



Article Apatite as a Record of Magmatic–Hydrothermal Evolution and Metallogenic Processes: The Case of the Hongshan Porphyry–Skarn Cu–Mo Deposit, SW China

Yao-Wen Zhang ^{1,2}, Jing-Jing Zhu², Li-Chuan Pan², Ming-Liang Huang², Dian-Zhong Wang^{2,*} and Zhi-Chao Zou^{1,*}

- ¹ College of Earth and Planetary Sciences, Chengdu University of Technology, Chengdu 610059, China
- ² State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China
- * Correspondence: wangdianzhong@mail.gyig.ac.cn (D.-Z.W.); zouzhichaoten@126.com (Z.-C.Z.)

Abstract: Apatite, as a common accessory mineral found in magmatic-hydrothermal deposits, effectively yields geochemical insights that facilitate our understanding of the mineralization process. In this research, multiple generations of magmatic and hydrothermal apatite were observed in the Hongshan porphyry-skarn Cu-Mo deposit in the Yidun Terrane in SW China. The geochemical compositions of the apatite were studied using in situ laser ablation-inductively coupled plasma mass spectrometry and an electron probe microanalysis to understand the magmatic-hydrothermal processes leading to ore formation. The apatite (Ap1a) occurs as subhedral to euhedral inclusions hosted in the phenocrysts of the granite porphyry. The Ap1b occurs later than Ap1a in a fine-grained matrix that intersects the earlier phenocrysts. Increases in F/Cl, F/OH, and F/S and decreases in ΣREE and $(La/Yb)_N$ from Ap1a to Ap1b suggest the exsolution of a volatile-rich phase from the magma. The skarn hosts three types of hydrothermal apatite (Ap2a, Ap2b, and Ap3), marking the prograde, retrograde, and quartz-sulfide stages of mineralization, respectively. The elemental behaviors of hydrothermal apatite, including the changes in Cl, Eu, As, and REE, were utilized to reflect evolutions in salinity, pH, oxygen fugacity, and fluid compositions. The composition of Ap2a, which occurs as inclusions within garnet, indicates the presence of an early acidic magmatic fluid with high salinity and oxygen fugacity at the prograde skarn stage. The composition of Ap2b, formed by the coupled dissolution-reprecipitation of Ap2a, indicates the presence of a retrograde fluid that is characterized by lower salinity, higher pH, and a significant decrease in oxygen fugacity compared to the prograde fluid. The Ap3 coexists with quartz and sulfide minerals. Based on studies of Ap3, the fluids in the quartz-sulfide stage exhibit relatively reducing conditions, thereby accelerating the precipitation of copper and iron sulfides. This research highlights the potential of apatite geochemistry for tracing magmatic-hydrothermal evolution processes and identifying mineral exploration targets.

Keywords: apatite; magmatic-hydrothermal evolution; mineral exploration; Hongshan Cu-Mo deposit

1. Introduction

Skarn-type deposits yield a variety of major and precious metal resources, such as Fe, Cu, Pb, Zn, W, Mo, Au, and Sn, making them one of the most economically important deposits globally [1–3]. Skarn-type deposits typically form in magmatic–hydrothermal systems and are characterized by long-duration and multi-stage hydrothermal activity [2,3]. The mechanism of the transition of ore-forming metals from magma to hydrothermal fluids, the evolution of hydrothermal fluids, and mineralization processes have always been the focus of the research for those deposits [4–7]. Currently, quantitative analyses



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). based on individual fluid inclusions can directly reflect compositional changes in magmatichydrothermal fluids [6,8,9]. However, due to numerous challenges, such as the modification of primary fluid inclusions by later metamorphism and the migration of easily diffusing elements between host minerals and fluid inclusions, these requirements are not always fulfilled [10–12]. Recent studies have shown that the physicochemical and isotopic features of ore-forming magmas and fluids can be estimated via mineral compositions [13–20]. However, most hydrothermal minerals crystallize under specific physicochemical conditions and cannot provide comprehensive information regarding the ore-forming environment. For instance, prograde minerals, such as garnet and wollastonite, which form from relatively high-temperature fluids, are often used to trace early conditions of magmatic–hydrothermal fluid systems [2]. Therefore, identifying widely occurring accessory minerals is crucial for addressing these issues.

Apatite, with the chemical formula $[Ca_5(PO_4)_3(F, Cl, OH)]$, belongs to the hexagonal crystal system. Compared to whole-rock samples or other minerals, apatite has several advantages: (1) it is widely distributed and can be found in most geological environments and rock types [21–24]; (2) its unique crystal structure can accommodate a variety of elements, including trace elements, rare earth elements (REEs), volatile elements, and redox-sensitive elements [25–27]; (3) it is chemically stable and strongly resistant to weathering and erosion, preserving its original information regarding the magma and fluid compositions [28,29]; (4) it has remarkable sensitivity to changes in its surrounding environment during crystallization, revealing the crystallization conditions and shedding light on the various processes that affected the magma and hydrothermal fluids [16,17,29–34]. Therefore, apatite is an effective indicator mineral and is widely used in evaluating the magma oxygen fugacity, volatile content, and ore deposits or rock types and in tracing the ore-forming potential and magmatic–hydrothermal evolution processes [17,19,29,30,32,35–39].

In this research, we studied apatite in the Hongshan Cu–Mo deposit in SW China. To understand the evolution from the magmatic stage to the hydrothermal stage, the elemental behaviors of apatite, including the changes in F, Cl, Eu, As, and REE, were utilized to reflect physicochemical conditions such as the salinity, pH, oxygen fugacity, and magmatic composition. We show that apatite can reflect the magmatic–hydrothermal evolution at different stages and can effectively be used to discriminate between deposit types and assess the mineralization potential of host rocks. Overall, our study provides an effective method for tracing petrogenic metallogenic processes using the chemical composition of apatite.

2. Geological Background

2.1. Regional Geology

The Sanjiang (Three Rivers) region in southwestern China is enveloped by the Jinshajiang, Lancangjiang, and Nujiang rivers. Geologically, the region is situated in the eastern segment of the Paleo-Tethys tectonic domain at the junction of the Gondwana and Laurasia continents and has a complex history of tectonic evolution [40,41]. The Yidun Terrane is located west of the Ganzi-Litang suture zone, east of the Jinshajiang suture zone, and in the Zhongza region, with a general north–south orientation (Figure 1a). The Yidun Terrane underwent two significant porphyry mineralization events. The early event occurred during the Late Triassic (~216 Ma) and was marked by the development of large-scale porphyry Cu deposits. Representative deposits include large to super-large porphyry Cu-Au deposits such as in Pulong and Xuejiping and smaller deposits or occurrences such as in Songnuo and Lannitang. The conventional view suggests that mineralization during the Indosinian period occurred in a subduction setting [40,42–44]. However, in recent years, scholars have proposed that this mineralization occurred in a collisional environment following ocean closure [37,45]. The latter event corresponds to the Yanshanian period (~88–79 Ma), marked by the development of large- to medium-sized porphyry-skarn Mo-Cu-W deposits. Representative deposits include the Hongshan, Tongchanggou, Xiuwacu, and Relin deposits.



Mineralization primarily occurred during the late Yanshanian stage of crustal thickening and subsequent extension [43,46–49].

Figure 1. The study area's geology: (**a**) tectonic setting of Yidun Terrane and Hongshan deposit (after Li et al. [50]); (**b**) geological map of Hongshan Cu–Mo deposit (after Peng et al. [48]); (**c**) geological cross-section of Hongshan deposit, showing the spatial relationship of orebodies, strata, and intrusions (after Peng et al. [48]).

2.2. Geology of the Hongshan Deposit

The Hongshan Cu–Mo polymetallic deposit is located ~35 km northeast of Shangri-La City in Yunnan Province, China. It comprises three main ore segments—Hongshan, Hongniu, and Enka. Currently, the proven metal reserves include 1.4 million tons of Cu and 40,000 tons of Mo, along with associated metals such as Ag, Pb, Zn, and W [51]. This deposit is the largest skarn-type Cu deposit explored within the Yidun Terrane [50].

Triassic strata outcrops occur extensively in the mining area (Figure 1b,c), with the Qugasi Formation of the Upper Triassic Series serving as the main ore-bearing host rock. The stratigraphic sequence includes limestone, sandstone, argillaceous slate, siliceous rocks, and volcaniclastic rocks. The mining area is characterized by two sets of faults, trending northwest and northeast (Figure 1b). The northwest-trending fault plays a major role in controlling ore distribution due to its large scale. In contrast, the smaller northeast-trending fault, which post-dates mineralization, cuts through both the early faults and ore belt. The ore bodies are similar in orientation, aligning with the layers of the rock formation. The Hongshan deposit hosts Cu and Mo mineralization, primarily composed of chalcopyrite and molybdenite associated with pyrrhotite, magnetite, pyrite, sphalerite, and galena. The gangue minerals include garnet, diopside, epidote, wollastonite, apatite, calcite, and quartz.

In the Hongshan deposit, two stages of igneous rock were identified (Figure 1b,c). The first is the diorite porphyry (200 Ma), which formed during the Indosinian period [52]. The second includes quartz monzonite porphyry (77 Ma) and granite porphyry (76 Ma), which formed during the Yanshanian period [49,52]. The Yanshanian granite porphyry is genetically related to skarn formation and mineralization [46,47,51]. The quartz monzonitic porphyry primarily intrudes into the Qugasi Formation and occurs as stock strains along the bedding, often directly contacting marble. The phenocrysts and matrix of the quartz monzonite porphyry are composed of plagioclase, K-feldspar, quartz, and biotite. The quartz monzonitic porphyry has undergone pronounced potassic, albitic, and sericitic alterations [53]. The granite porphyry has a porphyritic structure, with plagioclase, Kfeldspar, biotite, and quartz comprising the majority of the phenocrysts and quartz, Kfeldspar, and plagioclase comprising the matrix (Figure 2a). There is no clear intersecting relationship between the granite porphyry and quartz monzonite porphyry, which may be a product of magmatic activity during the same period [51]. The granite porphyry intrusion (> 800 m thick) was discovered by deep drilling in recent years. This intrusion has experienced different degrees of potassic, phyllic, weak propylitic, and argillic alterations, affecting the distribution and grade of the typical porphyry Cu–Mo mineralization.

The wall rock of the Hongshan ore field is highly modified by thermal metasomatism, resulting in the formation of calc–silicate skarn containing a mineral assemblage of garnet, diopside, epidote, chlorite, actinolite, and quartz (Figure 2b–h). The mineralization, skarn, hornfels, and marble are visible outside the intrusion of the quartz monzonitic porphyry and granite porphyry (Figure 1b,c). Mineralization is closely related to skarn, which is primarily found in the contact zone between marble interlayers, meta-sandstones, and hornfels. The skarn formation process can be divided into several stages based on the relationship between the ore texture and mineral paragenetic assemblage (Figure 3).

(1) Prograde skarn stage: Anhydrous silicate mineral assemblages, including garnet, diopside, wollastonite, and vesuvianite, formed in the early high-temperature hydrothermal metasomatic wall rock (Figure 2c). According to Peng et al. [54], garnet has large grain sizes (0.1–2 cm), an Al-rich core acyclic zone, and an Fe-enriched rim with a strong oscillatory zoning. At this stage, the granite porphyry and quartz monzonite porphyry underwent potassic alteration. The homogenization temperature of fluid inclusions in the garnets was determined to be between 450 and 550 $^{\circ}$ C [51].

(2) Retrograde skarn stage: As the hydrothermal temperature decreased, the early high-temperature anhydrous silicate minerals were replaced by many hydrous silicate minerals (tremolite, actinolite, chlorite, and epidote; Figure 2d–g). Furthermore, the garnet and diopside were also replaced by feldspar, which is associated with chlorite, quartz, and sulfides (Figure 2e,f). We recognized a small amount of Cu mineralization as disseminated chalcopyrite at this stage (Figure 2e–g). The hydrothermal temperature range was estimated to be 300–450 °C [51].

(3) The quartz–sulfide stage: This is the primary mineralization stage when the majority of sulfides, such as chalcopyrite, pyrite, pyrrhotite, sphalerite, and other minerals, began to precipitate. Gangue minerals, such as quartz, calcite, and fluorite, as well as actinolite and chlorite, began to precipitate during this period as well (Figure 2b,g–h). The skarn, hornfels, and granite porphyry were cut by quartz sulfide veins. Minerals from prograde skarn such as garnet and diopside, as well as retrograde skarn-like epidote, actinolite, and K-feldspar, were altered by quartz and sulfides. At this stage, the hydrothermal temperature was estimated to be more than 300 $^{\circ}$ C [51].

(4) The quartz–calcite stage: The mineral assemblage was dominated by the formation of calcite, quartz, and minor fluorite. The skarn and ore bodies were cut using unmineralized quartz–calcite veins. During this stage, the hydrothermal temperature was estimated to be below 300 $^{\circ}$ C [51].



Figure 2. Photographs of major mineral assemblages in the Hongshan Cu–Mo deposit: (**a**) granite porphyry with large phenocrysts of plagioclase, quartz, K-feldspar, and biotite; (**b**) garnet skarn is replaced by massive chalcopyrite, pyrrhotite, and quartz inclusions from the quartz–sulfide stage; (**c**) euhedral garnet grains with oscillatory zoned rim (cross-polarized light); (**d**) diopside and euhedral allanite grains are replaced by sulfide (cross-polarized light); (**e**) massive K-feldspar inclusions coexist with sulfide (cross-polarized light); (**f**) diopside is overprinted by K-feldspar and actinolite, which is replaced by guartz (reflected light); (**g**) garnet is overprinted by K-feldspar and chlorite, which is replaced by quartz (reflected light); (**h**) fluorite coexists with chalcopyrite, calcite, and quartz (reflected light). Mineral abbreviations: Act is actinolite; Aln is allanite; Ap is apatite; Cal is calcite; Ccp is chalcopyrite; Chl is chlorite; Di is diopside; Fl is fluorite; Grt is garnet; Kfs is K-feldspar; Pl is plagioclase; Po is pyrrhotite; Qtz is quartz.



Figure 3. Paragenetic sequence diagram for alteration assemblages in the Hongshan skarn. The widths of lines indicate relative abundance levels of minerals. Narrow lines show minor minerals. Dotted lines indicate traces or uncertainties at the stage.

3. Sampling and Analytical Methods

The granite porphyry samples were collected from drill holes, while the skarn samples were collected from mine pits.

3.1. Scanning Electron Microscope and Electron Probe Microanalyzer

The tests were conducted at the State Key Laboratory of Ore Deposit Geochemistry (SKLODG), Institute of Geochemistry, Chinese Academy of Sciences (IGCAS), Guiyang, China. A JSM-7800F scanning electron microscope (SEM), which is produced by Japanese company JEOL (Japan Electron Optics Laboratory, Peabody, MA, USA), was used to acquire the BSE and cathodoluminescence (CL) images of the apatite. The operating conditions were a 20 kV accelerating voltage and 10 nA beam current. The major elements of the apatite were analyzed using a JEOL JXA 8530F-plus electron probe microanalyzer (EPMA) at SKLODG. Selected elements (F, Na, Si, P, S, Cl, Ca, Fe, Mn, Sr, Y, La, and Ce) were quantified at a 25 kV accelerating voltage with a large beam size range (5–10 μ m) and low beam current (10 nA). The apatite compositions were calculated based on 26 anions per formula unit (apfu) [55]. The volatiles' X-position occupancies were calculated using the measured F and Cl data, assuming F + Cl + OH = 1 for OH [33].

3.2. In Situ Trace Element Analysis of Apatite

In situ trace element concentrations of apatite grains were measured over previous major element analysis positions. A trace element analysis of the apatite was performed with laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) at SKLODG. The LA-ICP-MS system consists of an Agilent 7700x ICP-MS, which is produced by Agilent Technologies in the USA and a Geolas Pro 193 nm ArF excimer laser ablation system, which is produced by Coherent in Germany. A helium flow rate of 450 mL/min carried the ablated material to the ICP. Argon, the makeup gas, was mixed with the carrier gas via a T-connector before entering the ICP system. An additional 3 mL/min of N_2 gas was added downstream from the cell to enhance the signal sensitivity. A laser fluence of 4 J/cm^2 , repetition rate of 6 Hz, and spot size of 24 μ m were used during the analyses. Each experiment was performed for 60 s for sample data acquisition and ~30 s for background acquisition. The elements selected were Na, Mg, Al, Si, Ca, Ti, Mn, Fe, Cu, Zn, Ge, As, Rb, Sr, Y, Zr, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb, Th, and U. External NIST610 and NIST612 glass standards were used for calibration. The calcium content was measured using ⁴³Ca and normalized to the concentration determined from the electron probe analysis. Offline data reduction was then performed using the ICPMSDataCal 10.2 software [56].

4. Results

4.1. Apatite Petrography and Origin

Five types of apatite were identified in the granite porphyry and skarn samples based on the mineral assemblage, microstructure, and chemical composition. Of these, three (Ap2a, Ap2b, and Ap3) were detected in the skarn samples and the other two (Ap1a and Ap1b) were found in the granite porphyry samples (Table 1).

Table 1. Characteristics of different apatite types.

Apatite Type	Formation Stage	Mineral Assemblage	REE_N Signature	Element Signature
Ap1a	Magma stage	Plagioclase, K-feldspar, biotite, quartz, titanite	Right incline with high ΣREE; negative Eu anomalies	High LREE, F, Cl, (La/Yb) _N ; low HREE
Ap1b	Magma stage	Plagioclase, quartz, titanite	Right incline with high ΣREE; negative Eu anomalies	High LREE, F, Cl, (La/Yb) _N ; low HREE
Ap2a (core)	Prograde skarn stage	Garnet, diopside	Right incline with high ΣREE; large negative Eu anomalies	High HREE, Ce, Nb, Y, Fe, F, Cl, As; low Sr, (La/Yb) _N
Ap2b (rim)	Retrograde skarn stage	K-feldspar, chlorite, actinolite	Convex (high MREE) with low ΣREE; small negative Eu anomalies	High MREE, F, Sr; low HREE, LREE, Ce, Nb, Y, Cl, Fe
Ap3	Quartz-sulfide stage	Quartz, calcite chalcopyrite, pyrrhotite	Right incline with high ΣREE; large negative Eu anomalies	High HREE, Y, F, Cl, Fe; low Sr, As

Apatite Ap1a exhibits subhedral to euhedral granular crystals that are primarily found as mineral inclusions hosted in biotite, plagioclase, titanite, and zircon (Figure 4a–d). This suggests that they were formed during the early stages of magmatic evolution and that late hydrothermal alteration had a minimal effect on them.



Figure 4. Photomicrographs of various apatites: (**a**) euhedral apatite (Ap1a) inclusion inside magmatic biotite phenocryst (plane-polarized light); (**b**) an assemblage of magnetite and apatite (Ap1a) inclusions in plagioclase (reflected light); (**c**) euhedral apatite (Ap1a) inclusion in titanite phenocryst (cross-polarized light); (**d**) quartz phenocryst with apatite (Ap1a) inclusion transected by a matrix of titanite, K-feldspar, quartz, and apatite (Ap1b) along fractures (cross-polarized light); (**e**) apatite (Ap1b) grains in the matrix (plane-polarized light, BSE and CL images); (**f**) euhedral garnet with apatite inclusion is replaced by K-feldspar (BSE image); (**g**) euhedral garnet with apatite inclusion is replaced by K-feldspar, with insert showing the apatite's core (Ap2a) and rim (Ap2b) (BSE and CL images); (**h**) euhedral apatite (Ap3) coexists with quartz, sulfide, and calcite from quartz–sulfide stage. The residual garnet and diopside can also be seen (BSE image). Mineral abbreviations: Ap is apatite; Bi is biotite; Cal is calcite; Grt is garnet; Kfs is K-feldspar; Mag is magnetite; Pl is plagioclase; Po is pyrrhotite; Qtz is quartz; Ttn is titanite.

The crystals in Ap1b vary in shape from subhedral to euhedral and occur along the fractures of quartz phenocrysts within the matrix composed of titanite, K-feldspar, and quartz (Figure 4d,e). The edges of the quartz phenocrysts are marked by their corrosion morphology. The titanites associated with Ap1b are mainly euhedral, ranging 60–100 μ m in size and with regular oscillatory zoning. The presence of acicular apatite inclusions with typical magmatic properties was noted. Based on observations using optical microscopes, CL, and BSE, this type of apatite has a pristine surface, a visible growth zone, and other unaltered characteristics (Figure 4e). These phenomena indicate that Ap1b apatite grains formed during late magmatic stages.

The Ap2 apatite grains, which occur as inclusions in garnet, have distinct core–rim structures. Because the CL images of the rim and core differed significantly (Figure 4f,g), these apatite grains were separated into two stages: Ap2a in the core and Ap2b on the rim. The cores (Ap2a) showed brilliant and homogeneous CL images with no discernible alterations. Considering the association of Ap2a with garnet, which formed during the prograde skarn stage, Ap2a is, thus, of hydrothermal origin. The CL images of the rims (Ap2b) are often black. Under backscattering, there are a lot of pores or mineral inclusions with noticeable alterations or dissolution–recrystallization [29]. Moreover, we found that the garnet enclosing apatite is unevenly cut by K-feldspar. The K-feldspar mainly formed in the retrograde skarn stage, in association with actinolite and chlorite (Figure 2e–g). Based on the petrological observations mentioned above, it can be inferred that hydrothermal processes altered the garnet, resulting in the dissolution–recrystallization of the early crystallized apatite (Ap2a) and the formation of the rim (Ap2b) of apatite during this stage.

The Ap3 apatite grains, which are mainly associated with quartz, calcite, and sulfides, are subhedral to euhedral (Figure 4h) and are thought to have formed during the quartz–sulfide stage. However, only four of these apatite grains were detected and evaluated due to their rarity and small size range (10–40 μ m).

4.2. Geochemistry of Apatite

The major compositions of the apatite samples are listed in Supplementary Table S1. The five kinds of apatite have similar concentrations of CaO and P_2O_5 (average CaO = 54.79 \pm 0.43 wt%, P₂O₅ = 42.4 \pm 0.36 wt%). All of the apatites are fluorine apatites, rich in F and poor in Cl, with the contents of SiO_2 being lower than the detection limit. For halogens, the F concentrations increase from Ap1a (average F = 3.08 ± 0.17 wt%, 1.64 \pm 0.089 apfu) to Ap1b (average F = 3.31 \pm 0.16 wt%, 1.75 \pm 0.082 apfu), Ap2a (average F = 3.46 ± 0.26 wt%, 1.88 ± 0.14 apfu), and Ap2b (average F = 3.66 ± 0.18 wt%, 1.92 ± 0.085 apfu), whereas the Cl concentrations show an opposite trend. Ap1a has the highest Cl concentration (average Cl = 0.141 ± 0.041 wt%, 0.040 ± 0.012 apfu), while Ap2b has the lowest (below the detection limit, mean of 0.01 wt%). Ap3 has F and Cl concentrations similar to those of Ap2a. Based on Ap1a, using the apatite melt partition model proposed by Li and Hermann., [57], we calculated that the original magma contained a moderate amount of chloride (average Cl: 1514 ± 299 ppm) and a relatively large amount of fluoride (average F: 1962 \pm 293 ppm). Among the hydrothermal apatites, Ap3 has the highest FeO concentrations (average FeO = 0.44 ± 0.152 wt%, 0.061 ± 0.040 apfu), while Ap2b has the lowest (average FeO = 0.15 ± 0.037 wt%, 0.021 ± 0.005 apfu).

The REE and trace element compositions of all apatite types are listed in Supplementary Table S2. The ΣREE content decreases from Ap1a (average $\Sigma REE = 6588 \pm 1824$ ppm) to Ap2a (average ΣREE = 5089 \pm 1124 ppm) and then to Ap2b (average ΣREE = 1135 \pm 355 ppm), while there is an increase in Ap3 (average $\Sigma REE = 3992 \pm 316$ ppm). The magmatic apatites (Ap1a and Ap1b) show much stronger fractionation levels between LREE and HREE (average (La/Yb)_N = 82.3 ± 21.9 and 77.4 ± 10.8 , respectively) with weaker negative Eu anomalies (average Eu_N/Eu_N* = 0.51 ± 0.070 and 0.53 ± 0.034 , respectively) than those of Ap2a (average (La/Yb)_N =14.3 \pm 8.74; average Eu_N/Eu_N* = 0.44 \pm 0.18) and Ap3 (average (La/Yb)_N = 7.77 \pm 0.31; average Eu_N/Eu_N* = 0.35 \pm 0.038) (Figure 5a,b). Ap2b shows convex REE patterns due to the high MREE level relative to LREE and HREE (average $(La/Sm)_N = 0.49 \pm 0.094$; average $(Gd/Yb)_N = 24.9 \pm 10.1$), with small negative Eu anomalies (average Eu_N/Eu_N^* = 0.60 ± 0.047). None of the apatites have obvious Ce anomalies but Ap2b has slightly negative Ce anomalies (average (Ce/Ce^{*})_N = 0.93 ± 0.02) (Figure 5b,c). The Sr content decreases from Ap1a (average Sr = 865 ± 229 ppm) to Ap2a (average Sr = 641 ± 361 ppm) and then to Ap3 (average Sr = 401 ± 68.0 ppm) and increases significantly to Ap2b (average Sr = 1128 ± 344 ppm). Ap1a and Ap1b have high Sr/Y ratios (average Sr/Y = 3.61 ± 1.08 , 3.06 ± 0.39 , respectively), Ap2a has the lowest (average $Sr/Y = 1.04 \pm 1.09$), and Ap2b has the highest (average $Sr/Y = 4.36 \pm 1.45$).



Figure 5. Chondrite-normalized rare earth element (REE) patterns: (**a**) apatites (Ap1a and Ap1b); (**b**) Ap2a; (**c**) Ap2b; (**d**) Ap3. Chondritic values are from Sun and McDonough [58].

5. Discussion

5.1. Apatite as a Recorder of Magmatic Volatile Evolution

The granite porphyry in our samples was weakly affected by potassic and phyllic alterations. The elements of primary igneous apatite, such as REE, Y, and Mn, are commonly extracted by the magmatic–hydrothermal fluids that relate to potassic and phyllic alterations [34]. Specifically, the substitution of Mn in apatite by Mg + Fe + Sr + Pb from the fluids occurs during alterations in porphyry deposits, leading to a negative correlation between Mn and Mg + Fe + Sr + Pb [20]. Thus, the trend changes in these graphs can indicate whether a hydrothermal alteration has occurred to the apatite (Figure 6a,b) [20,34]. The plotting results show that there are no discernible hydrothermal alterations in Ap1a and Ap1b apatites. This likely reflects that the apatite shows strong resistance to weathering and alterations [28,29], which may have preserved the original information of the melt. As a result, we consider that the abundance of elements in Ap1a and Ap1b can be used to identify the magmatic compositions.



Figure 6. Geochemical signatures of apatite: (a) Mg + Fe + Sr + Pb vs. Mn; (b) Σ REE + Y vs. Mn/Fe. Trend lines adapted from Cao et al. [20] (a) and Bouzari et al. [34] (b).

Apatite is a major volatile-bearing mineral phase in magmas and is widely used to track magmatic volatile evolution [17,33,36,59]. The Ap1a mineral inclusions occurred in silicate phenocrysts, which consequently preserved the early volatile information of the parent magma. The F and Cl concentrations in the ore-forming magma were calculated following the apatite melt partition model of Li and Hermann [57]. The results showed that the Hongshan pluton has relatively high F (1962 ppm) and moderately high Cl (1514 ppm) levels, which were consistent with previous research [60]. We compiled the F and Cl data for magmatic apatite from various deposit types and non-mineralized plutons in the same tectonic setting of the Yidun Terrane, including the Cu-Mo mineralized biotite granite porphyry (Tongchanggou, 87 Ma), W–Mo mineralized biotite granite porphyry and monzonitic granite porphyry (Xiuwacu, 85Ma), and non-mineralized biotite granite (Cilinco, 86 Ma) [46,60,61]. The data are listed in Supplementary Table S4. Compared to the non-mineralized intrusion (Cilincuo) and the W–Mo ore-related intrusion (Xiuwacu), the apatite of the Cu-Mo ore-related intrusions (Hongshan and Tongchanggou) contain relatively higher Cl levels (Figure 7a). The apatite of the W-Mo ore-related intrusion (Xiuwacu) contains more F than the others. The apatite in the non-mineralized intrusion (Cilincuo) has lower F and Cl levels than the others. This suggests that Cu-mineralized magma tends to have a high Cl content, whereas W-mineralized magma tends to have a high F content. Conversely, magma with low levels of both F and Cl may not be conducive to mineralization. It follows that relatively Cl-rich magmas are fertile for the generation of porphyry-skarn Cu deposits, as the Cl concentration in magma plays a crucial role in promoting the efficient extraction of copper from magma [62,63]. Analogously, the presence of magmatic F is crucial for controlling the fertility of porphyry–skarn tungsten (W) deposits. This probably happens because F is instrumental not only in facilitating the strong enrichment of W in the residual melt [64] but also in facilitating the transportation of W by oxyfluoride complexes [65]. Furthermore, the Ap1a and Ap1b from the Hongshan deposit are mostly plotted in the ore deposits field in the DP1-1 vs. DP1-2 diagram (Figure 7b) [19], indicating that apatite geochemistry can be effectively used distinguish between mineralization types and the potential of plutons [19,35].



Figure 7. Magmatic apatite geochemical plots: (**a**) Cl vs. F, including data for ore-related porphyries (Tongchanggou and Xiuwacu) from Pan et al. [61] (points with values of less than 3.77 were selected) and for non-mineralization rock (Cilincuo) from Liu et al. [60]; their major compositions are listed in Supplementary Table S4; (**b**) DP1-2 vs. DP1-1 (after Mao et al. [19]).

In the process of intermediate to felsic magma rising or cooling crystallization, the water content in the magma gradually reaches a saturated state and undergoes exsolution, during which Cl and S enter the fluid more easily than F [33,66,67]. The F/Cl, F/OH, and F/S ratios of Ap1b are significantly greater than those of Ap1a (Figure 8a,b), suggesting that volatiles (S and Cl) were removed during the evolution of the granite porphyry. Furthermore, compared to Ap1a, Ap1b has lower levels of Σ REE and (La/Yb)_N (the Σ REE mean values for Ap1a and Ap1b are 6587ppm and 5472ppm, respectively; the (La/Yb)_N mean values for Ap1a and Ap1b are 82.3 and 77.4, respectively), suggesting that fluid

exsolution happened before Ap1b formed. This is because high-temperature and highsalinity fluids can effectively carry away REEs in magma and it is relatively easy to extract LREE [68–70], leading to further reductions in Σ REE and (La/Yb)_N in residual magma during the saturated exsolution of volatiles. Previous studies showed that the Hongshan pluton has high magmatic water contents and forms from deep to shallow magma chambers with decreasing pressure levels (5.6–2.5 kbar) [60,71], which may facilitate the formation of exsolved hydrothermal fluids [72,73]. These magmatic–hydrothermal evolutions allow the transport of economic metals (Cu and Mo) between melts and fluids, contributing to the formation of the Hongshan Cu–Mo deposit.



Figure 8. Volatile characteristics in magmatic apatite: (**a**) F/Cl vs. F; (**b**) XF/XCl vs. XF/XOH; calculated following the thermodynamic partitioning model from Li and Hermann [57].

5.2. Unveiling Changes in Hydrothermal Halogens through the Cl and F Contents of Hydrothermal Apatite

The partition coefficient for the distribution of halogens (Cl and F) between apatite and the aqueous phase is a complex function of the composition, F and Cl concentrations, temperature, and pressure of the hydrothermal fluids [66,74]. In general, the Cl and F contents in apatite are related to the Cl and F concentrations in the hydrothermal fluids. The values of the $D_{Cl}^{apatite/fluid}$ vary from 0.07 to 2.3 [66,74] and the $D_{F}^{apatite/fluid}$ values vary from 52 to 453 [74,75].

The three types of hydrothermal apatite in the Hongshan skarn have distinct F and Cl contents (Figure 9a). For instance, Ap2b (rim) has higher F and lower Cl contents than Ap2a (core), suggesting that retrograde hydrothermal fluids have higher F and lower Cl concentrations than those of prograde hydrothermal fluids. The decreasing salinity may be the cause of a decrease in Cl in the H₂O–NaCl hydrothermal fluid system, indicating that the hydrothermal salinity in the retrograde skarn stage is lower. This conclusion is supported by the fluid inclusion data. According to Peng et al. [51], diopside and Fe-rich garnet formed in a high-salinity hydrothermal solution during the prograde skarn stage, whereas a low to moderate-salinity hydrothermal solution formed during the syn-ore stage (corresponding to the retrograde skarn stage and the quartz–sulfide stage in this paper). The above explanation can be verified by the Fe and Cl contents of the apatite. Previous studies have shown that in high-temperature magmatic-hydrothermal fluids, Fe is mainly transported as Fe–Cl complexes, such as FeCl₂ and FeCl₄^{2–} [76,77]. The Cl contents of Ap2a and Ap2b are positively correlated with the Fe content (Figure 9b). Furthermore, the Fe and Cl contents of Ap2a are higher than those of Ap2b, suggesting that the salinity of the fluids in the prograde skarn stage is higher than in the retrograde skarn stage.



Figure 9. Hydrothermal apatite halogens and Fe characteristics: (**a**) Cl vs. F; (**b**) Fe vs. Cl. Note: apfu is per formula unit.

The Cl content of Ap3 in the quartz–sulfide stage is greater than that of Ap2b and marginally higher than that of Ap2a (Figure 9a). Possibly, this increase is associated with decomposition of the Cl complexes. Cu is mainly transported as Cu-Cl complexes, such as $CuCl_{2}^{-}$ [63,78]. The solubility of Cu and other metals in the hydrothermal fluids will decrease exponentially when the physical and chemical hydrothermal parameters change, such as the temperature dropping [79]. A large number of metal-sulfides such as pyrite, pyrrhotite, and chalcopyrite formed in the quartz-sulfide stage, indicating that decomposition of the complexes occurred between metals (Cu, Fe, Mo) and Cl. This process also increases the Cl⁻ concentration in the hydrothermal fluids, which may lead to an increase in the Cl content of the apatite [77,80]. Although Ap3 is rare, it has the highest Fe content, and the Cl content is inversely correlated with the Fe content (Figure 9b). The inverse correlation between the Fe and Cl contents of Ap3 may be a sign of the cocrystallization of metal in the late stage of the skarn. In addition, Ap3 has a lower F content than Ap2b, indicating a lower F concentration in the ore fluids. During the ore precipitation stage, a significant amount of fluorite crystallized (Figure 2h), which mostly regulated the change in the F content of the hydrothermal fluids [65,81]. Thus, fluorite crystallization could be the cause of the decrease in the F content in Ap3.

As a result, the concentrations of halogen in hydrothermal fluids are closely related to mineral crystallization and salinity, which can be reflected by halogens of apatite.

5.3. Apatite as a Recorder of Hydrothermal Origin and Evolution5.3.1. Ap2a as a Recorder of Early Hydrothermal Origin

Previous studies have revealed that REEs in magma can be effectively mobilized by exsolution fluids with high salinity levels and at high temperatures [68–70]. Petrographic observations indicate that apatite (Ap2a) occurs as minute mineral inclusions within garnet and diopside during the prograde skarn stage. This evidence suggests that the Ap2a formed within the early magmatic–hydrothermal fluid [2,51]. The chondrite-normalized REE patterns of Ap2a, exhibiting a right incline and negative Eu anomalies, are similar to the whole-rock samples [53]. However, there are small differences in the REEs between Ap2a and the whole-rock samples. Ap2a exhibits a less fractionated REE distribution pattern (with a mean $(La/Yb)_N$ value of 14.3) compared to the whole-rock samples (with a mean $(La/Yb)_N$ value of 54.1; the data are listed in Supplementary Table S3 [53]).

Possible controls for the observed differences include (1) the partition behavior of the REEs between the hydrothermal fluid and apatite $(D_{REE}^{apatite/fluid})$ [24], (2) the partition behavior of the REEs between the magma and magmatic fluid $(D_{REE}^{melt/fluid})$ [68,70,82,83], and (3) the solubility of the LREE in the hydrothermal fluid [24,84–87]. First, the partition coefficient of The LREE between the apatite and hydrothermal fluid is slightly higher than that of HREE, ranging from 15 to 33 in the order Yb<Ce<Gd [24]. This indicates that during apatite crystallization, there is a slight enrichment of LREE rather than a depletion of (La/Yb)_N, contrary to our initial expectations. Additionally, the fractionation

of REEs can result from the processes of magmatic fluid exsolution and hydrothermal transport. The partitioning behavior of LREE between the melt and exsolving fluids is slightly higher than for HREE ($D_{LREE}^{fluid/melt} > D_{HREE}^{fluid/melt}$), causing more LREE to be extracted into the fluids [70,83]. This also suggests that the differences in distribution coefficients are not the cause of the differences in REE compositions between Ap2a and magmatic rocks. We suggest that the stability of REE–Cl in magmatic–hydrothermal fluids may play a more significant role in the differences in (La/Yb)_N ratios between Ap2a and magmatic rocks. In high-salinity fluids, REEs primarily combine with Cl to form REE-Cl complexes [85,86]. Due to the fact that LREE–Cl complexes are more stable than HREE–Cl, LREE can migrate further than HREE [70,85]. Decoupling of the HREE–Cl complexes will preferentially begin when the hydrothermal conditions change, leading to more HREE entering the apatite. As a result, the level of (La/Yb)_N in the Ap2a is lower than that of the granite porphyry.

5.3.2. Apatite as a Recorder of Hydrothermal Ph and Compositions

The trace element behaviors in apatite, particularly those of REE, Sr, and Eu, have been used to reveal changes in hydrothermal conditions such as the fluid temperature, redox reactions, and pH [14,18,20,29,38,77,80]. Previous studies have shown that the valence states of Eu in hydrothermal fluids are primarily controlled by H⁺ activity [88]. In acidic hydrothermal solutions, Eu^{2+} forms stable complexes with Cl⁻ and migrates [89], whereas under high-pH hydrothermal solutions, Eu^{3+} complexes are increasingly dominant [88]. Considering that Eu^{3+} with an appropriate icon radius more easily replaces Ca²⁺ in apatite [21,25], apatite formed in a more alkaline environment may have weaker negative Eu anomalies. Additionally, the Eu content of hydrothermal apatite also increases in tandem with the increase in Eu concentration in the hydrothermal fluids [19,90].

In the absence of Eu-rich mineral formation, the strong negative Eu anomalies of Ap2a suggest that the hydrothermal fluids during the prograde skarn stage were acidic. (Figure 5b). Simultaneously, there is a clear inverse correlation between Eu_N/Eu_N^* and REE+Y in Ap2a (Figure 10a). Considering that large amounts of garnet, diopside, wollastonite, and other minerals were formed in this stage, the decarbonization may have resulted in an inverse correlation between Eu_N/Eu_N^* and REE+Y. This is because calcite can absorb the acid from the hydrothermal fluids during the water–rock reaction [91], which leads to a decrease in temperature and increase in pH. The solubility of the REEs in hydrothermal solutions weakens with a decrease in temperature or increase in pH when the salinity does not vary considerably [70,86]. It is hypothesized that the pH of the acidic hydrothermal fluids gradually increases and the temperature decreases, resulting in a decrease in the REE concentration during the prograde skarn stage. It is worth noting that despite the increase in pH, the hydrothermal fluids may still be acidic.

Ap2b has higher Eu_N/Eu_N^* ratios relative to Ap2a (Figure 10a), and there may be two reasons for this. One possibility is that the fluids during the retrograde skarn stage have higher pH values compared to those during the prograde skarn stage, as mentioned earlier, which would lead to higher Eu_N/Eu_N^* ratios in apatite. Another possibility is that the fluids during the retrograde skarn stage have higher Eu concentrations. Published studies have shown that Eu-rich fluids with high Sr/Y ratios can form during the dissolution of Eu- and Sr-rich minerals such as plagioclase and feldspar [77,90,92]. In our samples, plagioclase and K-feldspar, primary phenocrysts in the Hongshan granite porphyry, were generally modified during hydrothermal alterations, such as K-silicate alterations and sericite alterations. The mean Sr/Y ratio in Ap2b is 4.36, indicating that the hydrothermal fluids are enriched in Sr and depleted in Y. Additionally, Ap2b exhibits depleted levels of Ce, Y, and Nd (Figure 10b,c). A similar phenomenon was thought to be caused by a potassic–phyllic alteration [34]. Thus, Ap2b might have originated from the dissolution–reprecipitation of Ap2a in Eu-rich fluids.



Figure 10. Hydrothermal apatite geochemical signatures and relationships of trace elements: (a) Eu_N/Eu_N^* vs. $\Sigma REE + Y$; (b) Ce vs. Y; (c) Ce vs. Nd; (d) chondrite-normalized $(Gd/Yb)_N$ vs. $(La/Sm)_N$; (e) $(Gd/Yb)_N$ vs. $(La/Yb)_N$; (f) arsenic (As) vs. $\Sigma REE + Y$. $Eu/Eu^* = Eu_N \times (Sm_N \times Gd_N)^{-0.5}$. Chondritic values are from Sun and McDonough [58].

Furthermore, Ap2b exhibits a convex REE pattern, being relatively enriched in MREE and displaying clear differences between Ap2a and Ap3 (Figures 5b–d and 10b–e). These features are comparable to those of late hydrothermal apatite in the Australian Olympic Dam iron oxide Cu–Au (IOCG) ore system, which has been interpreted to be associated with hematite–sericite alteration [90]. In the retrograde skarn stage, we observed many euhedral allanite grains with hydrothermal oscillatory zoning (Figure 2d), suggesting that the earlier crystallization of LREE-rich minerals results in a decrease in LREE concentration in the hydrothermal fluids. The modification of Ap2a by depleted LREE fluids forms Ap2b, which may be the reason for the lower (La/Sm)_N ration in Ap2b (Figure 10d). Nevertheless, no HREE-rich minerals were discovered, hinting that the HREE of the Ap2b drop may not be due to symbiotic mineral crystallization. Instead, a greater F content likely facilitates the continued formation of HREE–F complexes that remain mobile in the strong F-rich fluids [84,90]. Considering that the high F content in Ap2b reveals strong F-rich retrograde fluids, the HREE and Y may decreasingly enter into Ap2b (Figure 10e,f). Thus, the low salinity and elevated F levels in retrograde hydrothermal fluids could be the reason for the deficit of HREE in Ap2b.

The pronounced negative Eu anomalies in Ap3 may indicate acidic conditions (Figures 5d and 10a). The significant negative Eu anomaly in apatite is attributed to the prevalence of Eu^{2+} in acidic hydrothermal fluids. If this hypothesis holds true, the hydrothermal fluids will contain higher levels of H⁺. Elevated H⁺ activity can enhance the stability of Cl complexes and inhibit sulfide precipitation [93]. Nevertheless, the extensive sulfide mineralization observed in this stage might be influenced by other dominant factors such as the temperature and oxygen fugacity [8,94].

5.3.3. Apatite as a Recorder of Hydrothermal Oxygen Fugacity Evolution

Several studies have shown that various trace elements of apatite, including polyvalent metals that occur in different oxidation conditions, can be utilized to identify magmatic oxidation states [14,18,35,95]. Among them, As is predominantly in the As⁵⁺ and As³⁺ forms. Under oxidized conditions, As⁵⁺ is more likely to replace P⁵⁺, whereas under reduced conditions, As³⁺, having a larger ion radius, is less compatible [18,26].

In our results, the As content in Ap3 was lower than that in Ap2a, whereas the As contents in Ap2b varied greatly (Figure 10f). Ap2a, having a higher As content, demonstrates the greater oxidized state of the hydrothermal fluids in the prograde skarn stage. The variable As contents in Ap2b indicate the large fluctuations in oxygen fugacity in the retrograde skarn stage, which may be related to magnetite crystallization. According to Peng et al. [48], the crystallization of magnetite in this stage causes the hydrothermal fluids to change from an oxidation to reduction state. Ap3, having a lower As content, displays lower oxygen fugacity in the quartz–sulfide stage. This relatively reduced condition is particularly evident for ore fluids from this stage, considering the presence of H₂S, CH₄, HS⁻, and C₂H₆ within the fluid inclusions [51]. The S would become S⁻ or HS⁻ in such an environment, which accelerates the precipitation of Cu and Fe sulfides [8,94]. Consequently, based on the changes in the As content of apatite, we discovered that the precipitation of metal sulfides may be driven by the increasingly reduced condition during the quartz–sulfide stage.

6. Conclusions

The apatite in the Hongshan porphyry–skarn Cu–Mo deposit shows magma degassing and fluid saturation, as well as changes in salinity, pH, redox, temperature, and composition associated with multi-stage hydrothermal fluids. Furthermore, it exhibits significant potential for identifying mineral exploration targets.

The volatile concentrations of the apatite indicate that the ore-forming magma incorporates moderately high Cl and relatively high F, which facilitate the transportation of copper during magmatic–hydrothermal evolution. The volatiles in the magma gradually reach a saturated state and undergo exsolution during magma ascent or cooling crystallization. The high volatile contents of the parent magma play a crucial role in the formation of the Hongshan deposits.

The fluid salinity shifts in the prograde and retrograde skarn stages are closely correlated with the Cl concentrations of apatite. Compared to the retrograde hydrothermal fluids, the prograde hydrothermal fluids have a higher salinity level. In the quartz–sulfide stage, an increase in salinity or decomposition of metal–chloride complexes may cause an increase in the halogen concentration of the apatite.

The apatite (Ap2a) crystallized in the early acidic and high-salinity fluids in the prograde skarn stage and its rim (Ap2b) was created by the decreasing salinity and increasing pH fluids that altered the Ap2a in the retrograde skarn stage. Together with metal sulfide mineralization, Ap3 crystallized in the quartz–sulfide stage. The precipitation of sulfides is controlled by the decrease in oxygen fugacity.

This work supports the concept that hydrothermal apatite can be effectively applied as a tracer to characterize the properties of porphyry–skarn hydrothermal fluids. The partitioning behaviors of trace elements between apatite and hydrothermal fluids may require further investigation. Additionally, our work further demonstrates that alongside the decrease in temperature, the decrease in oxygen fugacity can be important for sulfide precipitation in the porphyry–skarn system.

Supplementary Materials: The following supporting information can be downloaded at https: //www.mdpi.com/article/10.3390/min14040373/s1. There are four connected tables in the Supplementary Date. Table S1: EMPA data [55]. Table S2: LA-ICP-MS data. Table S3: Whole-rock data [53]. Table S4: Major apatite elements in Tongchanggou, Xiuwacu, and Cilincuo [60,61].

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