in northeastern Zijinshan contains 1.4 Mt Cu @ 0.3% and 110 kt Mo @ 0.036% (Zhong et al., 2014).

The Neoproterozoic Louziba Group is the oldest stratum in the Zijinshan ore field, which comprises meta-clastic rocks (Fig. 1b). These rocks are unconformably overlain by Upper Devonian and Carboniferous sedimentary rocks. The Lower Cretaceous Shimaoshan Group volcanic rocks are exposed across the Zijinshan orefield (Fig. 1b), which yielded zircon U–Pb ages of 113–93 Ma (Jiang et al., 2013).

Intrusions in the Zijinshan ore field were emplaced in the Mesozoic, including the Zijinshan granite complex (zircon U–Pb age: 154–165 Ma; Li et al., 2015), Caixi monzogranite (zircon U–Pb age: 157–150 Ma; Jiang et al., 2013), Sifang granodiorite (zircon U–Pb age: 112 ± 1 Ma; Jiang et al., 2013), Luoboling granodiorite porphyry (zircon U–Pb age: 97–103 Ma; Huang et al., 2013), and the Zhongliao porphyritic granodiorite (zircon U-Pb ages of 95.9 ± 0.6 Ma; Li and Jiang, 2014). The Luoboling granodiorite porphyry intrudes the Sifang granodiorite and Caixi monzogranite (Fig. 1b). The Zhongliao porphyritic granodiorite was revealed by drilling to underly the Luoboling granodiorite porphyry (Fig. 2).

Porphyry mineralisation occurred mainly in the Luoboling granodiorite porphyry. There are three main hydrothermal alteration stages (I to III) at Luoboling: (I) potassic–silicic (K-Q) alteration; (II) phyllic (Phy) alteration; and (III) alumite-dickite (Alu-Di) alteration, which are spatially associated with pyrite, bornite, and digenite mineralization (So et al., 1998, Zhong et al., 2014). This alteration is generally located in the exocontact of the Zhongliao porphyritic granodiorite (Fig. 2).

The porphyry Cu–Mo mineralisation generally occurred (as veinlet or disseminated sulfides) where the K-Q alteration was overprinted by Phy alteration (K-Q+Phy). Ore
minerals at the Luoboling deposit include mainly pyrite, chalcopyrite, and molybdenite.

3. Sample Description

Luoboling granodiorite porphyry samples (LBL-82 and LBL-77) were collected from drill holes ZK405 at 680 m and 682 m depth, respectively. The granodiorite porphyry includes phenocrysts (>0.5 mm) of plagioclase (~25 vol.%), biotite (~5 vol.%), and quartz (~5 vol.%) within a groundmass of quartz (~25 vol.%), K-feldspar (~25 vol.%), biotite (~10 vol.%), plagioclase (~5 vol.%), and anhydrite (<5 vol.%). Zircon occurs in the groundmass (Fig. 3a) as inclusions within other phenocryst phases (Fig. 3c). Zircons in the groundmass are more elongate than those hosted in the phenocrysts, and their length-width ratios are >3 for the former (Fig. 3b) and 2-3 for the latter (Fig. 3c). Tiny apatite inclusions widely occur within the zircon grains (Fig. 4). Apatite crystals occur mainly as inclusions within plagioclase (Fig. 3c) and biotite phenocrystals (Fig. 3d) or in the groundmass (Fig. 3e-f). The groundmass-hosted apatites are either enclosed by other phases (i.e., quartz and K-feldspar) or as interstitials among other minerals (Fig. 3e). Most apatite crystals are euhedral and clear without fluid or mineral inclusions (Fig. 3c-e). Some apatite grains, especially the apatite micro-phenocrysts (> 200 µm) in the groundmass, were altered and contain abundant fluid inclusions and monazite inclusions (Fig. 3f).

In this study, we divided the primary apatite inclusions into three types based on their occurrences, namely those (1) included in zircon; (2) included in phenocrysts; (3) in the groundmass.

4. Sample Preparation and Methods
4.1 Sample preparation

Polished thin sections were made from each sample. About 1 kg of the
granodiorite porphyry was crushed and sieved to extract zircon microphenocrysts
from the 300–350 μm size fraction using conventional density and magnetic
separation techniques. Euhedral, clear zircon crystals (> 200μm) were handpicked
under a binocular microscope, which were then mounted in epoxy and polished before
the analysis. Cathodoluminescence (CL) imaging was performed (with 10 kV
acceleration voltage) to reveal zircon zoning textures and zircon-hosted apatite
inclusions.

4.2 Apatite minerology

CL imaging and in situ element mapping were carried out at the iCRAG Lab in
Trinity College Dublin, Ireland. Samples were first coated with 12 nm of carbon
before being introduced to a TESCAN S8000 field emission scanning electron
microscope (FE-SEM) operating with TESCAN Essence software platform (2018).
The SEM was used for imaging and performing a fully quantitative energy dispersive
x-ray spectroscopy (EDX) chemical analysis of the apatites. The instrument is
equipped with Bright Beam SEM column technology, backscatter electron (BSE)
imaging, colour CL detectors, and four Oxford Instruments X-Max 170 mm²
detectors, with AZtec software version 5.1 used to interpret the EDX results. The CL
imaging was conducted on carbon-coated thin sections using a colour
cathodoluminescence detector at an acceleration voltage of 15 kV, a beam current of
3nA, a working distance of 15 mm, and an image scanning speed of 320 μs per pixel.
The EDX analysis was carried out with an acceleration voltage of 20 kV, a beam
current of 3 nA, and a working distance of 15 mm.

4.3 Electron probe microanalysis
Apatite inclusions

Before the geochemical analysis, we observed the sample and crystal texture using an optical microscope and BSE imaging. The BSE imaging was conducted on carbon-coated thin sections, using an accelerating voltage of 15 kV. Only the inclusion-free, euhedral plagioclase-/biotite-hosted apatite inclusions and groundmass-hosted apatite grains with homogeneous or zoned texture under BSE imaging were selected for further study. Cathodoluminescence was conducted on the apatite-host zircon to reveal the zircon internal texture. The zircon grains were briefly polished before analysing the apatite inclusions to mitigate any potential beam damage.

Major element compositions of the apatite inclusions were determined on a JEOL JXA-8100 electron probe microanalyser (EPMA) at the State Key Laboratory for Mineral Deposits Research, Nanjing University (China). Analysis was conducted under 15 kV, 20 nA, and 2 μm beam size to generate sufficient counts to quantify the low Cl content in the tiny apatite inclusions. Although these analytical conditions risk minor electron-beam-induced sample damage (Goldoff et al., 2012; Stock et al., 2015; Stormer et al., 1993), F and Cl were analysed first using shorter analysis times to minimise this effect. The peak/background elemental counting times were 10/5 s for P, Ca, Cl and F, 20/10 s for Si. The standards used for the analysis included the Durango apatite for Ca, P, and F, almandine for Si, barite for S, and tugtupite for Cl. Previous studies have revealed the time-dependent variation in apatite halogen X-ray counts during EPMA analysis (Goldoff et al., 2012; Stock et al., 2015). The effect is most pronounced when the electron beam is oriented parallel to the crystallographic c-axis, whereas it is minimal when the beam is parallel to the a- or b-axis (Goldoff et al., 2012; Stock et al., 2015). The grains whose c-axis is parallel to the beam were
discarded to minimise the problem induced by the apatite anisotropy. We discarded
the apatite grains with a hexagonal symmetry (whose c-axis is likely beam-parallel;
crystals marked with white circles in Fig. 4b) and selected only the elongated apatite
grains (whose c-axis is likely beam-perpendicular; crystals marked with yellow, red,
and green circles in Fig. 4b). Analytical accuracy is <1\% for P, <2\% for Ca and F, and
<5\% for Cl. Relative precision, quantified through repeated analyses of the
Wilberforce apatite, is ±2\% for Ca, P, and F and ± 4\% for Cl (Table DR 1). The mole
fractions of fluorapatite and chlorapatite are calculated directly from the concentration
of F and Cl, with the mole fraction of hydroxyl-apatite (apatite OH content) estimated
using the approach in Ketcham (2015).

**Biotite and plagioclase phenocrysts**

Major element compositions of the apatite-hosting biotite and plagioclase were
analysed on a JXA-8230 EMPA at the Key Laboratory of Mineralogy and
Metallogeny (KLMM), Guangzhou Institute of Geochemistry, Chinese Academy of
Science (GIG CAS). The analysis was carried out using a 15 kV accelerating
voltage, 20 nA probe current, and 1 μm beam diameter. Peak/background counting
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,
and 20 s for Ca. The calibration standards include biotite for Si, magnetite for Fe,
olivine for Mg, almandine for Al, rutile for Ti, rhodonite for Mn, orthoclase for
K, albite for Na, Cr-diopside for Ca, BaF$_2$ for F, and tugtupite for
Cl. ZAF (Z: atomic number; A: absorption; F: fluorescence) calibration procedures we
re used to reduce the matrix effect.

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

**analysis**
Trace element contents of zircon were analysed on an ELEMENT XR (Thermo Fisher Scientific) ICP-SF-MS coupled with a 193-nm (ArF) Resonetics RESOlation M-50 laser ablation system at GIG CAS. The analysis consisted of a 33 μm laser spot size with a repetition rate of 5 Hz and an energy fluence of 4 J/cm². NIST SRM 610 glass (Jochum et al., 2011; Pearce et al., 1997) and Temora zircon (Black et al., 2003) standards were used for external calibration. A detailed analytical procedure is described by Zhang et al.(2019).

We used LA-ICP-MS to analyse the apatite trace element contents at the School of Resources and Environmental Engineering, Hefei University of Technology, using an Agilent 7900 ICP-MS coupled with a 193-nm (ArF) Analyte HE laser-ablation system. The analysis used a 30 μm beam with a repetition rate of 8 Hz and an energy fluence of 4 J/cm². NIST SRM 610, NIST SRM 612, and BCR-2G were used for external standards. The Ca concentration determined by EMPA was used as the internal standard. The offline data processing, time-drift correction, and quantitative calibration of both the zircon and apatite data were carried out with the ICPMSDataCal program (Liu et al., 2008).

5. Results

5.1 Host mineral compositions and saturation temperature

Biotite phenocrysts are euhedral and un-zoned (Fig. 3d) and have near-homogeneous interagrain compositions (Fig. DR2). They have high Mg# (molar Mg/(Mg+Fe): 0.69–0.72; Table DR3) and TiO₂ content (3.65–4.82 wt.%), indicating a magmatic origin (Rasmussen and Mortensen, 2013) despite weak alteration. Following Henry et al. (2005), we calculated the Ti-in-biotite saturation temperature to be 759–789 °C (mean= 777 ± 8 °C, n=25; Table DR3). The Al-in-biotite barometer for granites was used to estimate the crystallisation pressure (Uchida et al., 2007). The
pressures at the time of biotite crystallisation are 167–249 MPa (mean 205 ± 24 MPa).
The water solubility at this pressure was estimated with the equation by Tattitch et al.
(2021), which yielded 6.14 ± 0.49 wt.% (n = 25; Table DR3).

Plagioclase phenocrysts are euhedral and concentric oscillatory-zoned (Fig. 3a, 3c). They are andesine in composition, with An values (100 × molar CaO/(CaO + Na₂O + K₂O) of 37–46 (Table DR4), and display a progressive decrease from core (An₄₁–₄₆) to rim (An₃₇–₄₃). The An in plagioclase is sensitive to the magmatic water content and temperature, but less sensitive to pressure (Water and Lange, 2015). The plagioclase hygrometer is used to estimate the magmatic water content at the time of plagioclase crystallisation (Water and Lange, 2015). Since the plagioclase and the biotite phenocrysts should have both crystallised in the magma chamber, the biotite thermobarometer (205 MPa) and the Ti-in-biotite saturation temperature (777 °C) were used to estimate the water content. The average magmatic water content for the sample was estimated to be 6.62 ± 0.07 wt.% (n = 16), similar to the results from biotite.

Our zircon samples show oscillatory zoning in CL images (Fig. 4b). They have ∑REE and Y concentrations of 727 to 1339 ppm (Table DR2) with strong LREE depletion and positive Ce anomalies typical of igneous zircons (Fig. DR1), indicating a lack of hydrothermal alteration (Fu et al., 2009; Hoskin, 2005). Following Loucks et al. (2020), we calculated the Ti-in-zircon saturation temperature with pressure correction. As quartz is a matrix constituent in the granodiorite porphyry, this suggests that αSiO₂ = 1. The presence of titanite indicates that αTiO₂ should be ~0.7 (Chelle-Michou et al., 2014). In our calculation, we used 1.0 and 0.7 for αSiO₂ and αTiO₂, respectively. The estimated pressure for correction is 205 MPa (Table DR3, Uchida et al., 2007). The analysis yielded apparent temperatures of 722–818 °C.
(mean 766 ± 29°C, n = 13; Table DR2), broadly consistent with the Ti-in-zircon saturation temperatures reported from other porphyry deposits (e.g., 750-650 °C at Bajo da la Alumbrera (Argentina); Buret et al., 2016; 850-700°C at Yanacocha (Puru), and Yerington (Nevada); Dilles et al., 2015). The zircon oxybarometer in Loucks et al. (2020) was used to calculate the oxygen fugacity of the magma, which yielded ΔFMQ + 0.9 to ΔFMQ + 1.6 (mean = ΔFMQ + 1.2, n = 13).

5.2 Cathodoluminescence features and Cl distribution

The magmatic apatite grains in groundmass (Fig. 5a-c), biotite phenocryst (Fig. 5d-f), and plagioclase phenocryst (Fig. 5g-i) are texturally homogeneous under BSE imaging and display pink to purple luminescence under CL imaging. Some grains contain brown luminescence patches (Fig. 5b). The unaltered magmatic apatite grains consistently show a homogeneous intragrain Cl concentration (Fig. 5c, f, and i), regardless of their luminescence.

The altered apatite grains are characterized by containing fluid inclusions or monazite inclusions and voids in BSE images (Fig. 5j), and complex textures under the CL imaging (Fig. 5k). They consist of the remnants of magmatic apatite with brown or pink luminescence, and the hydrothermal apatite with blue-grey luminescence (Fig. 5k). The hydrothermal apatite form euhedral rims with light-blue luminescence, overgrown on a grey-dark luminescence core (Fig. 5k). Monazite inclusions in the grey-dark luminescence core indicate a fluid-coupled dissolution-reprecipitation process within apatite during the alteration (Harlov et al., 2002; Harlov and Förster, 2003). Element distribution in the altered apatite shows a sharp compositional boundary, with the hydrothermal replaced/altered parts having a much lower Cl content than the magmatic apatite remnants (Fig. 5l). This reflects the
interaction with hydrothermal fluids where Cl partitions into the fluid phase (Webster et al., 2009).

### 5.3 Apatite trace element composition

Trace element composition of 17 unaltered magmatic apatite grains (7 phenocryst-host and 10 in groundmass) and 4 altered apatites measured by LA-ICP-MS are shown in Fig. 6 and listed in Table DR5.

The 17 unaltered apatite in phenocrysts phases yield REE+Y contents of 3433-5412 ppm (mean 4289 ppm, n = 7) and slight LREE-enriched patterns ((La/Yb)_N = 2.41-3.04) (Fig. 6). The apatite in the groundmass has REE+Y contents of 3017-6024 ppm, (mean 4422 ppm, n = 10) and (La/Yb)_N = 2.43-3.08, comparable to those of the apatite in phenocrysts.

The altered apatite has much lower REE+Y contents (449-1482 ppm) with higher (La/Yb)_N (5.04-16.1) than those of the unaltered apatite (Fig. 6). This composition is consistent with the altered apatite in other porphyry systems (Bouzari et al., 2016), indicating REE dissolution and remobilisation by the hydrothermal fluids.

### 5.4 Apatite volatile compositions

The EPMA volatile element compositions of the apatite inclusions in zircon microphenocrysts, apatite inclusions in phenocryst phases, and apatite in the groundmass are summarised in Table 1, shown in Fig. 7, and detailed in Table DR6-DR8.

**Apatite inclusions in zircon microphenocrysts**

We further divided the zircon-hosted apatite inclusions into three textural subgroups (Fig. 4b): (1) apatite fully enclosed in the zircon core; (2) apatite fully enclosed in the zircon rim; (3) apatite partially enclosed in zircon. In total, we analysed 93 apatite inclusions in 25 zircons, and the results are listed in Table DR6.
Zircon-hosted apatite inclusions display significant intragrain variation in their halogen contents (Fig. 7; Table 1).

Apatite from the zircon core has 0.78–1.51 wt.% (mean 1.05 wt.%, n = 15) F, 1.40–2.72 wt.% (mean 1.96 wt.%) Cl, and 1.12–1.79 wt.% (mean 1.38 wt.%) OH. 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 0.5–1.8, respectively (where $X_F^{AP}$, $X_{Cl}^{AP}$, and $X_{OH}^{AP}$ are mole fractions of F, Cl, and OH in apatite, respectively).

Apatite from the zircon rim has slightly higher F (0.67–2.61 wt.%, mean 1.20 wt.%), similar Cl (0.20–2.97 wt.%, mean 1.98 wt.%), and lower OH (0.69–1.65 wt.%, mean 1.20 wt.%) contents than apatite from the zircon core. Their $X_F^{AP}/X_{OH}^{AP}$, $X_{Cl}^{AP}/X_{OH}^{AP}$, and $X_F^{AP}/X_{Cl}^{AP}$ ratios are of 0.4–3.3, 0.1–1.5, and 0.5–21, respectively.

Apatite partly enclosed by zircon has higher F content (1.44–2.65 wt.%, mean 1.94 wt.%, n = 17), lower Cl (0.41–1.93 wt.% mean 1.21 wt.%), and lower OH contents (0.72–1.44 wt.%, mean 0.97 wt%) than apatite fully enclosed by zircon. 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, respectively.

**Apatite inclusions in phenocryst phases**

We analysed 41 apatite inclusions from 13 biotite phenocrysts and 18 apatite inclusions from 8 plagioclase phenocrysts (Fig. 7 and Table DR7). These apatite inclusions are all fully enclosed in their host phenocrysts. Apatite from the biotite phenocrysts exhibits a more restricted compositional range than the zircon-hosted inclusions, with 1.85–3.45 wt.% (mean 2.26 wt.%) F, 0.20–1.45 wt.% (mean 1.22 wt.%) Cl, and 0.07–1.01 wt.% (mean 0.67 wt.%) OH. This equates to $X_F^{AP}/X_{OH}^{AP}$.
$X_{Cl}^{Ap}/X_{O_H}^{Ap}$, and $X_{F}^{Ap}/X_{Cl}^{Ap}$ ratios of 1.7–38, 0.4–9.2, and 2.5–32, respectively. Apatite from the plagioclase phenocrysts has a volatile composition similar to those for apatite hosted by biotite, with 2.13–3.35 wt.% (mean 2.64 wt.%) F, 0.18–1.47 wt.% (mean 0.87 wt.%) Cl, and 0.06–0.84 wt.% (mean 0.49 wt.%) OH contents. This equates to $X_{F}^{Ap}/X_{O_H}^{Ap}$, $X_{Cl}^{Ap}/X_{O_H}^{Ap}$, and $X_{F}^{Ap}/X_{Cl}^{Ap}$ ratios of 2.4–49.0, 0.15–5.4, and 3.1–35, respectively.

Apatite crystals in groundmass

We analysed 49 apatite grains in the groundmass (Table DR8). They have 1.92–3.39 wt.% (mean 2.59 wt.%) F, 0.15–1.55 wt.% (mean 1.07 wt.%) Cl, and 0.04–0.87 wt.% (mean 0.44 wt.%) OH. This equates to $X_{F}^{Ap}/X_{O_H}^{Ap}$, $X_{Cl}^{Ap}/X_{O_H}^{Ap}$, and $X_{F}^{Ap}/X_{Cl}^{Ap}$ ratios of 2.1–78.8, 0.1–18.4, and 2.3–37.5, respectively.

6. Discussion

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

Porphyry mineralization accompanies hydrothermal alteration, which may alter the magmatic apatite and modify its geochemical composition (Bouzari et al., 2016; Xing et al., 2020). Therefore, only the primary apatite free from alteration would preserve the magmatic volatile record. Altered apatite is usually depleted in Mn, REE, and Y, and forms new REE phosphates (incl. monazite inclusions; Xing et al., 2019; Bouzari et al., 2016), due to the coupled dissolution-reprecipitation mechanism (Harlov et al., 2002; Harlov and Förster, 2003; Harlov et al., 2005). Since Mn and REEs are the most common CL activators in apatite (Barbarand and Pagel, 2001; Roeder et al., 1987), altered apatite usually shows replacement texture in CL images. Moreover, altered apatite in the porphyry systems is characterised by extremely low
Cl contents regardless of alteration types (Bouzari et al., 2016) because Cl partitions more strongly into fluids than apatite (Webster et al., 2009). In our study, the textures and geochemical compositions of zircon, biotite, and plagioclase phenocrysts indicate that these minerals are magmatic in origin and free of or weakly affected by hydrothermal alteration (section 5.1). Thus, the apatite inclusions in these minerals should be magmatic in origin and be isolated from hydrothermal alteration. The magmatic apatite grains analysed are free of fluid inclusions with homogeneous or zoned texture under BSE (Fig. 5a, d, g) and CL imaging (Fig. 5b, e, h). Compositionally, the apatite grains analysed yielded Mn/Fe >1 and much higher REE+Y contents (>3000 ppm) than those of the altered apatite (<1000 ppm), further indicating that they are unaltered (Bouzari et al., 2016). Besides, the apatite in our study yielded Cl contents > 0.1 wt.% and plot on a continuous composition trend in the ternary F–Cl–OH plot (Fig. 7g). Such a compositional trend is inconsistent with the low Cl content for the apatite altered by hydrothermal fluids (Bouzari et al., 2016), which should have recorded the magmatic volatile evolution. Since our apatite grains should record magmatic volatile compositions (either the timing of entrapment or re-equilibration), compositional comparison of apatite with different textures could provide relative temporal constraints on the magmatic volatile evolution. Phenocrysts are crystallised in the magma chamber, whereas the groundmass phases are formed by rapid crystallisation during the magma ascent or degassing in the roof of the magma chamber (Burnham, 1967). Thus, unless their host phenocrysts did not provide an effective barrier from re-equilibration, apatite inclusions that are fully enclosed by phenocrysts should have recorded the volatile composition of melt at an earlier stage compared with apatite in the groundmass,
which can re-equilibrate with their host magma (and the exsolved fluid) until a late
stage.

Some zircon microphenocrysts contain more than one apatite inclusion, which
may be fully or partially enclosed by the host zircon. The former may preserve a
record of melt volatile evolution, whereas the latter may record the volatile
equilibration with the ambient magma. For these zircons, we assume that apatite fully
enclosed in the zircon core was entrapped before those in the zircon rim, and that both
crystal-melt partitioning is non-Nernstian and can be described by a
inclusion types would preserve the volatile record at the time of entrapment. In
contrast, apatite partly enclosed by a zircon microphenocryst was likely in contact
with the ambient melt until solidification and could re-equilibrate with volatiles from
a later-stage melt, similar to the case of groundmass apatite.

6.2 Apatite compositional evolution in an H₂O-saturated porphyry magma
chamber

As F, Cl, and OH are stoichiometric constituents in the crystal structure of
apatite, their crystal-melt partitioning is non-Nernstian and can be described by a
series of exchange reactions in the form:

\[ X_{\text{Cl}}^{\text{Ap}} + X_{\text{Cl}}^{\text{M}} \rightleftharpoons X_{\text{Cl}}^{\text{M}} + X_{\text{Cl}}^{\text{Ap}} \]  

(1)

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

The equilibrium relationship between the volatile composition of apatite crystals
and their host melt can be expressed by \( K_D \) exchange equations of the form:

\[ K_D^{\text{Ap-M}}(P, T) = \frac{x_{\text{Ap}}^{\text{Cl}}}{x_{\text{Ap}}^{\text{Cl}}} \times \frac{x_{\text{OH}}^{\text{Cl}}}{x_{\text{OH}}^{\text{Cl}}} \]  

(2)

where the exchange coefficients (\( K_D \)) are constant at a given pressure and
temperature (Piccoli and Candela, 1994). Equation 2 assumes that F–Cl–OH exchange
in apatite behaves as an ideal solid solution; although this may not be strictly true, it is
consistent with the available experimental data (see the discussion in Stock et al. 2018). A comparison of ideal vs non-ideal apatite thermodynamic models suggests that any non-ideality must be small (Humphreys et al., 2021).

Stock et al. (2016, 2018) proposed a thermodynamic model to calculate the apatite compositional evolution during H\(_2\)O-undersaturated and H\(_2\)O-saturated magmatic crystallisation by varying the modelling parameters (incl. crystal–melt and fluid–melt volatile partition coefficients, initial melt volatile content, and melt H\(_2\)O solubility). The modelling compositional trends can be compared with datasets of natural apatite to determine whether the magma, the apatite crystallised from, was H\(_2\)O-saturated.

Regarding our textural constraints, \(X^{Ap}_{Cl}/X^{Ap}_{OH}\) appears to decrease while \(X^{Ap}_{F}/X^{Ap}_{OH}\) and \(X^{Ap}_{F}/X^{Ap}_{Cl}\) appears to increase during magma evolution, from apatite fully enclosed by zircon (esp. apatite in the zircon core, which was isolated from the earlier melt) to apatite partly enclosed by zircon (which re-equilibrated with the later melt) (Fig. 7c, f). The compositional trajectory recorded by zircon-hosted apatite is inconsistent with cooling at a constant melt composition, which would generate a positive \(X^{Ap}_{Cl}/X^{Ap}_{OH}\) vs. \(X^{Ap}_{F}/X^{Ap}_{OH}\) correlation (Piccoli and Candela, 1994; Stock et al., 2018). The compositional trajectory is also inconsistent with volatile-undersaturated crystallisation models, which are characterised by decreasing \(X^{Ap}_{F}/X^{Ap}_{Cl}\) and away from the F apex in the ternary F–Cl–OH plot during magma evolution (Stock et al., 2018). This is because F partitions more strongly into common hydrous minerals (e.g., apatite, biotite, and amphibole) than Cl, while Cl partitions more strongly than OH (i.e., \(D^{Cl/M}_F > D^{Cl/M}_{Cl} > D^{Cl/M}_{OH}\); Benard et al., 2017; Li and Hermann, 2015; Mathez and Webster, 2005; Van den Bleekken and Koga, 2015). This is especially true, if the Cl
partition coefficient between the mineral and the melt \( \bar{D}_{\text{Cl}}^{C/M} \) is extremely low, the water under-saturated evolution would produce increasing \( X_{\text{Cl}}^{Ap} / X_{\text{OH}}^{Ap} \) with decreasing \( X_{F}^{Ap} / X_{\text{OH}}^{Ap} \) and \( X_{F}^{Ap} / X_{\text{Cl}}^{Ap} \), similar to the negative correlation trends observed in our zircon-hosted apatite inclusions (Fig. 7c and 7f; Stock et al., 2018). However, this is inconsistent with that of a porphyry magma, which should have a relatively high \( \bar{D}_{\text{Cl}}^{C/M} \) due to the crystallisation of abundant Cl-bearing biotite and amphibole (Richards et al., 2012). Besides, the decreasing F and increasing Cl content of the melts during water-undersaturated evolution with low \( \bar{D}_{\text{Cl}}^{C/M} \) would drive apatite compositionally away from the F apex and towards the Cl apex in F-Cl-OH space (Stock et al., 2018), which is opposite to the trend shown by our samples (Fig. 7g). Instead, the compositional trend of our apatite inclusions closely matches those of the H\(_2\)O-saturated crystallisation models (Fig. 7g), where Cl is partitioned from the melt into an exsolving vapour phase while F is retained in the felsic melt (Candela, 1986; Cassidy et al., 2022; Doherty et al., 2014; Stock et al., 2018; Webster et al., 2009). As the solubility of H\(_2\)O in a magmatic system is mainly pressure-dependent, the trajectory of apatite volatile evolution should be different during isobaric and polybaric (decompressed) H\(_2\)O-saturated crystallisation. After H\(_2\)O saturation in the isobaric scenario (i.e., second boiling), the melt water concentration remains constant, water is exsolved due to continuous crystallisation, and changes in apatite volatile concentration are driven primarily by partitioning of Cl into the vapour phase. In the F-Cl-OH ternary space (Fig. 7g), following H\(_2\)O-saturation under isobaric conditions, apatite compositions would move directly towards the F–OH binary, as Cl is strongly partitioned into the vapour, before moving towards the F apex (Stock et al., 2018).
After H$_2$O saturation in the polybaric scenario (i.e., first boiling), the melt H$_2$O concentration drops due to its decreasing solubility during decompression. The Cl partition coefficients for fluid-melt are pressure dependent (Tattitch et al., 2021) but always larger than 1 in felsic melts (Aiuppa et al., 2009; Webster et al., 2009), thus the melt Cl still partitions into the vapour phase. The apatite compositions are influenced by the decrease of both H$_2$O and Cl in the melt. In the ternary F-Cl-OH plot, following H$_2$O-saturation under polybaric conditions, the apatite compositions would move closer to the F apex than the trends created by the isobaric scenario, as the H$_2$O is extracted from the melt alongside Cl (Fig. 7g; Stock et al., 2018). The pressure dependence of apatite–melt K$_D$ values would be superimposed on these compositional changes, but the variation caused by this dependence is expected to be small over the normal crustal pressure range (Riker et al., 2018).

The apatite fully enclosed by zircon displays a steep drop in $X_{Cl}^{Ap}$ at approximately $X_{OH}^{Ap}$ in the ternary F–Cl–OH plot (Fig. 7g), consistent with the trajectories modelled by isobaric H$_2$O-saturated (the continuous lines in Fig. 7g) and the slowly-decompressed H$_2$O-saturated crystallisation (red dashed line in Fig. 7g, Stock et al., 2018). This indicates that the apatites were entrapped by zircons at relatively constant magmatic H$_2$O content/solubility, which likely took place in the magma chamber. Therefore, we suggest that the apatite grains fully enclosed by zircons recorded the volatile exsolution in the magma chamber. The fertile Zijinsan porphyry magma likely reached water saturation during/before zircon crystallisation in the magma chamber.

An alternative explanation is that the compositional trends of apatite in zircons are controlled by the assimilation of Cl-depleted or F-enriched material, which would...
increase the apatite $X_{F}^{Ap}$ and drive crystals towards higher $X_{F}^{Ap}/X_{O^{2-}}^{Ap}$ and $X_{F}^{Ap}/X_{Cl}^{Ap}$ ratios. However, a large amount of Cl-depleted or F-enriched material would be required to decrease the apatite $X_{Cl}^{Ap}$ by 80% (according to our data) within the time frame of zircon growth. Furthermore, the most probable Cl-depleted and F-enriched endmember in the Zijinshan district is the Proterozoic sedimentary rocks. Zircon Hf isotopic analysis of the Luoboling granodiorite porphyry indicated that their assimilation was insignificant (Huang et al., 2018; Jiang et al., 2013; Li and Jiang, 2014). This further suggests that assimilation of Cl-depleted or F-rich materials is unlikely the cause of decreasing $X_{Cl}^{Ap}$ and $X_{Cl}^{Ap}/X_{O^{2-}}^{Ap}$, and increasing $X_{F}^{Ap}/X_{O^{2-}}^{Ap}$ and $X_{F}^{Ap}/X_{Cl}^{Ap}$ in zircon hosted apatite.

The thermobarometer for the biotite (Uchida et al., 2007) indicates that the pressure of the Zijinshan fertile magma chamber was ~205 MPa (eqv. ~6.8 km depth) and comparable to those of most porphyry magma chambers around the world (5~15km, Sillitoe, 2010). Since our fertile porphyry magma has achieved water saturation in the chamber, the water solubility estimated by the pressure should represent the water content (~6.14 wt.%). The result is close to the water content estimated by the plagioclase phenocryst compositions (~ 6.62 wt.%). Both results suggest that the fertile porphyry magma was characterized by a significantly higher water content than the common arc magmas (~ 4 wt.%; Plank et al., 2013). The high-water content should therefore be the key factor contributing to the water saturation in the magma chamber at the time of the zircon-apatite crystallisation. Meanwhile, a high magmatic water content is not unique for fertile porphyry systems. Similar magmatic water contents (> 6 wt.%) have been reported in many subduction-related porphyry ore systems, such as the Rio Blanco in Peru (Chen et al, 2022), and the
Santo Tomas II, Black Mountain, Clifton, and Bumolo in the Philippines (Huang et al, 2023a).

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

Given that the Ti-in-biotite saturation temperatures (mean 777 ± 7 °C) are similar with the Ti-in-zircon saturation temperatures (mean 766 ± 29 °C), and that plagioclase likely reaches the liquidus substantially earlier than zircon, we would expect the biotite and plagioclase phenocrysts hosted apatite inclusions to record a period during magmatic volatile evolution that was simultaneous with or earlier than that of the fully enclosed zircon-hosted apatite inclusions (i.e., equal or higher $X_{Ap}$ and $X_{Cl}$, and lower $X_{Ap}^{F}/X_{Ap}^{OH}$ and $X_{Cl}^{F}/X_{Cl}^{OH}$). In fact, despite having some compositional overlap with fully enclosed zircon-hosted inclusions, apatite inclusions in the biotite and plagioclase phenocrysts extend to markedly higher $X_{Ap}^{F}/X_{Ap}^{OH}$ (Fig. 8b) and $X_{Cl}^{F}/X_{Cl}^{Ap}$ (Fig. 8e), and lower $X_{Ap}^{Cl}$ and $X_{Ap}^{OH}$ (Fig. 7g), similar to the apatite partly enclosed by zircon or that in the groundmass (Fig. 7).

While groundmass apatite crystals may have grown from a late-stage melt, after significant degassing and shortly before emplacement, we might expect inclusions within phenocrysts and zircon microphenocrysts to preserve a volatile record earlier in magmatic evolution, at or before their entrapment. Their compositional correlation with groundmass crystals can be explained by diffusional re-equilibration with the late-stage melt and exsolved fluid, which can occur within days to months under magmatic conditions (Stock et al. 2016; Li et al, 2020). In the case of zircon-hosted inclusions which were not fully enclosed by their host crystals, diffusive re-equilibration is possible because crystals had not been isolated from their
host magma. In terms of inclusions within plagioclase and biotite phenocrysts, these phases are weakly altered in our porphyry samples (Fig. 3), likely due to interaction with exsolved Cl-rich magmatic fluids. This might have compromised them as an inclusion host and permitted re-equilibration of apatite inclusions (Krause et al., 2013).

The complexity of apatite volatile compositions in porphyry system might also be explained by the slower cooling and the longer lifespan (100,000 to several million years; Sillitoe, 2010) of the porphyry systems, which is long enough for volatile diffusion to achieve re-equilibrium under high (magmatic) temperatures (Brenan, 1994; Costa et al., 2008; Costa et al., 2020). This is in contrast to previous analyses of non-porphyry volcanic apatite inclusions, where common phenocrysts appear to be reliable host phases, permitting apatite inclusions to retain a volatile record at their time of entrapment (Stock et al., 2018). Nevertheless, our data indicate that zircon could robustly shield the fully enclosed apatite inclusions from diffusive re-equilibration in porphyry systems, allowing them to preserve their primary volatile composition at the time of entrapment. This is consistent with the recent experimental study, which indicates that zircon can resist alteration by Cl-rich fluids at magmatic conditions (900°C and 1000 MPa; Harlov et al., 2023).

The steep decreases in $X_{Cl}^{Ap}$ and $X_{OH}^{Ap}$ between apatite inclusions which are fully enclosed by zircon host crystals and those in other textural associations (i.e. all of our crystals which are not fully enclosed within zircon; Fig. 7g) indicates a substantial depletion of Cl in the melt by the exsolving H$_2$O-rich fluids. This is consistent with the volatile compositions of the melt calculated to be in equilibrium with the apatite crystals using the model Li and Costa (2020) (Fig. 8). Melt
equilibrium with zircon-hosted apatite has higher $\frac{X_{OH}}{X_F}$, $\frac{X_{Cl}}{X_F}$, and $\frac{X_{OH}}{X_{Cl}}$ than those in equilibrium with apatite crystals in other textural associations, suggesting that the zircon hosted crystals record an earlier stage in magmatic evolution, where the melt had undergone less volatile degassing. Apatite inclusions within biotite and plagioclase phenocrysts, apatite inclusions which are only partly enclosed by zircon, and groundmass apatite crystals preserve a later-stage volatile record compared to apatite inclusions which are fully enclosed in zircon (Fig. 9a), after significantly more volatile exsolution in the magma chamber (Fig. 9b).

Previous experimental studies indicated that Cu in the melt partitions strongly into the sulphide (Li and Audétat, 2012) and fluid phases (Zajacz et al., 2008). Our porphyry magma is highly oxidized (~ ΔFMQ+1.2), where sulphate (S$^{6+}$) should be the dominating sulphur phase (Jugo et al., 2009), and the fractionation of sulphides should be depressed (e.g., Lynton et al., 1993; Ballard et al., 2002; Sun et al., 2014). In such an oxidized environment, Cu and Mo readily form Cl-complexes and partition into H$_2$O-rich fluids (Audétat, 2019; Audétat and Simon, 2012; Candela and Holland, 1986; Williams-Jones and Migdisov, 2014). Therefore, we suggest that, along with the Cl, most of the Cu and Mo in the magma should have been extracted by the fluids during the volatile exsolution in the magma chamber.

7. Implications

Previous research has suggested that volatile exsolution in magma chambers controls the metal budgets of porphyry ores, based on the observation that fluid inclusions, bulk ore, and volcanic gases have metal ratios comparable to those in the sulfide melts (Halter et al., 2002; Nadeau et al., 2010; Rottier et al., 2019; Stavast et al., 2006). Moreover, modeling studies indicated that volatile exsolution in magma
chambers would benefit the fluid-melt chemical equilibrium, thereby enhancing extraction of the ore-forming materials (Cu, Mo, Cl, and S) from the melts (Candela, 1986, Huber et al., 2012).

Our results indicate the zircon-hosted apatite inclusions can provide a direct record of the volatile evolution and exsolution in a porphyry magma chamber, and that their water-saturated compositional patterns indicate that Cl and H$_2$O (and associated Cu and Mo) were extracted from the melt by isobaric degassing (Fig. 9a). Besides, recent research indicates that some other porphyry systems have achieved water saturation in their magma chamber(s) at the time of zircon-apatite crystallisation, such as at the Quellaveco porphyry deposit, Peru (Nathwani et al., 2023) and the Yulong porphyry deposit, Tibet (Huang et al., 2023b). Since volatile exsolution in the magma chamber is an essential prerequisite for porphyry ore magma fertility, zircon-hosted apatite with water-saturated compositional patterns could be a novel mineral-geochemical indicator for potential porphyry mineralization.

Our study also indicated that some resilient minerals, such as zircon, can shield apatite inclusions from hydrothermal alteration and post-entrapment diffusion in the porphyry system, whereas other minerals (e.g., plagioclase and biotite phenocrysts) may not shield the apatite inclusions from the diffusive volatile re-equilibrium after apatite entrapment due to the propensity for hydrothermal alteration, or volatile diffusion at a magmatic temperature during an up to millions years’ time window of cooling in the porphyry system (Brenan, 1994). This contrasts with phenocryst-hosted apatite inclusions in rapid cooling volcanic systems, which can retain the volatile composition at the time of entrapment even when the melt inclusion record has been reset by post-entrapment diffusive re-equilibration (Stock et al., 2016, 2018). Hence, reconstruction of magmatic volatile compositions using apatite inclusions from
porphyry systems should be performed with caution, and post-entrapment re-
equilibrium with the melt or the exsolved magmatic fluids must be considered.

Finally, although the zircon can resist the Cl-rich fluid metasomatism in
porphyry systems, it can be altered, or replaced by another mineral in alkali- and F-
rich fluids at crustal temperature-pressure conditions (i.e. Harlov et al., 2023; Huang
et al., 2020). Therefore, the application of zircon-host apatite inclusions in other
magmatic-hydrothermal systems (such as the pegmatites and highly evolved granites)
should be performed with caution, and systemic mineralogical and geochemical
studies are necessary before interpreting data from these mineral inclusions.

Acknowledgements

The data of this work are available in the article and its online supplementary
material. This study was funded by the National Natural Science Foundation of China
(42072088) and the National Key R&D Program of China (2018YFA0702600). We
thank Changming Xing, Yonghua Cao and Wenlan Zhang for their help with the
electron microprobe analyses. We thank Daniel E. Harlov for handling the
manuscript, and Andreas Audétat and Chetan Nathwani for the constructive
suggestions, which helps to significantly improve the manuscript. WH acknowledges
the support from the China Scholarship Council (CSC) Scholarship (No.
202104910197). MS was supported by a Frontiers for the Future grant (20/FFP-
P/8895), co-funded by Science Foundation Ireland and Geological Survey Ireland. PG
was supported by SFI Research Centre for Applied Geosciences, Ireland (iCRAG,
13/RC/2092_2).
Figure Captions

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

**Figure 2** Geological cross section of the Luoboling porphyry Cu-Mo deposit (modified after Li and Jiang, 2017).

**Figure 3** BSE images showing (a) mineral assemblage of the Luoboling granodiorite porphyry, (b) zircon in the groundmass, (c) zircon inclusion in plagioclase phenocryst, (d) apatite inclusion enclosed by biotite phenocryst, (e) primary apatite in the groundmass, and (f) altered apatite in the groundmass. Abbreviation: Anh = anhydrite; Ap = apatite; Bi = biotite; Mon = monazite; Pla = plagioclase; Qtz = quartz; Pl = plagioclase; Zr = zircon.

**Figure 4** Transmitted-light (a) and cathodoluminescence (b) microphotographs of apatite inclusions enclosed by zircon. Abbreviations: AFIZC = apatite inclusions fully enclosed by a zircon core; AFIZR = apatite fully enclosed by a zircon rim; APIZ = apatite partially enclosed by zircon.

**Figure 5.** Apatite textural association under BSE imaging (left) and CL imaging (middle) and EDS Cl distribution (right) in the Luoboling granodiorite porphyry. Primary apatite in the groundmass (a-c), biotite phenocryst (d-f), and plagioclase phenocryst (g-i) show homogeneous texture under BSE and CL imaging, with even Cl distribution. Hydrothermally altered apatite from the groundmass in which monazite inclusions formed (j). Complex replacement texture in CL (k). The altered part shows a lower Cl content than the primary apatite (l). Abbreviation: Ap = apatite; Anh =
anhydrite; Bi = biotite; Cal = calcite; Kfs = K-feldspar; Nfs = Na-feldspar; Mon = monazite; Pla = plagioclase.

Figure 6 Chondrite-normalised rare earth elements (REEs) patterns for the apatite inclusions in the Luoboling granodiorite porphyry. The normalising values are from Sun and McDonough (1989).

Figure 7 Scatter plots of apatite compositions in (a, b, and c) $X_{CI}^{AP}/X_{OH}^{AP}$ vs. $X_F^{AP}/X_{OH}^{AP}$; (d, e, and f) $X_{CI}^{AP}/X_{OH}^{AP}$ vs. $X_F^{AP}/X_{CI}^{AP}$, and (g) ternary F–Cl–OH space. The insets in (c, f, g) show modelled apatite compositional trajectories from Stock et al. (2018). Black solid line shows one potential trajectory of apatite compositional evolution during volatile-undersaturated crystallisation. Colored lines distinguish the volatile-saturated models with $D_{F}^{Cl/m} = 0.7$, and $D_{F}^{Cl/m} = 50$ (dark blue), $D_{F}^{Cl/m} = 20$ (red), $D_{F}^{Cl/m} = 10$ (green), and $D_{F}^{Cl/m} = 4$ (orange). The line types illustrate the difference between isobaric and polybaric conditions. Continuous lines show the trajectories modelled by the isobaric volatile-saturated crystallization (with 0% water loss per unit crystallisation); Dashed lines denote the trajectory of apatite compositional evolution during decompression with 0.1 wt.% water loss per unit crystallization; Dotted line shows a higher $H_2O$ loss rate at 0.25 wt.% per unit crystallisation. Note that the fluids and melts partition coefficients of F and Cl applied in the green lines ($D_{Cl}^{fluid/melt} = 10$ and $D_{F}^{fluid/melt} = 0.7$) are similar to the experimental results of the dacite melts at similar pressure and temperature to our granodioritic porphyry ($D_{Cl}^{fluid/melt} = 11.1 \pm 3.5$; $D_{F}^{fluid/melt} = 0.8 \pm 0.8$ at 50-150 MPa and 800-1000 °C; Cassidy et al., 2022).
Figure 8 Scatter plots of calculated volatile ratios equilibrated with apatites following Li and Costa (2020). (a) $X_{OH}^M / X_P^M$ vs. $X_{Cl}^M / X_P^M$, and (b) $X_{OH}^M / X_{Cl}^M$ vs. $X_{Cl}^M / X_P^M$.

Symbol legend is the same as for Figure 7.

Figure 9 Schematic diagram summarising the volatile evolution during porphyry Cu ore formation, based on the apatite composition (modified after Richards, 2016). The F–Cl–OH ternary diagram illustrates apatite composition changes during different magmatic processes in the porphyry ore system. (a) Magma achieved volatile saturation and began to generate separated fluid phases that extracted S, Cu, Mo, and Cl from the magma chamber at a relatively steady pressure. The apatite grains captured by plagioclase, biotite phenocrysts, and zircon at this stage should have plotted on the compositional trends consistent with isobaric H$_2$O-saturated crystallization; (b) The magma exsolved large amounts of fluids during its ascent and emplacement, and caused the steep drop in the magma H$_2$O-Cl contents. The zircon resisted the fluid metasomatism and the apatite grains fully enclosed by zircon cores and rims preserved the primary volatile record of isobaric H$_2$O-saturated crystallization. The reset of apatite inclusions (partly enclosed by zircon, in the groundmass, and fully enclosed by the plagioclase and biotite phenocrysts) achieved re-equilibrium with the post-exsolution melts, thereby falling on a compositional trend toward the F apex in the F–Cl–OH ternary diagram.

Abbreviations: AFIZC = apatite inclusions fully enclosed by a zircon core; AFIZR = apatite fully enclosed by a zircon rim; APIZ = apatite partially enclosed by zircon; AFIB = apatite inclusions in biotite phenocryst; AFIP = apatite inclusions in plagioclase phenocryst; AMG = apatite in the groundmass. Ap = apatite; Bio = biotite; Pla = plagioclase; Kfs = K-feldspar; Qtz = quartz; Zr = zircon.
Table 1: Summarization of the volatile composition of apatite from the Luoboling granodiorite porphyry

<table>
<thead>
<tr>
<th>Type</th>
<th>In zircon</th>
<th></th>
<th></th>
<th>In phenocryst phases</th>
<th></th>
<th></th>
<th>In groundmass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zircon core</td>
<td>Zircon rim</td>
<td>Partly included</td>
<td>Biotite</td>
<td>Plagioclase</td>
<td>In Quartz</td>
<td>In K-feldspar</td>
</tr>
<tr>
<td>Amount</td>
<td>range</td>
<td>avg.</td>
<td>range</td>
<td>avg.</td>
<td>range</td>
<td>avg.</td>
<td>range</td>
</tr>
<tr>
<td>F (wt.%)</td>
<td>0.78-1.51</td>
<td>1.05</td>
<td>0.67-2.61</td>
<td>1.2</td>
<td>1.44-2.65</td>
<td>1.94</td>
<td>1.85-3.45</td>
</tr>
<tr>
<td>Cl (wt.%)</td>
<td>1.40-2.72</td>
<td>1.96</td>
<td>0.20-2.97</td>
<td>1.98</td>
<td>0.41-1.93</td>
<td>1.21</td>
<td>0.20-1.45</td>
</tr>
<tr>
<td>OH(wt.%)*</td>
<td>1.12-1.79</td>
<td>1.38</td>
<td>0.69-1.65</td>
<td>1.21</td>
<td>0.72-1.44</td>
<td>0.97</td>
<td>0.07-1.01</td>
</tr>
<tr>
<td>X_F/X_OH</td>
<td>0.4-1.2</td>
<td>0.4-3.3</td>
<td>0.9-3.2</td>
<td>1.7-38</td>
<td>2.4-49.0</td>
<td>2.1-23.9</td>
<td>2.2-66.4</td>
</tr>
<tr>
<td>X_Cl/X_OH</td>
<td>0.4-1.0</td>
<td>0.1-1.5</td>
<td>0.2-1.0</td>
<td>0.4-9.2</td>
<td>0.15-5.4</td>
<td>0.5-6.1</td>
<td>0.5-14.0</td>
</tr>
<tr>
<td>X_F/X_Cl</td>
<td>0.5-1.8</td>
<td>0.5-21</td>
<td>1.5-12.1</td>
<td>2.5-32</td>
<td>3.1-35</td>
<td>2.7-13.0</td>
<td>2.7-34.9</td>
</tr>
</tbody>
</table>
Supplementary Materials

Figure DR1 Chondrite-normalized REE patterns of the zircon-hosted apatite inclusions.

Figure DR2 Chemical compositional diagrams of biotite phenocryst (after Rieder et al., 1998).

Table DR1 Composition of the Wilberforce secondary apatite standard.

Table DR2 Trace element composition and Ti-in-zircon temperature of zircon in Luoboling granodiorite porphyry

Table DR3 Major element composition of biotite phenocrysts from the Luoboling porphyry Cu-Mo deposit

Table DR4 Major element composition of plagioclase phenocrysts from the Luoboling porphyry Cu-Mo deposit

Table DR5 Trace element composition of primary and altered apatite grains in the Luoboling granodiorite porphyry

Table DR6 Composition of apatite inclusions in zircon from the Luoboling porphyry Cu-Mo deposit

Table DR7 Composition of primary apatite in the biotite and plagioclase phenocrysts from the Luoboling porphyry Cu-Mo deposit

Table DR8 Composition of primary apatite in the groundmass from the Luoboling porphyry Cu-Mo deposit

References cited


system, SW Fujian Province, China: Constrains from the geochronology and
geochemistry of the igneous rocks. Ore Geology Reviews, 53, 287-305.

Jochum, K.P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q.C., Raczek, I., Jacob,
Determination of Reference Values for NIST SRM 610-617 Glasses Following ISO
Guidelines. Geostandards and Geoanalytical Research, 35(4), 397-429.


Geology, 37(5), 415-418.

Kendall-Langley, L.A., Kemp, A.I.S., Hawkesworth, C.J., Craven, J., Talavera,
in granitic melts from apatite inclusions in zircon. Contributions to Mineralogy and
Petrology, 176(7), 58.

data for apatite and other phases with mixing on monovalent anion sites. American
Mineralogist, 100(7), 1620-1623.

and clinopyroxene as tracers for metasomatic processes in nepheline clinopyroxenites
of Uralian-Alaskan-type complexes in the Ural Mountains, Russian Federation.


Li, B., and Jiang, S.Y. (2014) A subduction-related metasomatically enriched
mantle origin for the Luoboling and Zhongliao Cretaceous granitoids from South
China: implications for magma evolution and Cu–Mo mineralization. International
Geology Review, 57(9-10), 1239-1266.


Piccoli, P., and Candela, P. (1994) Apatite in Felsic Rocks - a Model for the Estimation of Initial Halogen Concentrations in the Bishop Tuff (Long Valley) and...


Figure 1

This figure illustrates the geological map of the Zijinshan Au-Cu and Luoboling Cu-Mo deposit areas. The map shows the distribution of various geological formations, including:

- **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**
- **Dacite porphyry**
- **Cryptoexplosive breccia**
- **Early Cretaceous volcanic rocks**
- **Deposits**
- **Faults**
Figure 4
Figure 5

(a) Ksf, Ap, Nsf

(b) Cl

(c) Cl

(d) Ksf, Ap, Bi, Anh

(e) Cl

(f) Cl

(g) Anh, Pla, Ap, Ksf

(h) Cl

(i) Cl

(j) Bi, Anh, Cal

(k) Cl

(l) Cl
Figure 6

[Graph showing lanthanide patterns for apatite/chondrite with different markers for Plagioclase phenocryst-hosted, Biotite phenocryst-hosted, In groundmass (unaltered), and In groundmass (altered).]
Figure 7

Undersaturated →
Saturated

**Iso-baric**
- D\text{cl}^{20} ≤ 50
- D\text{cl}^{20} = 10
- D\text{cl}^{20} = 20
- D\text{cl}^{20} ≤ 4

**Decompressed** (D\text{cl}^{20} = 20)
- 0.1 wt% H\text{2}O loss per 1% crystallization
- 0.25 wt% H\text{2}O loss per 1% crystallization

**Apatite inclusion in zircon**
- Fully included by zircon core
- Fully included by zircon rim
- Partly included by zircon

**Apatite inclusions in phenocrysts**
- Plagioclase
- Biotite
- *Apatite in groundmass*

Always consult and cite the final, published document. See http://www.minsocam.org or GeoscienceWorld
Figure 9

Argillic-altered rocks

Igneous intrusions

Porphyry ore body

Apatite
- AFIZC
- AFIZR
- APIZ
- AFIB&AFIP
- AMG

Apatite water-saturated compositional evolution trend
- Volatile exsolution in magma chamber
- Re-equilibrium with post-exsolution melt

Re-equilibrium

Always consult and cite the final, published document. See http://www.minsocam.org or GeoscienceWorld