Mechanisms of fluid degassing in shallow magma chambers control the formation of porphyry deposits

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Abstract

Magmatic fluid degassing within shallow magma chambers underneath the ore bodies is critical to the formation of porphyry Cu–Au deposits (PCDs). Yet, it remains unclear that how the ways of fluid degassing influence on the development of PCDs. Here, geochemical data of apatite, amphibole and plagioclase from ore-forming and coeval barren porphyries have been analyzed in Sanjiang metallogenic belt, China. The ore-forming porphyries normally exhibit high and wide $X_F/X_{Cl}$ (31.76–548.12) and $X_F/X_{OH}$ (0.779–7.370) ratios of apatites, which are evidently higher than those of the barren porphyries ($X_F/X_{Cl}$ of 1.03–26.58; $X_F/X_{OH}$ of 0.686–3.602). Combined with the continuous variation features of Cl/OH ratios and H$_2$O contents of melts calculated by amphiboles, as well as fluid migration models, we constrained the mechanisms of fluid degassing within shallow magma chambers underneath PCDs. There are three different ways of fluid degassing, while only fluid degassing via fluid channel stage can migrate and focus the metal-rich fluids effectively, conducive to the development of PCDs. The mechanisms of magmatic fluid degassing processes are further controlled by the storage depths of magma chambers and initial H$_2$O contents of the magmas revealed by the compositions of amphibole, plagioclase and
thermodynamic modelling. Magmas, with shallower storage depth and higher
initial H$_2$O content, are more likely to experience extensive and focused fluid
degassing, leading to the generation of PCDs. This study demonstrates the
potential utility of integrated mineral analyses, the thermodynamic modelling for
investigating the mechanisms of magmatic fluid degassing in porphyry systems,
as well as identifying prospective buried PCDs.

Keywords: porphyry deposit, magma degassing, magma chamber,
thermodynamic modelling, apatite, amphibole

Introduction

Porphyry Cu–Au deposits (PCDs), representing a typical type of magmatic–
hydrothermal deposit, currently provide ~75% and ~20% of the global demand
for Cu and Au, respectively (Sillitoe, 2010). Their ore bodies are typically around
the apical tips of small volume (< ~5 km$^3$) pipe- or dyke-like porphyries at depths
of ~1–4 km. Such small porphyries could not be able to provide enough ore-
forming metals and fluids (enriched in H$_2$O, HCl, H$_2$S, SO$_2$ and other volatile
components) for the development of large PCDs. Thus, it is commonly believed
that the ore-forming metals and fluids are dominantly derived from a larger
magma chamber (> ~100 km$^3$) underneath the porphyries at depths of ~4–10 km
(e.g., Richards., 2018). Consequently, the tonnages of PCDs could be closely
associated with the volumes of fluids (> ~10 km$^3$) degassed from the shallow
magma chambers (e.g., Cline and Bodnar, 1991; Chelle-Michou et al., 2017;
Richards., 2018), while the processes of fluid degassing may also play critical roles in the development of PCDs as shown by numerical simulations (Parmigiani et al., 2016, 2017; Degruyter et al., 2019; Lamy-Chappuis et al., 2020). These various processes that govern the transport and extraction of magmatic fluids, as they leave their shallow magma chambers and reach the mineralization sites, are difficult to be well constrained directly by geological samples, and remain a major challenge to our understanding of magmatic–hydrothermal systems of PCDs. Apatite and amphibole are common phases in ore-forming porphyries that can incorporate Cl, F and OH in their structure and known to have a relatively high crystal–melt partition coefficients of them. They have been used to elucidate the behavior of magmatic fluids, owing to their ability to dynamically re-equilibrate their volatiles contents in response to changes in melt compositions (Piccoli and Candela, 2002; Humphreys et al., 2009). Therefore, the compositions of apatite and amphibole might have great potential to provide well constrains on the mechanisms of fluid degassing within the shallow magma chambers underneath PCDs (e.g., Humphreys et al., 2009; Stock et al., 2016, 2018; Popa et al., 2021). The comparisons of apatite and amphibole from ore-forming and barren magmas, combined with correlative thermodynamic models, could be used to reveal the significance of fluid degassing mechanisms in the development of PCDs and their tonnages.

The Cenozoic Cu–Au metallogenic belt in Sanjiang region (Sanjiang metallogenic belt), southwestern China, hosts numerous PCDs (Figure 1). They show broad similarities in their formation ages, metal components and alteration patterns, and
are all related to adakite-like porphyries (Lu et al., 2013a, 2013b; Huang et al., 2019), while the tonnages of these PCDs vary significantly. Meanwhile, there are also some coeval adakite-like porphyries without mineralization (barren) in this metallogenic belt. Collectively, these facts make the Sanjiang metallogenic belt an excellent opportunity to examine how the mechanisms of fluid degassing in shallow magma chambers control the formation of PCDs and provide the guidance for PCDs mineral exploration.

Geological setting

The eastern Tibet Plateau, lying to Yangtze and Songpan–Ganze block, is built on a tectonic collage of continental blocks resulted in progressive Triassic to Cretaceous closures of the Paleo- and Neo-Tethyan Oceans (Figure 1). The Cenozoic evolution of the eastern Tibet Plateau was largely controlled by Indian–Asian collision, which was initiated at ca. 55 Ma (e.g., Najman et al., 2010; Deng et al., 2014, 2021). The Indian–Asian continental collision caused crustal thickening in Tibet (e.g., Najman et al., 2010), with continuing impingement of the Indian plate on Asian causing the extrusion of elongated crustal blocks in Sanjiang region, along the eastern Tibet Plateau (Figure 1; Tapponnier et al., 1982).

During the Indian–Asian collision, the Eocene Sanjiang metallogenic belt formed along Jinshajiang–Ailaoshan suture zone (JAS), which is largely composed of relics of the Jinshajiang–Ailaoshan Paleo–Tethys oceanic plate (Figure 1; Deng et al., 2014, 2021). The Sanjiang metallogenic belt clustered abundant Eocene
potassic felsic intrusions and potassic-ultrapotassic mafic volcanic rocks. There
are numerous PCDs along Sanjiang metallogenic belt, including two giant PCDs
of Yulong and Beiya as well as a series of large- to small-sized deposits (Lu et al.,
2013b; He et al., 2015; Hou et al., 2017; Huang et al., 2019; Xu et al., 2021;
Wang et al., 2022). The proven resources currently include >16 Mt Cu, >450 t
Au, ~6 Mt Mo (Lu et al., 2013b; Deng et al., 2014, 2021; He et al., 2015; Wang et
al., 2022). These PCDs were formed at ca. 34–43 Ma sharing similar metal
components and alteration patterns, and genetically related to adakite-like felsic
porphyries (ore-forming porphyries). Many Eocene adakite-like porphyries (32–
43 Ma) with no features of alteration and mineralization (barren porphyries) have
also been identified in this belt (Figure 1).

The ore-forming and barren adakite-like porphyries have similar outcrop area
(typically 0.5–1 km$^2$), dominated by pipe- or dyke-like intrusive bodies (Figure
1). The popular model proposes that these adakite-like porphyries were produced
by partial melting of sulfide-rich arc cumulates in the lower crust (e.g., Lu et al.,
2013; Hou et al., 2017; Huang et al., 2019; Shen et al., 2021). Additionally, some
scholars have also suggested that these adakite-like porphyries could be derived
from the fractionation of potassic mafic magmas derived from lithospheric mantle
(Jiang et al., 2006; Chang et al., 2023a). While there are potassic mafic rocks with
high La/Yb and Dy/Yb ratios similar to the felsic rocks, the scarcity of
corresponding high La/Yb and Dy/Yb samples in the intermediate-transitional
range undermines the credibility of the potassic mafic magmas fractionation
model (Supplementary Figure 1a, b). The elevated La/Yb and Dy/Yb ratios
observed in these adakite-like porphyries can be effectively explained by the presence of residual garnet in the source (Davidson et al., 2007; Macpherson, 2008). Considering the similarities in geochemical signatures (e.g., adakite-like; Supplementary Figure 1c, d) and isotopic compositions ($\varepsilon_{Hf}(t)$: -9.1–8.5; $^{87}$Sr/$^{86}$Sr): 0.7050–0.7097; $\varepsilon_{Nd}(t)$: -11.2–1.43; Supplementary Figure 2), we are inclined to believe that both ore-forming and barren adakite-like porphyries were derived from partial melting of a juvenile lower crust resulting from previous underplating of Neoproterozoic–Paleozoic arc magmas. The subduction of Indian continent disturbed the asthenosphere of Asian continent, causing the upwelling of mantle flow. The hot mantle flow rose through the mantle and widely emplaced at crust–mantle boundary, resulting in large-scale partial melting of the lower crust (e.g., Hou et al., 2021). The Jinshajiang–Ailaoshan suture zone, having spatial correspondence with this hot mantle flow, dominates the emplacement of potassic intrusions, forming the north-northwest trend 2000-km-long magmatic belt (Figure 1; Hou et al., 2021; Deng et al., 2021).

Sample description

Combined with our previously data, systematic whole-rock and mineralogical data from four ore-forming porphyries of PCDs, including two giant PCDs (Beiya and Yulong) and two large PCDs (Machangqing and Yao’an), as well as six barren porphyries (Shigu, Weishan, Ninglang, Yanyuan, Nangqian and Mangkang) in the Sanjiang metallogenic belt have been analyzed in this paper (Supplementary Table 1–7). The Yulong and Machangqing deposits contain Cu–
Mo mineralization (Yulong: ~6.5 Mt Cu, 0.4 Mt Mo; Machangqing: 0.3 Mt Cu, 0.1 Mt Mo) within the ~43 Ma and ~35 Ma porphyries. The Beiya and Yao’an deposits exhibit Au mineralization (~320 t and ~10 t Au) related to the ~36 Ma and ~33 Ma porphyries, respectively. The barren porphyries have been dated at ~33 to 40 Ma, showing spatial and temporal correspondence with the ore-forming porphyries.

The ore-forming and barren porphyries have similar mineral assemblages. The phenocrysts contain plagioclase, K-feldspar, amphibole, biotite and quartz, and some apatite micro-phenocrysts. Groundmass of these porphyries are composed of plagioclase, K-feldspar and quartz with sizes mostly < 0.5 mm. The plagioclase (0.2–4 mm) occurs as euhedral to subhedral laths (Figure 2a–g). Some plagioclase grains preserve oscillatory zoning (Figure 2b, f). K-feldspar is mostly anhedral with occasional cross-hatched (tartan) twinning. The biotite phenocrysts, which are lath-shaped and range from euhedral to subhedral, exhibit yellowish to dark brown pleochroism (Figure 2b, f). The quartz phenocrysts are irregular and circular. Euhedral to subhedral amphibole phenocrysts are hexagon-shaped with dark brown to green pleochroism, ranging from the 0.3 to 5 mm in size (Figure 2a–g). Some slightly fluid altered amphibole phenocrysts have bleached colors corresponding to the patchy zoning observed in BSE images (Figure 2h), which were excluded from the experiment. Apatites occur as inclusions within biotite and K-feldspar phenocrysts apart from micro-phenocrysts (Figure 2j, 2k). Some apatites exhibit bright bands along fractures and edges in cathodoluminescence (CL) images (Figure 2l), indicating that these corresponding portions of apatite...
have undergone late-stage hydrothermal alteration. We excluded these hydrothermally altered apatites and took precautions during experiments to avoid fluid or mineral inclusions and fractures in apatite to ensure that the tested apatites are primarily magmatic origin (Supplementary Figure 3). Therefore, the selected amphiboles and apatites are of primary magmatic origin (Figure 2i, 2l), and capable of reflecting the corresponding magmatic processes and avoiding the influence of late-stage hydrothermal alteration.

Results

Major element compositions of apatite, amphibole, and plagioclase from ore-forming and barren porphyries in Sanjiang metallogenic belt were obtained using an electron probe microanalyzer (EPMA). The results are presented in Supplementary Table 1–3, including compiled data for Yao’an, Yulong, Nangqian and Mangkang (e.g., Bi et al., 2009). For detailed information about the analytical methods employed, please refer to the Supplementary materials.

Amphibole compositions

The analyzed amphibole phenocrysts in both ore-forming and barren porphyries are unaltered, showing no bleached colors (Figure 2i). The quality of their compositions was verified using AMFORM.xlsx (Ridolf et al., 2018). These amphiboles are all calcic (Ca$_B$ > 1.5) and can be further classified as actinolite, magnesiohornblende, edenite and pargasite (Supplementary Figure 4a, b; Leake et al., 1997). The amphibole phenocrysts in ore-forming porphyries demonstrate
variable contents of Na$_2$O (0.54–2.24 wt%), CaO (10.91–12.56 wt%), and Al$_2$O$_3$ (1.99–8.48 wt%). The amphibole phenocrysts in barren porphyries display narrower ranges in Na$_2$O (1.45–3.01 wt%), CaO (10.91–11.94 wt%), and Al$_2$O$_3$ (6.63–12.12 wt%). The Al$^{VI}$ contents of the amphiboles in ore-forming and barren porphyries are 0.28–1.44 and 0.97–1.87, respectively. They exhibit similar ranges of Cl contents (0.01–0.24 wt% and 0.02–0.19 wt%, respectively), with no observed correlation between Cl and Mg$#$ (Supplementary Table 2).

**Apatite compositions**

Apatites in the ore-forming and barren porphyries exhibit similar CaO, P$_2$O$_5$ and SO$_3$ contents (52–59 wt%, 38–43 wt% and 0.03–1.44 wt%, respectively). Apatites from ore-forming porphyries show much higher F (1.60–3.22 wt%) and lower Cl (0.01–0.17 wt%) contents relative to those from barren porphyries (1.15–2.76 wt% F, 0.18–2.10 wt% Cl; Supplementary Table 1). These differences can be translated to $X_F$, $X_{Cl}$ and $X_{OH}$ (Supplementary Figure 4c), which are the mole fractions of F, Cl and OH, respectively.

Apatites from ore-forming porphyries tend to have a low and narrow range of $X_{Cl}/X_{OH}$ (0.003–0.148), high and wide extents of $X_F/X_{Cl}$ (31.76–548.12) and $X_F/X_{OH}$ (0.779–7.370), showing a negative correlation between $X_F$ and $X_{Cl}$, $X_F$ and $X_{OH}$, respectively. In contrast, the counterparts from barren porphyries have high and wide $X_{Cl}/X_{OH}$ ratios (0.073–1.041), low and narrow $X_F/X_{Cl}$ (1.03–26.58) and $X_F/X_{OH}$ (0.686–3.602) ratios, with a negative correlation between $X_{Cl}$ and $X_{OH}$ (Supplementary Table 1).
Feldspar compositions

Some plagioclase phenocrysts in ore-forming and barren porphyries are zoned. The plagioclases we selected are those with no zone or the rims of the zoned plagioclase phenocrysts, which could be in equilibrium with the residual evolved melt. In ore-forming porphyries, the plagioclase phenocrysts range in composition from albite to anorthoclase and oligoclase (An content = 0.6-34.0% and Or content = 0.5-24.0%). Among them, the plagioclase phenocrysts in the Beiya ore-forming porphyry have the lowest An content (0.6-2.8%). The compositions of plagioclase phenocrysts in barren porphyries are comparable to those in ore-forming porphyries, ranging from albite to oligoclase (An content = 2.4-30.7% and Or content = 0.5-8.6%; Supplementary Figure 4d, Table 3).

Pressure, temperature and H$_2$O content estimates

The method of Ridolfi and Renzulli (2012) has been used to estimate the physical (P, T) and compositional conditions (e.g., melt H$_2$O contents) at the time of amphibole crystallization, based on amphibole compositions (Figure 3). This method is recommended for studies aiming to discern the pre-eruptive conditions and sub-volcanic processes such as magma storage for both calc-alkaline and alkaline magmatic series (Ridolfi and Renzulli. 2012; Chelle-Michou et al., 2015; Gorini et al., 2018), which is consistent with our samples. The amphibole compositions in this study match those of the experimental amphiboles from Ridolfi and Renzulli (2012). However, there are much debate surrounds the
accuracy of the calculated intensive variables (e.g. Walker et al., 2013; Erdmann et al., 2014). Therefore, the methods of amphibole–plagioclase barometer and feldspar–liquid hygrometer have been conducted to estimate the physical and compositional conditions (especially P and melt H₂O contents) and verify the credibility of these results (Anderson et al., 2008; Putirka, 2008). The results for individual analyses can be found in Supplementary Table 2–4.

The pressures and temperatures calculated using the methods of Ridolfi and Renzulli (2012) indicate that amphiboles from ore-forming porphyries record lower crystallization temperatures (680–831 °C with uncertainties ± 23.5 °C) and pressures (0.39–1.56 Kbar with uncertainties ± 11.5%), whereas amphiboles from barren porphyries yield evidently higher temperature and pressure, except for Shigu and Yanyuan barren porphyries (739–940 °C and 0.97–4.35 Kbar, with uncertainties ± 23.5 °C and ± 11.5%, respectively; Figure 3; Supplementary Fig 5, Table 2). We also calculated pressures using amphibole–plagioclase barometer (Anderson et al., 2008), and obtained a range of pressures of 0.3–4.4 Kbar, which is similar to the results estimated by the methods of Ridolfi and Renzulli (2012) (Supplementary Table 4). The pressures calculated by these two methods of the same porphyry are relatively consistent within this study (Supplementary Fig 5). The new temperature-independent Al-in amphibole geobarometer of Méard and Le Pennec (2022) returns similar pressure ranges for ore-forming and barren porphyries and suggests a shallower storage depths for the ore-forming magmas.

Overall, the melt H₂O contents of ore-forming porphyries (4.2–6.3 wt% with uncertainties ± 0.78 wt%) are slightly lower than those of barren porphyries (4.0–
8.1 wt% with uncertainties ± 0.78 wt%) by the methods of Ridolfi and Renzulli (2012) (Figure 3; Supplementary Table 2). These results are also consistent with the melt H$_2$O contents calculated using feldspar–liquid hygrometer (Putirka, 2008), except for Beiya ore-forming porphyry (Supplementary Fig 6, Table 3). The higher melt H$_2$O contents and temperatures calculated by plagioclase–liquid in the Beiya porphyry may indicate the physical and compositional conditions for the early crystallization of plagioclases, while the lower melt H$_2$O contents and temperatures calculated by amphibole-only represent the conditions for the later stage of magma evolution with the crystallization of amphiboles.

Discussion

Modelling fractionation and fluid saturation

According to the different pressures and temperatures estimated by amphiboles from ore-forming and barren porphries in Sanjiang metallogenic belt, the evolutions of ore-forming and barren magmas have been modeled, over the pressure of 1.2 Kbar (corresponding to ore-forming magmas) and 3 Kbar (for barren magmas) by the Rhyolite-MELTS thermodynamic software (Gualda et al., 2012). Because these magmas are attributed to the partial melting of a thickened juvenile lower crust (Figure 3a; Supplementary Figure 1, 2; Lu et al., 2013a, 2013b; He et al., 2015; Hou et al., 2017; Huang et al., 2019; Wang et al., 2022), the melt composition from partial melting experiments on a synthetic has been used as the starting composition, which is close to the average lower continental crust (Qian and Hermann, 2013; details in supplementary materials). Models were
run at the Ni-NiO buffer and with H$_2$O concentration of 4 wt% according to the results calculated by amphibole compositions (Figure 3c, 4b), and were also the best ones reproducing the stable phase assemblages observed in ore-forming and barren porphyries (Figure 3a; Lu et al., 2013a, 2013b; He et al., 2015; Huang et al., 2019; Wang et al., 2022).

The model results confirm the crystallization sequence: plagioclase (~980°C) + amphibole (~920°C) + quartz (~760°C) + biotite (~750°C) + apatite (~730°C) + K-feldspar (~740°C) at 1.2 Kbar, and plagioclase (~970°C) + amphibole (~910°C) + quartz (~800°C) + biotite (~780°C) + apatite (~760°C) at 3 Kbar (Figure 5a). These match the observed phase assemblage in ore-forming and barren porphyries. Apatites arrive on the liquidus as a late phenocryst phase at both 1.2 and 3 Kbar, which is consistent with the high SiO$_2$ contents of the melt inclusions trapped by apatites in Yulong porphyries (Chang et al., 2018). During fractionation, modeled melt MgO contents have similar variation characteristics at 1.2 and 3 Kbar, which decrease when amphiboles arrive on the liquidus (Figure 5a). Pressures greatly affect the behaviors of dissolved H$_2$O contents. At 3 Kbar, modeled melt H$_2$O contents increase from the beginning to 6.9 wt% before fluid saturation is achieved at ~50% crystallization, whereas the fluid saturation is achieved much earlier at ~7% crystallization, with melt H$_2$O contents around 4 wt% at 1.2 Kbar (Figure 3c; 5a). We have also modeled sulfide saturation processes at 1.2 and 3 Kbar with initial S concentration ~100 ppm (Smythe et al., 2017; Yao and Mungall, 2020). The saturation conditions occur at 15% crystallization, and the modeled melt S contents decrease
with fractionation at both 1.2 and 3 Kbar. Pressures affect the modeled down-
temperature S evolution of the melt, that the melt S contents at 3 Kbar are a bit
higher than those at 1.2 Kbar after S saturation is achieved (Figure 5a).

Fluid enrichment and degassing of ore-forming and barren magmas

The crystallization pressures and temperatures calculated by amphibole from ore-
forming porphyries (pink trend; 0.39–1.56 Kbar; 680–831 °C) are lower than
those of barren porphyries (gray trend; 0.97–4.35 Kbar; 739–940 °C; Figure 4c
and d), suggesting that amphibole crystallization in ore-forming magmas (with
lower crystallization pressure conditions) is relatively later than that in barren
magmas. These are consistent with the thermodynamic modelling, that modeled
melt amphiboles arriving on the liquidus at 3 Kbar is earlier than that at 1.2 Kbar
(Figure 5a, 6a and c).

During crystallization process with H₂O-undersaturation, Cl/OH ratios of the
melts [(Cl/OH)ₘ] will decrease with increasing H₂O contents of melts, whereas
(Cl/OH)ₘ and H₂O contents of melts could decrease together under H₂O-
saturation condition, according to the experimental exchange partition coefficient
of Cl/OH and Cl/H₂O ratios between fluid and melt (Sato et al., 2005). In the
Sanjiang metallogenic belt, though the (Cl/OH)ₘ decrease through cooling
process within both ore-forming and barren magmas (Figure 4c), H₂O contents of
the ore-forming magmas first increase then decrease with the falling of (Cl/OH)ₘ
as revealed by amphiboles (Figure 4b). Conversely, H₂O contents of the barren
magmas are characterized by rising consistently, lacking of falling in H₂O
contents (Figure 4b). These features indicate that H$_2$O contents were enriched in both of the ore-forming and barren magmas during the processes of amphibole crystallization. However, H$_2$O saturation did not occur within the barren magmas, while the ore-forming magmas experienced obvious H$_2$O saturation and degassing processes. According to the thermodynamic modelling, amphibole crystallization occurs at relatively early stages of magmatic evolution at both 1.2 and 3 Kbar (Fig 5a and 6a, c). Amphiboles could record the degassing processes of most of the ore-forming magmas, while the degassing processes of some ore-forming magmas (such as Yao’an) are not recorded by amphiboles, due to degassing processes taking place after amphibole crystallization instead of there being no degassing processes. The obvious changes of F, Cl and OH contents of apatites indicate that they may have higher potential to record degassing processes than amphiboles. That is, the crystallization of apatites could be at later magmatic fractionation stage, which is consistent with the results of thermodynamic modelling (Fig 5a and 6a–d; Supplementary Figure 4c). Together with their application to elucidate the volatile contents of melts (Stock et al., 2016; 2018), models can be built to estimate the evolution of melt volatile composition, relying on apatite–melt exchange coefficients (K) between F–OH and Cl–OH. Decreasing in $X_F/X_{Cl}$ and $X_F/X_{OH}$ with the falling of $X_{Cl}/X_{OH}$ ratios for apatites should represent H$_2$O-undersaturated crystallization, when the order of crystal–melt partition coefficients from high to low is F, Cl and H$_2$O. In contrast, H$_2$O-saturation crystallization could be characterized by a strong decrease in apatite $X_{Cl}/X_{OH}$,
with increasing $X_F/X_{Cl}$ ratios (Figure 7a; Supplementary Figure 4c), owing to
much higher fluid–melt partition coefficients for Cl than those for F (Webster et al., 2014). Therefore, as shown in Figure 7, a modal represents ~50% crystallization at H$_2$O-undersaturated conditions starting from 4 wt% H$_2$O content (according to our Rhyolite-MELTS thermodynamic modelling; the initial melt Cl and F concentrations are set at 0.4 wt % and 0.15 %, based on the melt inclusion data from the Sanjiang porphyries; Chang et al., 2023b), with crystal–melt partition coefficients $D_{c/m} F \approx 0.99$, $D_{c/m} Cl \approx 0.9$ and $D_{c/m} OH \approx 0.01$. During the next differentiation under fluid-saturation conditions to 90% crystallization, there are three trajectories of apatite compositional evolution, which show gradually increasing $X_F/X_{Cl}$ and $X_F/X_{OH}$ ratios, indicating an increased degree of fluid degassing. The fluid–melt partition coefficient has been set as $D_{f/m} F \approx 0.9$ and $D_{f/m} Cl \approx 35$, consistent with alkali melt–fluid halogen partitioning experiments under magmatic conditions (Figure 7a; e.g., Borodulin et al., 2009; Hsu et al., 2019).

Much higher $X_F/X_{Cl}$ and lower $X_{Cl}/X_{OH}$ ratios of apatites from ore-forming porphyries suggest that the ore-forming magma crystallization were reached H$_2$O-saturation and degassed extensive fluids during magmatic evolution (Figure 7a), according to the apatite thermodynamic modelling. The H$_2$O contents calculated by amphiboles from ore-forming porphyries are decreasing with increase of apatite $X_F/X_{Cl}$ ratios, which further restricts the fluid degassing of ore-forming magmas (Figure 8b). The fluid saturation and degassing processes will be greatly affected by the magma storage depths, because pressure is the most important
variable controlling the solubility of H$_2$O (e.g., Zhang et al., 1999; Ghiorso and Gualda, 2015; Collins et al., 2020). The lower crystallization pressures (shallower storage depths) of ore-forming magmas estimated by amphiboles indicate lower H$_2$O solubility (easier to reach H$_2$O saturation) of them (Figure 3b), which also concurs with the features of apatites, amphiboles and our Rhyolite-MELTS modelling (Figure 4d; 5a).

Very low X$_{Cl}$/X$_{OH}$ ratios of apatites from ore-forming porphyries are consistent with sufficient isobaric H$_2$O-saturated fractionation at high Df/m Cl, where Cl is efficiently extracted from the melt into the extensive fluid phase. The ratios of X$_F$/X$_{OH}$, however, remain relatively low throughout this isobaric crystallization process according to no H$_2$O loss (Figure 7b; Stock et al., 2018). Under the following polybaric H$_2$O-saturation fractionation, which is a fast process with violent H$_2$O loss (fluid degassing) from shallow magma chambers, the X$_F$/X$_{OH}$ ratios of apatites from ore-forming porphyries then curve towards higher values immediately, resulting in wide ranges of X$_F$/X$_{OH}$ ratios (Figure 7b; 8c, d; Stock et al., 2018). Low X$_{Cl}$/X$_{OH}$ and wide ranges of X$_F$/X$_{OH}$ and X$_F$/X$_{Cl}$ ratios of apatites and low crystallization pressures estimated by amphiboles, therefore, suggest that the ore-forming magmas experienced focused extensive fluid degassing with shallower storage depths of magma chambers.

Being different from ore-forming magmas, the barren magmas, with higher crystallization pressures estimated by amphiboles (Figure 3a, b; Supplementary Figure 5), show fluid enrichment during crystallization process at H$_2$O-undersaturated conditions (gradual increase of H$_2$O contents with relatively low
$X_F/X_{Cl}$ ratios of apatites; Figure 3c; 4b; 7a; 8a, b), followed by fluid exsolution under isobaric H$_2$O-saturation condition (with no H$_2$O loss; continuous reduction of X$_{Cl}$/X$_{OH}$ with low $X_F/X_{Cl}$ and $X_F/X_{OH}$ ratios of apatites; Figure 7b).

Mechanisms of fluid degassing within shallow magma chambers

The ore-forming and barren magmas experienced polybaric and isobaric H$_2$O-saturation fractionation, respectively, according to the features of apatites and amphiboles. However, the different ways of fluid degassing under H$_2$O-saturation processes cannot be explained only by H$_2$O solubility of melts according to pressure conditions of magma chambers. Here, three different ways of fluid degassing have been identified in the Sanjiang metallgenic belt according to thermodynamic modelling (Figure 5b) and apatite and amphibole compositions (Figure 5c–e), (1) by discrete bubbles that roughly account for a few percentages of the total amount of fluid degassing, which could be recorded by the early crystallized amphiboles characterized by decreasing (Cl/OH)$_m$ with increasing H$_2$O contents (Figure 5e); (2) by permeable degassing via fluid channel formation that contributes to about 40–50% of the degassing, which could be indicated by high $X_F/X_{Cl}$ and $X_F/X_{OH}$ ratios of apatites. The together decreasing (Cl/OH)$_m$ ratio and H$_2$O contents calculated by some relatively late crystalline amphiboles can also indicate this degassing stage (Figure 5c); and (3) degassing stops because there is not enough fluid to form/stabilize connected pathways (bubbles remain trapped in the mush), which could be recorded by the decreasing X$_{Cl}$/X$_{OH}$ with low $X_F/X_{OH}$ ratios of apatites, representing isobaric fluid exsolution (Figure 5d).
The storage depth of magmas play an important role in controlling the mechanisms of fluid degassing. At 3 Kbar (~10 km in depth), the simulated melts can achieve H$_2$O-saturation at ~41% crystal volume fractions (~50% crystallization), and finally exsolves a large amount of fluids (~3.5 wt%), but all the exsolved fluids belongs to the third stage which remain trapped in the mush with no degassing (green region in Figure 5b). At 1.2 Kbar (~4 km in depth), however, H$_2$O-saturation is achieved at very early stage with ~6% crystal volume fractions (~7 wt% crystallization), and the degassing occurs through stage 1 and stage 2 and finally to stage 3. Up to 3.4 wt% H$_2$O can be exsolved controlled by discrete bubbles and fluid channel degassing processes (Figure 5b; Parmigiani et al., 2017). Conclusively, shallower storage depths (for ore-forming magmas) would enhance the amount of fluid degassing before the trapped bubbles stage. However, the Yanyuan and Shigu exhibit shallow storage depths, similar to those of the ore-forming magmas, showing weak or no fluid degassing (Figure 7a, b; 8b, d), which could be caused by the melts with relatively lower initial H$_2$O contents.

The initial H$_2$O content of magmas may also play an important factor affecting the mechanisms of fluid degassing (Chiaradia, 2020; Rezeau and Jagoutz, 2020). The same starting compositions with different initial H$_2$O contents (1–7 wt%) at 1.2 and 3 Kbar have been modeled (Figure 6a, c). The model results confirm that the crystallization sequences are similar with different initial H$_2$O contents. The crystallization of quartz and plagioclase will be delayed and the process of H$_2$O-saturation will be enormously advanced, with higher initial H$_2$O contents (Figure 6a, c).
At 1.2 Kbar, the initial H$_2$O content required for fluid degassing is greater than 2 wt% (Figure 6a, b). ~85% fluid contents (3.4 wt%) could degas after ~90 wt% crystallization, when the initial H$_2$O content is 4 wt%. Almost all fluid contents could undergo degassing process, if the initial H$_2$O content is 6 wt% (Figure 6b). In contrast, at 3 Kbar, degassing process cannot occur unless the initial H$_2$O content is more than 4 wt%. ~80% fluid contents (4.8 wt%) are able to degas after ~87 wt% crystallization, if the initial H$_2$O content is 6 wt% (Figure 6d). These results imply that higher initial H$_2$O contents would increase the amount of fluid degassing before the trapped bubbles stage.

Collectively, magmas with shallower storage depths and higher initial H$_2$O contents can reach fluid saturation at earlier stages of crystallization processes and undergo more intense fluid degassing through fluid channel stage. The deeper storage depths and lower initial H$_2$O contents of magmas will block the degassing processes via the trapped bubbles stage.

**Extensive focused fluid degassing driving the formation of porphyry deposits**

Cu, Au and S will effectively partition into the fluids due to similarly elevated fluid/melt partition coefficients, which vary from 10 to 100, 2 to 100 and 20 to 280 (e.g., Zajacz et al., 2012; Audétat and Edmonds, 2020), respectively. Thus, the effective fluid exsolution, which could carry a large amount of metals, plays a primary role in the generation of PCDs. However, the barren porphyries in the Sanjiang metallgenic belt (e.g., Weishan and Nangqian) also experienced H$_2$O saturation processes with no porphyry mineralization, according to continuous
reduction of X\textsubscript{Cl}/X\textsubscript{OH} with low X\textsubscript{F}/X\textsubscript{Cl} and X\textsubscript{F}/X\textsubscript{OH} ratios of apatites (Figure 7a, b). This is possibly caused by the lack of effective migration and focusing of the exsolved fluids. The mechanisms of fluid degassing after exsolution within magma chambers, therefore, may finally determine whether the porphyries have the potential to form PCDs.

As shown above, the ore-forming magmas in the Sanjiang metallgenic belt experienced focused extensive fluid degassing revealed by the features of apatites and amphiboles. Shallower storage depths and higher initial H\textsubscript{2}O contents of ore-forming magmas made the magmatic fluid exsolution occur at very early stage. In consequence, these earlier exsolved fluids should enriched in Cu, Au and S, because less fractionation of sulfides could occur before earlier fluid saturation, leading to that higher proportion of those ore-forming elements can be extracted from the melt by these earlier exsolved fluids (Figure 5a; Smythe et al., 2017).

Most of these exsolved fluids could migrate efficiently through fluid channel stage. Meanwhile, for the ore-forming magmas with shallow storage depths, it is easy to form a stable tube ring network, a particularly efficient fluid transport pathway (Oppenheimer et al., 2015; Edmonds and Woods, 2018; Lamy-Chappuis et al., 2020). This stable tube ring network will establish within the magma chambers close to H\textsubscript{2}O saturation at the early stage of crystallization processes, requiring relatively low initial H\textsubscript{2}O contents (Figure 9b). Fluid exsolution of the entire ore-forming magmas took place mainly through fluid channel stage and laterally focused fluids flowed through the tube ring, and then focused degassed from spatially stable small region in the roof of the magma chambers, which is
consistent with wide ranges of $X_F/X_{OH}$ and low $X_{Cl}/X_{OH}$ ratios of apatites (Figure 9b). The metal sulfides were settled in relatively small volume rocks accordingly (porphyry mineralization) at the end.

Conversely, the barren magmas with deep storage depths could also undergo fluid saturation (Figure 9c, d), which occurred at late stage of crystallization processes. Most of the exsolved fluids would be trapped within the magma chambers at trapped bubbles stage. Even if the storage depths of the barren magmas from Yanyuan and Shigu are shallow, their low initial $H_2O$ contents (less than 2 wt%, according to our thermodynamic modelling with different initial $H_2O$ contents; Figure 6b) blocked the migration of exsolved fluids (mainly at trapped bubbles stage; Figure 6b; 9a). It is also difficult to form an integral tube ring network for the barren magmas with deep storage depths and/or low initial $H_2O$ contents (Figure 9a, c, d). Fluid degassing within the barren magma chambers is weaker, more radial and diffusive, recorded by slight increase in $X_F/X_{OH}$ with low $X_{Cl}/X_{OH}$ ratios of apatites (as in Shigu and Weishan barren magma chambers; Fig 9a, d), or there is no degassing at all, revealed by declining of $X_{Cl}/X_{OH}$ with low $X_F/X_{OH}$ ratios of apatites (Figure 9c). Without or with limited magmatic fluid degassing, the ore-forming elements cannot be effectively focused and migrated from the magma chambers, resulting in no porphyry mineralization.

Magmatic fluid degassing processes bridge the magmatic and hydrothermal systems of PCDs, during magma ascent and storage in the upper crust with cooling and crystallization at a fixed pressure (e.g., Parmigiani et al., 2016, 2017).

In the Sanjiang metallgenic belt, only magmas with shallow storage depths
(commonly less than ~5 km) and relatively high initial H$_2$O contents (at least ~2 wt%) allow effective migration, focusing and degassing processes of metal-rich exsolved fluids, which are pre-requisites to the precipitation of metal sulphides within a relatively small volume of rock, the final step in the formation of PCDs.

**Implications for exploration**

The mineral geochemical data and thermodynamic modelling presented here allow us to shed light on the control of the mechanisms of fluid degassing within shallow magma chambers on the formation of PCDs. This multiscale approach reveals that only if H$_2$O-saturation is achieved at the early stage of magmatic evolution, the exsolved fluids carrying ore-forming elements can migrate efficiently through fluid channel stage, focus through the tube ring and degas from spatially small region in the roof of shallow magma chambers. Magmas with shallower storage depths and higher initial H$_2$O contents can reach fluid saturation at earlier stages of crystallization processes and allow more substantial focused degassing, leading to significant ore-forming elements focusing and the formation of PCDs. Conversely, deeper storage depths and lower initial H$_2$O contents can be more prone to a late-stage fluid exsolution where fluids remain trapped in the mush with no degassing.

The combination of apatite, amphibole and plagioclase analyses and thermodynamic modelling represents a robust approach for assessing the mechanisms of fluid degassing in the upper crust, which could reveal the transformation processes from magmatic systems to hydrothermal systems. This
approach can significantly advance our understanding of the ore-forming processes of PCDs, which can be an effective exploration tool to reveal the degassing processes of magmas and the optimal storage depths conducive to porphyry mineralization, and thus to identify prospective buried PCDs.

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Figure 1. Topographic-geological map of the eastern Indian–Asian collisional zone (Xu et al., 2021). The thick gray dotted line is Jinshajiang–Ailaoshan suture (JAS), and the gray continuous line is Indus–Tsangpo suture. The PCDs are shown as red hammers, including the giant Yulong (age of 43–37 Ma), giant Beiya (age of 36–34 Ma), medium Machangqing (age of 36–34 Ma) and medium Yao’an (age of 33 Ma; Lu et al., 2013b; Huang et al., 2019). The barren porphyries along JAS are shown in orange. The black lines represent Cenozoic
faults (SGF: Sagaing fault; GLGF: Gaoligong fault; XSHF: Xianshuihe fault; RRF: Red-River fault; XJF: Xiaojiang faults; LMT: Longenshan thrust fault; KLF: Kunlun fault).
Figure 2. a–g, Photomicrographs of ore-forming and barren adakite-like porphyries in Sanjiang metallogenic belt. h and i, Backscattered-electron (BSE) images showing altered amphibole phenocryst (h) and amphibole phenocryst with no hydrothermal alteration (i). j and k, Backscattered-electron (BSE) images
showing apatite microphenocryst (j) and apatite inclusions (k). Cathodoluminescence (CL) images of apatite from ore-forming and barren adakite-like porphyries. Qtz, quartz; Kfs, K-feldspar; Pl, plagioclase; Bt, biotite; Am, amphibole; Ap, apatite.
Figure 3. **a,** The calculated P–T conditions for the adakite-like porphyries in Sanjiang metallogenic belt. Cross bars indicate the P–T uncertainties (Ridolfi and Renzulli, 2012). Liquidus and near liquidus fields for amphibole, garnet, clinopyroxene are delineated with black solid lines, labelled on their unstable side (Annen et al., 2006). The field of residual garnet amphibolite is shaded. The blue P–T path for partial melting of thickened juvenile lower crust (residual garnet amphibolite; Annen et al., 2006), according to regional tectonic background of Sanjiang region (Hou et al., 2017). The wet granite solidus line and wet basalt liquidus line are delineated with black solid line and dashed line, respectively (Collins et al., 2020). The steep grey dashed lines are undersaturated liquidus (with wt% H2O labelled) and the subhorizontal dashed lines are H2O solubility limits (also labelled as H2O saturated; Gualda et al., 2012; Collins et al., 2020). The cordilleran geotherm is also shown. Abbreviations: Cpx, clinopyroxene; Am, amphibole; Gt, garnet; Wgs, wet granite solidus. **b,** The calculated magma depth vs. magmatic H2O content for the adakite-like porphyries in Sanjiang metallogenic belt. Cross bars indicate the P–H2O uncertainties (Ridolfi and Renzulli, 2012). The colored dashed line show the H2O solubility curves from different methods (Newman and Lowenstern, 2002; Papale et al., 2006; Iacono-
Marziano et al., 2012; Ghiorso and Gualda, 2015). The calculated T–H$_2$O conditions for the adakite-like porphyries in Sanjiang metallogenic belt. Cross bars indicate the T–H$_2$O uncertainties (Ridolfi and Renzulli, 2012). The thick lines represent the melt compositional evolution modelling with 4% initial H$_2$O content at 1.2 Kbar (wathet dashed line) and 3 Kbar (blue dotted line), respectively.
Figure 4.  

**a**, Test for equilibrium between amphibole and melt based on the Fe-Mg exchange coefficient ($K_D$). $K_D$ values in the range of $0.28 \pm 0.11$ (Putirka, 2016). **b–d**, The calculated melt Cl/OH–H$_2$O, Cl/OH–T and Cl/OH–P, respectively. Melt Cl/OH is calculated by amphibole compositions according to Sato et al. (2005). The pink and gray thick lines illustrate continuous variation trends of ore-forming and barren porphyries.
Figure 5a, Rhyolite-MELTS thermodynamic modelling for the ore-forming and barren magmas in Sanjiang metallogenic belt. Summary of mineral phase and extent of crystallization at 1.2 Kbar (black dashed line) and 3 Kbar (black dotted line) for cooling and crystallizing. Residual melt MgO (gray) and H$_2$O (blue) are shown at 1.2 Kbar (dashed lines) and 3 Kbar (dotted lines). The brown dashed and dotted lines represent the trend of estimated sulfur concentration at sulphide saturation (SCSS) at 1.2 Kbar and 3 Kbar, respectively. Meanwhile, the brown continuous line traces the enrichment of sulfur within melts during magma evolutions at 1.2 Kbar and 3 Kbar. Apatites have joined the crystallizing assemblage before H$_2$O-saturation is achieved at both pressure conditions. b–e, Models of fluid migration in shallow magma chambers according to Parmigiani et al. (2017). The Bond number (Bo) is set as 0.5, which can describe the competition between buoyancy and capillary stresses on fluid bubbles in the hydrodynamics migration regime. The representative graphs around each model illustrate how apatite and amphibole compositional trend relate to different fluid
migration processes. Black dots and squares represent the liquidus of apatite and amphibole at different conditions, respectively.
Figure 6a and c, Isobaric $T$–$H_2O$ pseudosection for the ore-forming and barren magmas in Sanjiang metallogenic belt with different initial $H_2O$ contents. These phase diagrams are constructed at constant pressures (1.2 Kbar and 3 Kbar, respectively) and shows the influence of different initial $H_2O$ contents at temperatures of 730–1050 °C. The thin dashed lines show calculated crystal volume proportion. The thick dashed and dotted lines represent the boundary of $H_2O$-saturation at 1.2 and 3 Kbar, respectively. The filled colors represent the volumes of exsolved fluids. The thin continuous lines are the liquidus of minerals.

b and d, Models of fluid migration in shallow magma chambers with different initial $H_2O$ contents according to Parmigiani et al. (2017). Black dots and squares
represent the liquidus of apatite and amphibole at different conditions,
respectively.
Figure 7. Volatile compositions of apatites from the adakite-like porphyries in Sanjiang metallogenic belt. 

(a) Apatite volatile compositions in $X_{Cl}/X_{OH}$ versus $X_{F}/X_{Cl}$. (b) Apatite volatile compositions in $X_{Cl}/X_{OH}$ versus $X_{F}/X_{OH}$. The thermodynamic modelling of apatite compositional evolution is presented in a, b.

Apatite crystallization begins at the black point and continues to 50% crystallization under $H_2O$-undersaturated condition according to the black arrow (initial $H_2O$ content is 4%; $D_{m}F \approx 0.99$, $D_{m}Cl \approx 0.9$ and $D_{m}OH \approx 0.01$). Then apatite compositional evolution continues in the red arrows to 90% crystallization under $H_2O$-saturated condition. Line types illustrate the difference between isobaric (0% $H_2O$ loss; solid red line) $H_2O$-saturated crystallization and polybaric $H_2O$-saturated crystallization with 0.05 wt% (dashed line) and 0.09 wt% (dotted line) $H_2O$ loss per 1% crystallization (total $H_2O$ loss of 0%, 2 wt% and 3.5 wt%, respectively) according to the overall systems. The inset in b shows compositional trajectories during no degassing (black solid line), weak diffusive degassing (black dashed line) and extensive focused degassing (red dashed line) according to $X_{Cl}/X_{OH}$ versus $X_{F}/X_{OH}$ ratios of apatites.
Figure 8. Box and whisker plots of volatile compositions of apatites and P–T–H$_2$O calculated by amphiboles from the adakite-like porphyries in Sanjiang metallogenic belt. Boxes show first to third quartile range with bars showing extremes of data (excluding any outliers). Long and short lines in box show square and mean value, respectively. The points outside boxes represent their extremum values. The thermodynamic modelling of apatite compositional evolution as for Figure 6. The gray dashed lines (in a, c) are H$_2$O solubility limits (Ghiorso and Gualda, 2015; Collins et al., 2020). The grey squares in the insets show different data features between no/weak diffusive degassing and extensive focused degassing processes.
Figure 9. Classification of magma crystallization, fluid migration and degassing patterns as a function of magma storage depths and initial H$_2$O contents. Three principal mechanisms of degassing process can be distinguished as follows. Fluid exsolution starts at the late trapped bubble stage with no degassing (c); A small amount of degassing with weak fluid migration, forming discontiguous tube ring, and most of exsolved fluids are trapped according to high crystallization (a, d); Extensive fluid exsolution with intense migration and degassing with no trapped fluids, and the integral tube ring controlling focused degassing. Efficient focusing of fluids through a narrow window and cooling across a steep thermal gradient, could make sulphide mineral precipitation in a limited rock volume, creating rich mineralization, and form PCDs. (b). The representative graphs on the left
illustrate how apatite and amphibole compositional trend relate to different degassing processes.