Compositions of biotite, amphibole, apatite and silicate melt inclusions from the Tongchang mine, Dexing porphyry deposit, SE China: implications for the behavior of halogens in this mineralized porphyry system

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ABSTRACT

The Dexing deposit, located in the Circum-Pacific ore belt, is the largest porphyry copper deposit in eastern China. It is composed of 3 separate plutons, which host three individual mines (Tongchang, Fujiawu and Zhushahong). The porphyritic granodiorite samples studied in this investigation were collected from the Tongchang ore-forming pluton of this giant deposit. This paper presents electron microprobe analyses of biotite, apatite, amphibole, plagioclase, potassium feldspar and rehomogenized glassy melt inclusions from the Tongchang porphyritic granodiorites. Petrographic observations on these samples show that the portions of granodioritic magma represented by our samples were overprinted by potassic hydrothermal fluid which variably altered these minerals.

All of the studied micas are Mg-rich biotite. The biotites are separated into altered magmatic and secondary types based on their petrographic and geochemical characteristics. The phlogopite components of the secondary biotites are typically higher than those of the altered magmatic biotites, and the X_{Mg} values of all biotites correlate negatively with their Cl contents showing that they conform to the Mg-Cl avoidance principle. The X_{Mg} values also correlate negatively with the contents of (K_2O+Na_2O+BaO) , FeO and TiO_2 for both generations of biotites. The calculated log

($f\text{H}_2\text{O}/f\text{HCl}$) values (for 690K) of the coexisting potassic fluids, which are determined from the altered magmatic biotite compositions, range from 4.43 to 4.67, and are very similar to those of other major porphyry deposits. However, the $\log(f\text{H}_2\text{O}/f\text{HF})$ and $\log(f\text{HF}/f\text{HCl})$ values for the same batch of hydrothermal fluids are significant higher and lower than those of these other porphyry deposits, respectively.

The Cl concentrations of amphiboles and melt inclusions range from 0.18 to 0.32 wt.% and 0.15 to 0.44 wt.%, respectively. Most apatites trapped in biotite and plagioclase phenocrysts display a bimodal Cl distribution: 0.19 to 1.35 wt.% and 1.48 to 3.73 wt.%. Similarly, the S contents of the apatite also show a distinct bimodal distribution reflecting the effects of variable anhydrite saturation during evolution of the Tongchang melt and variable dissolution of anhydrite by saline aqueous fluids. The Cl contents of the apatites from the Tongchang system are typically higher than those of other studied porphyry deposits. Furthermore, the Cl contents of the melt inclusions are at or very near the Cl saturation levels for these melt compositions at shallow crustal pressures. These findings suggest that the area of the granodioritic magma represented by our samples, and perhaps the bulk of the Tongchang granodioritic magma was very enriched in Cl. The melt inclusion compositions further suggest that high-salinity, hydrosaline liquid might have exsolved from the granodioritic melt directly. This high-salinity hydrosaline liquid was likely very efficient at dissolving, transporting and precipitating ore metals in the mineralizing magmatic-hydrothermal system.

Key words: Dexing porphyry deposit; Tongchang pluton; potassic alteration; halogens; biotite; apatite; amphibole

1. Introduction

The giant Dexing porphyry copper deposit is an important source of copper and, to a lesser extent, molybdenum and gold for China (Zhu et al., 1983; Zhang et al., 2013).

In evolving magmatic porphyry systems, hydrothermal fluids exsolve from crystallizing intermediate-silica to highly silicic melts due to first and/or second boiling, and these processes determine the styles of mineralization and hydrothermal alteration of the deposits (Burnham, 1979; Cline and Bodnar 1991; 1995; Halter and Webster, 2004; Weis et al., 2012; Wilkinson, 2013; Hurtig and Williams-Jones, 2015; Spencer et al., 2015). Previous studies show that halogens in silicate melt can strongly influence the evolution of magmatic and magmatic-hydrothermal systems (Ulrich et al., 1999; Aiuppa et al., 2009; Bao et al., 2014; Kodêra et al., 2014). The characteristics of the Dexing deposit hydrothermal fluids have been studied and determined to be Cl enriched based on fluid inclusions (Pan et al., 2009, 2012), but more information is required to understand how the Cl-bearing magmatic fluids exsolved and how they affected the compositions of the hydrous minerals.

Magmatic biotite, a common gangue mineral in porphyry systems, readily exchanges OH, F and Cl in the hydroxyl site with coexisting melts and hydrothermal fluids (Munoz, 1984; Selby and Nesbitt, 2000). Prior research on porphyry deposits has used biotite chemistry to trace the composition and evolution of magmatic-hydrothermal fluids (Beane, 1974; Jacob and Parry, 1979; Munoz, 1984; Selby and Nesbitt, 2000; Ayati et al., 2008; Boomeri et al., 2009, 2010; Afshooni et al., 2013; Einali et al., 2014; Parsapoor et al., 2015), and we have expanded this approach to include data from coexisting amphiboles, apatites and rehomogenized glassy silicate melt inclusions. Following on the thermodynamic development of the partitioning of F-Cl-OH between biotite and hydrothermal fluids (Zhu and Sverjensky, 1991, 1992), Munoz (1992) formulated relevant relations to determine halogen fugacity ratios of the melt or aqueous fluid coexisting with biotite based on biotite compositions. Using the halogen compositions of biotites, we calculate the

log($f_{\text{H}_2\text{O}}/f_{\text{HF}}$), log($f_{\text{HF}}/f_{\text{HCl}}$) and log ($f_{\text{H}_2\text{O}}/f_{\text{HCl}}$) ratios of the potassic fluids from Tongchang, which is one of the three mineralized Dexing porphyries in China. These fluids contained abundant copper as shown by the existence of chalcopyrite-bearing fluid inclusions in potassium feldspar-quartz veins (Pan et al., 2009). We also compare these results to other porphyry deposits to distinguish and interpret the unique halogen characteristics of the hydrothermal fluids of the Tongchang mine, Dexing porphyry Cu-Mo-Au deposit.

Previous research on the Dexing porphyry Cu-Mo-Au deposit primarily concentrated on the petrogenesis, petrography, and geochemistry of its three constituent plutons and the origin of this deposit (He et al., 1999; Wang et al. 2006; Liu et al., 2012; Hou et al., 2013; Zhou et al., 2012, 2013; Zhang et al., 2013; Wang et al., 2015). To date, the role of magmatic volatiles in the ore-forming processes of this system has not been studied. Audétat and Pettke (2003) and Audétat et al. (2008) proposed, generally, that whether or not intermediate- to high-silica plutons are mineralized depends primarily on the salinity of the exsolved fluids which determine the efficiency of metal extraction from the coexisting silicate melt. High-salinity hydrothermal fluids with high contents of complexing ligands (chlorine) are more efficient at extracting the metals residing in the silicate melt than low-salinity fluids (Candela and Piccoli, 1995; Aiuppa et al., 2009; Zajacz et al., 2011; Bao et al., 2014). For most porphyry systems, high-salinity fluids are thought to form through the immiscible condensation of brine from a low-salinity Cl-bearing vapor that had exsolved directly from the silicate melt (Burnham, 1979; Hedenquist and Lowenstern, 1994; Bodnar et al., 2014). However, other studies show that such high-salinity aqueous fluids can also exsolve directly from the silicate melt (Cline, 1994; Webster, 2004). In this study, we will evaluate the likelihood and the consequences of the direct

exsolution of high-Cl hydrosaline liquids (with or without low-salinity vapor) from the Tongchang granodioritic magmatic system.

2. Geological setting and deposit geology

The Dexing porphyry copper ore deposit is located in the South China craton which is composed of the Yangtze and Cathaysia blocks (Fig. 1; Zhu et al., 1983). Li and McCulloch (1996) proposed that the South China craton was formed by a collision between Yangtze and Cathaysia at ca. 970 Ma. These two blocks are separated by the Jiangshan-Shaoxing (Jiang-Shao) fault system (Fig. 1), a major Neoproterozoic suture in southern China. The reactivation of the Jiang-Shao suture, during the Mesozoic, formed the NE-trending Gan-Hang rift system (Gilder et al., 1991).

There has been abundant magmatism in the South China craton, and primarily during three magmatic pulses: 183-168, 160-140 and 140-90 Ma (Fig. 1; Hou et al., 2013). The older magmatic rocks (183-168 Ma) are dominantly mafic. This suite consists of alkalic basalt and tholeiitic basalt. In addition, volcanic rocks of bimodal suites and A-type granites and syenites also formed during this period. In contrast, the intermediate granitoid rocks (160-140 Ma) are closely associated with W-Mo (Mao et al., 2004), Sn-W and Nb-Ta (Wang et al., 2003; Zhang et al., 2004; Hua et al., 2006) mineralization. As shown in Fig. 1, the most widespread magmatic activity occurred during the period from 140 to 90 Ma. A belt of volcanic-intrusive complexes formed along the coast and 260 granitic intrusions were emplaced along the LYMR (Lower-Middle Yangtze River metallogenic belt) during this period.

The Dexing copper ore deposit consists of three porphyritic plutons: Tongchang (middle), Fujiawu (southeast) and Zhushahong (northwest), which host the three separate mines (Fig. 2). The Neoproterozoic Shuangqiaoshan group country rocks

(metamorphic volcanic and sedimentary rocks and epizonal metamorphic rocks) were intruded by these three ore-forming granodiorite porphyries. The wall rocks are characterized by extensive hydrothermal alteration. The main alteration types are potassic, phyllic, argillic and propylitic, which is similar to the typical alteration types of porphyry deposits summarized by Sillitoe (2010). As shown in Fig. 2, our five porphyritic granodiorite samples were collected from the sole, ore-forming porphyritic granodiorite pluton that hosts the Tongchang mine of the Dexing porphyry deposit. We consider the samples to be representative of the bulk of this pluton because the sample locations span most of the porphyritic granodiorite pluton core.

3. Experimental and analytical methods

3.1. Sample preparation

Double-polished thick sections were prepared commercially and grain mounts were made with the objective of identifying amphibole, potassium feldspar and plagioclase phenocrysts and different generations of biotites, apatites and melt inclusions (MI) enclosed in the biotite, plagioclase and quartz phenocrysts. The epoxy-based, biotite and plagioclase grain mounts were polished to a depth in the phenocrysts that allowed access to the interiors of the host minerals and to apatite inclusions at the polished surfaces.

The crystallized MI required rehomogenization prior to investigation. We were concerned that, during rehomogenization of crystallized MI in the separated quartz phenocrysts, some of the groundmass materials attached to the phenocrysts might melt which would degrade the optical transparency of the quartz crystals. So, the quartz phenocrysts were soaked in cold dilute hydrofluoric acid for 22 hours to dissolve the attached materials. Afterward, the quartz grains were rinsed, dried and

then loaded into an open palladium-silver capsule and heated at temperatures of 790-910 degrees Celsius and 100 MPa for 5-8 hours during multiple runs in an internally heated pressure vessel (IHPV) at the American Museum of Natural History (AMNH), New York. If the MI in the heated grains were not fully homogenized at a given temperature, a new batch of quartz phenocrysts were heated at 100 MPa and at 30 degrees Celsius higher temperature. Once the appropriate range in homogenization temperatures was determined, all additional quartz phenocrysts were heated to these temperatures directly in the IHPV and held for 8 hours. After the heating process, the quartz phenocrysts were mounted, ground and polished to search for glassy MI. Multiple steps of polishing and searching were required to expose the glassy MI on the polished surfaces of quartz mounts for analyses (Student and Bodnar, 2004).

3.2. Electron probe microanalyses

Phenocrysts of biotite, amphibole and feldspar and inclusions of biotite (in plagioclase and quartz), apatite (in biotite and plagioclase) and glassy MI (in quartz) were analyzed by electron probe (EPMA), which were performed using a Cameca SX-100 at the AMNH. Two-step protocols were employed for all analyses.

Biotites were analyzed with the following conditions: F, Na, Cl and Fe were measured in the first pass using a 15-kV accelerating potential and a 10-nA beam current and Mg, Al, Si, K, Ca, Cr, Mn, Ba and Ti in the second pass utilizing a 15-kV accelerating voltage and a 20-nA beam current. Both passes used a 5- μ m diameter defocused electron beam. Because amphibole and plagioclase have many of the same primary components as biotite, we used the same standards and operating conditions to analyze these three minerals.

For the apatite analyses, F, Na and Cl were analyzed with a 4-nA beam current and a 10-kV accelerating voltage in the first instrumental pass and the other components

were measured with a 20-nA beam current and 15-kV accelerating potential in the second instrumental pass. Both passes used a 5- μ m diameter defocused beam. Stormer et al. (1993) determined that the F, Cl, Ca and P K α X-ray counting rates (EPMA) are highly time-dependent when exposed to an electron beam. Therefore, in our analyses, the apatite grains were moved under the electron beam during the analyses to prevent the migration of these components. In addition, the optimal analytical results are obtained when apatite crystals are oriented with their c-axes perpendicular to the electron beam (Stormer et al., 1993; Goldoff et al., 2012; Stock et al. 2015). In this study, we just perform the EPMA analyses with the c-axes of apatites normal to the electron beam.

The glass of the MI and potassium feldspars were analyzed with the following conditions: F, Na, K and Fe were measured in the first pass using a 15-kV accelerating potential and a 2-nA beam current; and Mg, Al, Si, P, Cl, S, Ca, Mn and Ti in the second pass using a 15-kV accelerating voltage and a 10-nA beam current. Due to the small size (the longest dimensions are commonly less than 12 microns) of some of the MI, they could not be moved under the beam during the EPMA analyses without the beam interacting with the host phase. For this situation, we employed the time-zero method for Na, K, and F which instead counts X-rays emitted from the samples in five-second intervals. The numbers of counts in each interval were plotted on a graph, a line was fitted to the points, and the line was extrapolated back to “time-zero” (i.e., the time immediately prior to the beam exposure and prior to potential changes in Na, K and F contents of the MI) to estimate the X-ray counts at the start of the analyses. Both passes used a 1- μ m diameter electron beam for these small MI. In contrast, for larger MI, we used the 5- μ m diameter defocused beam and moved the MI under the electron beam during the EPMA analyses.

4. Results

4.1. Petrographic observations

4.1.1. The porphyritic granodiorite

The five studied samples of the porphyritic Tongchang granodiorite include fresh to variably altered phenocrysts of plagioclase, biotite, amphibole, potassium feldspar, and small amounts of quartz. The groundmass is composed of quartz, potassium feldspar and small amounts of amphibole and biotite. In addition, the accessory minerals are rutile, monazite, sphene, zircon, magnetite, anhydrite and apatite. These textural characteristics of TC-21 are consistent with prior observations on Tongchang granodiorites (Wang et al., 2006).

The presence of secondary grains of biotite, magnetite, quartz, and potassium feldspar filling interstices and fine hydrothermal veinlets and replacing primary phases in the partially altered granodiorite samples indicates the main-stage metasomatism represents potassic alteration. Furthermore, some rare primary potassium feldspar phenocrysts show overgrowths of secondary potassium feldspar. We note that no pyroxenes are present in this sample, and we interpret this to mean that all pyroxenes were replaced during metasomatic alteration. These rocks contain alteration-phase rich pseudomorphs some of which likely formed after pyroxenes and others after amphiboles. In addition, parts of the studied samples are cut by fine hydrothermal veinlets, and one scanning electron microscope (SEM) image was taken of a small veinlet in TC-21 granodiorite that is representative of the veinlets. The included minerals, showing different brightnesses, were identified by SEM-EDS analyses (Fig. 3). This example veinlet is composed mainly of potassium feldspar, quartz and anhydrite. In summary, the general alteration characteristics of all studied

samples and the mineral constituents of the studied veinlets all manifest that this portion of the granodiorite was altered by potassic fluids except for sample TC-4, which shows strong biotitization alteration (Fig. 4D). For this sample, we can locate abundant alteration-phase rich pseudomorphs some of which likely formed by alteration of pyroxenes or amphiboles.

In addition, we found that weak lower-temperature sericitic (potentially deuteric) and argillic alteration has affected some plagioclase phenocrysts, but the extent of visible alteration is highly variable among different crystals. Most amphibole phenocrysts (0.5-2mm) are strongly altered to oxides and other silicate mineral(s). Less altered, somewhat well-preserved amphibole is rare; however, there are some relatively fresh relict amphibole cores left, and these were the amphiboles analyzed by EPMA in this study. The relatively fresh areas of these amphiboles exhibit obvious pleochroism ranging from green to yellow green. The quartz phenocrysts (1-2.5mm) in the granodiorite show variable forms. They vary from round to rectangular and also include more-complex polygonal shapes. Some quartz phenocrysts only exist as a round single quartz crystal while others occur as polycrystalline quartz aggregates. This characteristic is as same as that of the type-2 "quartz eyes" described in Harris et al. (2004) for quartz (in miarolitic cavities) of dacite porphyries in the Bajo de la Alumbrera porphyry deposit. These type-2 quartz phenocrysts in our sample are composed of small interlocking grains (50-200 microns diameter) that always occur with small iron oxides. These small quartz grains contain abundant fluid inclusions, and the more-rare MI are much more common within these smaller quartz grains.

4.1.2. Biotite petrography, paragenesis, and nomenclature

In this report, biotite was classified into altered magmatic and secondary genetic categories based primarily on their textural characteristics. The term "altered

magmatic biotite" is used to designate biotite that crystallized from the silicate melt directly and were altered by later hydrothermal fluids (Fig. 4A). The altered magmatic biotite occurs as euhedral to subhedral phenocrysts, and some are replaced by secondary biotites along their cleavage planes and the outer edges. Some biotites are completely recrystallized to smaller secondary biotite flakes that appear as anhedral clustered flakes (Fig. 4B). In addition to occurring as phenocrysts, altered magmatic biotite can also be trapped as micro-inclusions in other magmatic phenocrysts (e.g., plagioclase or quartz) (Fig. 4C). In contrast, the term "secondary" refers to biotites that precipitated from hydrothermal fluids. Secondary biotite partially or completely replaces magmatic biotite and amphibole phenocrysts and typically appears anhedral with rounded outlines. Partially replaced primary mica appears embayed with secondary micas and hydrothermal opaque minerals (magnetite with or without hematite) along their periphery. When the secondary biotites totally replace the biotite or amphibole crystals, they form clustered biotites, which co-exist with secondary magnetite with or without hematite. Individual anhedral grains of biotite in the clustered assemblage are always small and range from 10 to 200 microns in length. Besides this, some secondary biotites are distributed randomly in the groundmass as disseminated flakes (Fig. 4D). Prior research has determined that some biotite crystals of mineralized porphyries having textures that are similar to those of the disseminated secondary biotites can also be magmatic or they may represent a mixture of magmatic and secondary types (Jacobs and Parry, 1979). Therefore, the textural characteristics of biotite, sometimes, may not always serve as a fully applicable criterion for distinguishing between different generations of biotites. More complete characterization of the origin of biotites can be made by determining their compositional differences (Nachit et al., 2005) which we address for our Tongchang

porphyritic granodiorite samples below.

4.1.3. Apatite textures

Apatite occurs as hexagonal prismatic forms that are acicular and euhedral to subhedral. It is found as inclusions within biotite, plagioclase, and quartz phenocrysts and as individual microphenocrysts in the groundmass. When in plagioclase, apatite may occur together with magmatic biotite (Fig. 4C). Individual grains (or crystals) of apatite range from 12-200 microns in long dimension and 6-50 microns in short dimension. In this study, we mainly analyzed apatite (with c-axes parallel or nearly parallel to the polished surfaces of the grain mounts) poikilitically enclosed in biotite or plagioclase phenocrysts (Fig. 5A). In contrast, most apatites enclosed in quartz phenocrysts are too small to analyze (i.e., typically less than 10 microns in length).

4.1.4. Melt inclusion characteristics

Almost all MI analyzed in this study were trapped in the small quartz crystals of the big type-2 "quartz eyes". Before heating, they contain large proportions of crystallized materials with or without small amount of glass and obscure bubble(s). Owing to the different crystallographic orientations of the minerals in the inclusions, the MI show a few bright spots under cross-polarized light. Their strongly crystallized characteristics reflect that their cooling rates were quite slow after the MI were trapped (Frezzotti, 2001). They tend to be distributed in the host quartz randomly with diameters ranging from 5 to 20 microns. After heating in the IHPV, the MI show different extents of rehomogenization because of their various sizes and compositions. In addition, they commonly have round to negative-crystal shapes. In this report, we mainly analyzed crystal-free MI and those with minute quantities of residual crystallized minerals.

4.2. Mineral and glass (MI) analyses

4.2.1. Feldspar and amphibole compositions

The compositions of feldspar and amphibole phenocrysts are listed in Table 1 and 2. The An contents of the plagioclase in the Tongchang granodiorite have unimodal distribution and are located in the range of An₂₂ to An₄₈ (Fig. 6). Most plagioclase phenocrysts range from An₂₈ to An₄₂. Almost all of them are andesine plagioclases (e.g., An₃₀-An₅₀). The compositions of the alkali feldspar are in the range of Or₈₇ to Or₉₆, and the wt.% K₂O ranges from 14.77 to 16.27.

Table 1 and Fig. 7 show that all of the residual amphibole cores are Cl-enriched and F-deficient edenite compositions using the classification diagram proposed by Leake et al. (1997) and for ion numbers calculated on the basis of 23 oxygens. We calculated the Mg/(Mg+Fe²⁺) (each element represents cation numbers of amphiboles) ratios reporting all iron as FeO because we lack accurate information about the ratio of Fe²⁺/Fe³⁺. However, owing to the fact that part of the total Fe will occur as Fe³⁺, the actual Mg/(Mg+Fe²⁺) values should be larger than those in Fig. 7. However, all amphiboles are edenitic in composition regardless of changes in Mg/(Mg+Fe²⁺) values.

4.2.2. Biotite compositions

The compositions of the different biotite generations are presented in table 3 and the methods for calculating biotite formulas is in the appendix. The textural differences we have observed for the Tongchang granodioritic biotites show relationships with their compositions. The per formula unit Fe, Ti, and Ba numbers of the altered magmatic biotite are higher in comparison to those of the secondary biotite, for example. In contrast, the Mg numbers tend to increase from altered magmatic to secondary biotites (Fig. 8).

Based on the classification scheme of Rieder et al. (1998), we have projected the compositions of the biotites in our samples onto the quadrilateral field for phlogopite,

annite, siderophyllite and eastonite in micas. The Tongchang biotites are Mg-rich and fall near the phlogopite-annite join (Fig. 9), which is similar to the previous work of Boomeri et al. (2009) on all micas in potassic zone from the Miduk porphyry copper deposit, Iran. The mole fractions of phlogopite in secondary biotite from Tongchang range from 0.55-0.63, which is equivalent to and generally higher than those of the altered magmatic biotite (0.53-0.59) (Table 3). There is also an apparent, negative relationship between X_{Mg} and the tetrahedral Al content for all of the biotites (Fig. 9).

4.2.3. Apatite compositions

The compositions of apatites trapped in biotite and plagioclase phenocrysts are presented in table 4. For some very large apatites, that exceed 40 microns in short dimensions, we conducted EPMA analyses at the core and the rim. None of these analyzed apatites exhibit compositional zoning, which suggests that the primary magmatic equilibration of apatites trapped and armored within other phenocrysts was maintained, and hence that partial reequilibration of those components investigated did not occur or else that the large crystals were completely re-equilibrated.

The SO_3 contents of all apatites have a positive relationship with their SiO_2 contents (Fig. 10A), which is consistent with the coupled exchange reaction for apatites: $S^{6+} + Si^{4+} = 2P^{5+}$ (Streck and Dilles, 1998). Similarly, the SO_3 contents of all apatites also correlate positively with their Na_2O contents (Fig. 10C), which is consistent with the coupled substitution for apatites: $S^{6+} + Na^+ = P^{5+} + Ca^{2+}$ described by Piccoli and Candela (2002) and Parat and Holtz (2004). In contrast, it is shown that the Cl content of all apatites correlates negatively with their F and CaO contents (Fig. 10B, D), respectively. In addition, the Cl contents of most apatites display an obvious bimodal distribution (Fig. 10D).

Based on the method described in Piccoli and Candela (2002), the mole fractions of

volatile components in the halogen site of the apatites were calculated. The $X_{\text{Cl}}\text{-}X_{\text{F}}\text{-}X_{\text{OH}}$ ternary plot (Fig. 11A) for the Tongchang apatites shows that some apatites contain nearly subequal proportions of Cl, F, and OH. Others are fluorapatite rich, however. All apatites appear to contain substantial OH ranging from ca. 20-38 mole percent. In addition, we also construct a ternary plot (Fig. 11B) showing the F, Cl, and $10 \times \text{S}$ per formula unit numbers because Cl and S may have strongly influenced ore metal complexation and transportation in the mineralizing fluids of the Tongchang system. The compositions of the apatite trapped in the biotite define two groups; one is located near the F apex and the other clusters almost in the middle of the ternary in Fig. 11B (in the circle). These observations mean that the second population possesses higher relative S and Cl and lower relative F concentrations than those of the first group. And, the apatite existing as micro-inclusions in plagioclase phenocrysts has similar to slightly elevated Cl relative to those enclosed in the biotite crystals.

4.2.4. Melt inclusion compositions

In this report, we only analyzed crystal-free MI and those with small amount of residual crystals. The compositions of the MI are silicic to very silicic (i.e., $\text{SiO}_2 = 72.55$ to 78.84 wt%), and these compositions are more chemically evolved than the granodiorite whole-rock compositions (Table 5). The higher silica contents in some MI may have been influenced by incorporation of the host quartz into the melt during the rehomogenization process if the heating durations were too long or too high in temperature. The A/CNK (molar $\text{Al}_2\text{O}_3/(\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O})$) and the N/NK (molar $\text{Na}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})$) ratios of the glassy MI range from 0.97 to 1.16 and 0.64 to 0.87, respectively. For comparison, the whole rock sample has A/CNK of 0.96 and N/NK of 0.66. The MI contain from 1500 to 4300 ppm Cl, ≤ 500 ppm F, and ≤ 300

ppm SO₂. Thus, the MI compositions show that the Tongchang is a Cl-enriched, F-deficient system.

5. Discussion

5.1. Genetic, orthomagmatic model for the formation of mineralized porphyry systems

The dissolution, transport, and deposition of metals during the magmatic to hydrothermal transition are essential for the formation of mineralized porphyry deposits (Halter and Webster, 2004). These processes start at the initial separation of a magmatic volatile phase(s) from the evolving magmas and terminate at the solidus temperature of the corresponding magmatic systems (London, 1986; Halter and Webster, 2004). Owing to the high H₂O contents common to arc magmas (Burnham, 1979; Naney, 1983; Richards, 2005), the saturation of an aqueous magmatic volatile phase from a cooling and fractionating magma is an inevitable process. The separation of magmatic volatile phase(s) from the melt can occur in response to changes of temperature and pressure by first or second boiling processes. Prior studies show that the solubilities of most volatiles in magmas correlate positively with the confining pressure of the related magmatic system (Burnham, 1979; Newman and Lowenstern, 2002; Webster, 2004). Hence, with the ascent of parental magmas from the lower crust hot zone, the solubilities of volatiles in the cooling and evolving magmas will be lowered. When the combined contents of all volatiles components in the melt exceed their specific solubility in the melt at a given pressure and temperature, a volatile-rich phase (vapor or hydrosaline liquid) or phases (vapor plus hydrosaline liquid) will exsolve via first boiling (Burnham, 1979; Cline and Bodnar, 1994; Webster, 2004; De Vivo et al., 2005). Alternatively, the crystallization of volatile-free to volatile-poor

magmatic minerals will increase the volatile contents of the residual melt and with continued crystallization, the volatile contents of the residual melt eventually exceed their integrated solubilities, and a magmatic volatile phase exsolves via second boiling (Burnham, 1979; De Vivo et al., 2005).

After aqueous phase saturation in the magma chamber, certain ore metals in the melt will partition efficiently in favor of the exsolved aqueous phase(s) (Candela and Piccoli, 1995; Bai et al., 1999; Davidson and Kamenetsky, 2001, 2007; Harris et al., 2003, 2004; Davidson et al., 2005). Magmatic volatiles initially exsolve as either a film adhering to phenocryst surfaces or as bubbles (Candela, 1991). The lower density of the bubbles relative to melt and phenocrysts in the magma will drive the bubble-laden magma to ascend. Continued ascent of the exsolved fluid(s) will cause bubble expansion and coalescence. Magma ascent and vapor expansion may lead to rupturing of the magma carapace and fluid escape with or without brecciation (Burnham, 1979; Sillitoe, 2010). After vapor loss, the denser partially degassed magma may sink and be followed by the ascent of a new batch of bubble-laden magma (Cloos, 2001). The intimate mixture of melt and aqueous fluid(s) is advantageous for efficient extraction of metals from coexisting magma (Audétat and Pettke, 2003). Moreover, for most porphyry copper systems, the first exsolved magmatic fluid is generally considered to possess less than 10 wt.% NaCl equivalent (i.e., generally of low salinity) (Hedenquist and Lowenstern, 1994; Yardley and Bodnar, 2014), but with continued ascent and depressurization, the early exsolved vapor will intersect the fluid solvus and form coexisting low-salinity vapor and Cl-rich hydrosaline liquid (Hedenquist and Lowenstern, 1994; Bodnar, 1995). This high-Cl hydrosaline phase has proven to be essential to the transport of metals in some porphyry systems (Cline and Bodnar, 1994; Bodnar et al., 2014).

These fluids cause massive hydrothermal alteration as well as ore metal transport and deposition. Sillitoe (2010), for example, describes the classic alteration zoning patterns for porphyry Cu systems. Early potassic metasomatism spans from hyper-solidus through sub-solidus temperatures producing alteration assemblages of quartz, potassium feldspar, biotite with or without magnetite. Shinohara and Hedenquist (1997) proposed that fluids exsolved subsequently from the gradually cooling magmatic system may not intersect the vapor-hydrosaline liquid solvus with their evolution and hence may generate moderately saline fluids that produce sericitic alteration. The circulation of meteoric groundwater in the hydrothermal convection system generated by the hot magmatic intrusion may support large-scale propylitic alteration, which may overprint the earlier hydrothermal alteration. Finally, advanced argillic alteration occurring at shallow levels in the hydrothermal system, may be produced by low-salinity vapor phases enriched in acidic volatiles that separated physically from the coexisting hydrosaline liquid because of the strong density contrast between vapor and liquid (Richards, 2005). The highest Cu ore grades are always found at the outer edges of the potassic alteration region suggesting that temperature decreases associated with the potassic alteration stage (i.e., above but near-solidus temperatures to much lower temperatures) are significant for decreasing copper solubility in the potassic fluid (Cooke et al., 2014). A primary objective of this study is to investigate the levels of Cl enrichment in the latest-stage magmatic phases, the behavior of Cl and S during the magmatic-hydrothermal transition, and the potential role of these volatiles in magmatic and later-stage hydrothermal alteration associated with Cu, Mo and Au mineralization for the Tongchang granodioritic magma in the context of this described orthomagmatic model for porphyry ore formation.

5.2. Interpretation of the stages of crystallization of biotite and apatite and their subsequent reactions with hydrothermal fluids

5.2.1. Origins and compositions of the biotite

As described above, the altered magmatic biotite occurs as euhedral to subhedral phenocrysts, and they are partially to totally replaced by secondary biotites. In contrast, the secondary biotites partially to completely replaced the primary mafic biotite and amphibole forming clustered biotites, which may or may not co-exist with hydrothermal magnetite with or without hematite. The TiO_2 contents of the altered magmatic biotites and secondary biotites range from 4.08 to 5.81 wt.% and 2.02 to 3.67 wt.%, respectively. Nachit et al. (2005) proposed a qualitative ternary plot comprised of $10 \times \text{TiO}_2$ - FeO^* - MgO (where $\text{FeO}^* = \text{FeO} [\text{total iron}] + \text{MnO}$ and all oxide data are expressed in weight percent) for discriminating between primary magmatic, re-equilibrated magmatic, and secondary biotites, and we have adopted this approach (Fig. 12). The compositions of our biotites show a continuous spread from the primary to the re-equilibrated magmatic domains, but most of the studied Tongchang biotites are located in the domain of re-equilibrated magmatic biotite, indicating that they reacted (and may have partially to fully re-equilibrated) with magmatic or magmatic-hydrothermal hydrothermal fluids. Biotite inclusions trapped in the plagioclase and quartz are located in the same region of the ternary plot as the altered magmatic biotites and secondary biotites, respectively. Use of this method to distinguish the different generations of biotites in the Tongchang granodiorite also points to discrepancies between the textural and chemical constraints on biotite origins, however. For example, texturally characterized secondary biotite should project into the domain C of Fig. 12, but they are actually located in domain B. For this apparent discrepancy to occur, the secondary biotites of Tongchang must contain

much higher relative TiO_2 contents than those referred to in Fig. 12. Considering that the ratios of FeO^*/MgO of all analyzed Tongchang biotites remain relatively constant, it is temperature that must have influenced the measured TiO_2 contents of the biotite (Nachit et al., 2005). The temperature variation for reaction between primary magmatic biotite and potassic fluid and crystallization or last reaction of secondary biotite with potassic fluid should overlap partially. Hence, we hypothesize that the TiO_2 contents of these two generations of biotites should have a continuous spread, rather than have a large gap, due to the likely continuous decrease in temperature with progressive system cooling.

The X_{Mg} values of Tongchang biotites can also be applied to better interpret their different types and history. The X_{Mg} values of the secondary biotites vary from 0.63 to 0.68, which partially overlap with and are slightly higher than those of altered magmatic biotite (0.60 to 0.65) (Table 3). However, the X_{Mg} values of the two types of Tongchang biotites exhibit a continuous sequence rather than have an obvious gap between them. Trends like these were observed and reported, early on, by Beane (1974) and Jacobs and Parry (1979) for other mineralized porphyries.

As stated in Munoz (1984), biotites having higher X_{Mg} tend to contain lower Cl contents than biotites with lower X_{Mg} values (at the same temperature and fugacity ratios of the coexisting phases), which is due to a crystal-chemical effect defined as the Mg-Cl avoidance principle. The X_{Mg} values of the studied biotites correlate negatively with Cl contents for all biotites, showing that they are in agreement with the Mg-Cl avoidance principle (Fig. 13A). In contrast, those biotites containing higher X_{Mg} tend to incorporate higher F contents than biotite with lower X_{Mg} values (at the same temperature and fugacity ratios of the coexisting media), which is consistent with the Fe-F avoidance principle (Munoz, 1984). In Fig. 13B, the F contents for all

Tongchang biotites remain relatively constant with the variation in X_{Mg} of ca. 0.60-0.68 wt.%. This relationship appears to contradict the Fe-F avoidance principle, implying that some other variable or variables influence F incorporation in these biotites. Perhaps, this is because the high- X_{Mg} biotites reacted with relatively F-poor fluids and/or is due to subtle changes in temperature.

A negative relationship also exists between the BaO concentrations and the X_{Mg} values for all magmatic biotites (Fig. 13C) whereas the BaO contents of the secondary biotites stay relatively constant. Therefore, the BaO contents might also serve as a proxy for discriminating between re-equilibrated altered magmatic biotite and secondary biotite as proposed by Jacobs and Parry (1979). This suggests that the BaO contents of the altered magmatic biotites increase along with the alteration intensity, and meanwhile, the secondary biotites should contain more BaO than the altered magmatic biotites. In addition, the X_{Mg} values correlate negatively with the concentrations of (K₂O+Na₂O+BaO), FeO and TiO₂ (Fig. 13D, E, F) for the two types of biotites.

5.2.2. What do the compositions of the volatile-bearing phases represent?

The compositions of apatite can be used decipher the oxidized state of the coexisting magmas (Ding et al., 2015). In addition, igneous apatite can serve as a useful proxy for estimating the concentrations of F, Cl, OH/H₂O, S, and CO₂ in magmatic systems (Piccoli and Candela, 2002; Webster and Piccoli, 2015). However, the application of this geochemical tool requires knowledge on the timing of apatite crystallization, the occurrence of potential post-crystallization reactions with magmatic or hydrothermal fluids, and the extent to which apatite achieves equilibrium in its reactions with melts, fluids and/or other minerals. The volatile concentrations of other hydrous phases (e.g., micas and amphiboles) have also been determined for

mineralized and barren granites and applied to the interpretation of volatile behavior in melt with or without coexisting fluids (Selby and Nesbitt, 2000; Boomeri et al., 2009, 2010; Zhang et al., 2012; Teiber et al., 2015; Zhang et al., 2016).

The Tongchang apatites prove to be highly useful in this regard. As shown in Fig. 10D, 11 and 14, the highly variable Cl and SO₃ contents of the studied Tongchang apatites exhibit a distinctly bimodal distribution that provides evidence of volatile behavior during magma differentiation. Most of these apatites can be assigned to either a very low-S and variable but lower-Cl group or a group containing significantly greater and highly variable S and Cl contents. Regarding magmatic S, Hou et al. (2013) proposed that S and Cu were supplied to the Dexing magmatic systems by mantle-derived mafic magmas that were either injected into the shallow felsic magma chamber or were underplated beneath the hot zone of the lower crust. After emplacement of the Dexing magma at the magma chamber, subsequent fractional crystallization should have caused progressively increasing concentrations of S and Cl in residual Tongchang melt and apatite. Further evolution of the Tongchang mingled magmas eventually caused the crystallization of the magmatic anhydrites found as inclusions within plagioclase phenocrysts in the porphyritic granodiorite samples of this study and also other magmatic anhydrite phenocrysts in Tongchang porphyries described by Wang et al. (2006). Saturation in anhydrite indicates magmas that are sulfate-rich, and hence, highly oxidized (Luhr, 1990; Audétat et al., 2004; Stern et al. 2007), and this is true for the Tongchang magmatic system (Wang et al., 2006; Zhang et al., 2013). Importantly, the crystallization of anhydrite scavenged S from the Tongchang magmas which led to a sharp decrease in S contents of the magma. Hydrothermal experiments have shown that saturation in anhydrite will decrease and buffer the S concentrations of felsic melts and of

coexisting apatite (Parat and Holtz, 2005; Masotta and Keppler, 2015). Thus, any apatites in equilibrium with melt and anhydrite at this stage had their S contents buffered at very low values, which conforms with and explains the volatile contents of the very low-S group of apatites (Fig. 14). The observed variation in Cl of these lower-Cl apatites likely reflects magma evolution for conditions involving increasing and unbuffered Cl, and in particular, increasing Cl in residual melt (and in coexisting apatite).

Subsequently, at some unconstrained stage in the progressing evolution of the Tongchang system, and addressed in greater detail below, one or more saline fluids exsolved from the magma and the fluid(s) began to react with the existing phenocrysts. Prior experimental work shows that the solubility of anhydrite in aqueous fluid increases enormously with increasing NaCl and KCl (or CaCl₂) activities (Newton and Manning, 2005; Webster et al., 2009a), and prior petrographic study of natural systems has determined that early formed anhydrite can be dissolved by later-exsolved aqueous fluid (Streck and Dilles, 1998). Thus, in the Tongchang magmatic-hydrothermal system, either the direct exsolution of a high-salinity fluid or the condensation of high-salinity fluid from magmatic vapor would work to dissolve most of the phenocrystic anhydrites. Moreover, the penetration of such fluids along cleavage planes inside magmatic phenocrysts during metasomatism would allow contact with and partial to complete dissolution of anhydrite inclusions trapped inside plagioclase, amphibole and mica phenocrysts. One result of these hydrothermal processes of alteration and dissolution would be saline fluids that are variably enriched in S and Cl depending on the extent of reaction and approach to equilibrium between melt, amphibole, biotite, anhydrite, apatite, and the fluids. Another result of these processes would be the low SO₂ contents determined for the Tongchang MI

(Table 5). These SO₂ values are consistent with those of melts from the anhydrite-free, fluid-felsic melt experiments of Masotta et al. (2016), and the experimental data are applicable to the MI given the close similarity in bulk composition. For example, the SO₂ contents of anhydrite-free, fluid saturated experimental felsic melts range from 0.005 to 0.03 wt% at 900°C and 0.009 to 0.03 wt% at 800°C and 200 MPa, and in comparison the MI contain 0.01 to 0.03 wt% SO₂ (Masotta et al., 2016). In addition, an additional consequence of this high-S and high-Cl fluid would be the precipitation of anhydrite in the fine hydrothermal veinlets of our samples during cooling (Fig. 3). Finally, the reaction between this high-S and high-Cl fluid and early crystallized apatite would increase the S and Cl contents of the apatite, which can explain the high-S and high-Cl apatite occurrences.

Petrographic observations show that the majority of amphiboles in the granodiorite are strongly altered to secondary biotites with or without hydrothermal iron-oxide opaque minerals. The abundance of metasomatized amphiboles and micas suggests that hydrothermal alteration was pervasive and that the duration for hydrothermal fluid interacting with the existing primary magmatic minerals was long. We assume that the residual interiors of the altered amphiboles have potentially been variably influenced by alteration and some of these analyses may no longer represent primary magmatic compositions.

In addition, the rims of the primary magmatic biotite phenocrysts are nearly always altered to secondary biotites due to reactions with the potassic hydrothermal fluid. We expect that halogens were exchanged, to some extent, between magmatic biotite and this batch of fluid during the potassic alteration stage. To determine the extent of biotite phenocryst reaction and potential re-equilibration with the potassic fluid, we conducted traverses by EPMA across representative biotite phenocrysts to trace the

compositional changes from rim to core and then to opposite rim (Fig. 15). The extent of reaction of the hydrothermal potassic fluid was pervasive in the area of this deposit represented by our samples. It is also important to note that we could not locate any pyroxenes, but actually, pyroxenes should exist in granodiorites of this composition, so any primary magmatic pyroxenes were replaced by hydrothermal alteration. Considering that almost all amphiboles have been strongly altered by potassic fluid, that primary pyroxenes have been replaced and because of the presence of strong cleavage in the biotite, we suggest that there are likely few to no primary biotites left which did not react with the potassic fluid. In addition, although some biotites are located in the compositional boundary between domain A and B (Fig. 12), they are likely to have reacted with the fluid to some minor extent. For the traverse, we focus on the X_{Mg} values and K_2O , TiO_2 , and BaO contents of this biotite for the following reasons: (1) the K_2O contents of biotites should change during reactions between potassium-rich Cl-enriched fluid and biotite phenocrysts during compositional exchange reactions; (2) prior investigations discussed previously determined that X_{Mg} values and the TiO_2 (Nachit et al., 2005; and references therein) and BaO (Jacobs and Parry, 1979; and references therein) contents of biotites play a significant role in distinguishing different generations of biotites and in differentiating the alteration intensity. These parameters remain relatively constant from the rim to the core, and then to the opposite side rim of the selected biotite phenocryst (Fig. 15). So, we assume that this magmatic biotite phenocryst obtained equilibrium with the potassic hydrothermal fluid, and if it is indeed representative of the other altered primary micas, then we can use the EPMA biotite compositions to calculate the halogen fugacity ratios of the coexisting potassic fluids with confidence.

5.3. Comparison of Tongchang biotites and apatites with those of

other porphyry deposits

5.3.1. F, Cl and OH (H₂O) concentrations of biotites and estimated HF and HCl fugacity ratios for the potassic hydrothermal fluid

All Tongchang biotites contain from below the detection limit to 0.28 wt.% F and from 0.19 to 0.35 wt.% Cl. The ranges in halogen contents of the altered magmatic micas are equivalent to and consistent with those of the secondary biotites (Fig. 13A, B). The calculated water concentrations of these micas range from 3.72 to 3.99 wt%. We applied the method of Munoz (1992) and calculated halogen fugacity ratios for the fluids in equilibrium with biotite using new equations based on a revised thermodynamic interpretation of F-Cl-OH partitioning between biotite and hydrothermal fluids. These equations are:

$$\log (f_{\text{HF}}/f_{\text{HCl}})^{\text{fluid}} = \log (X_{\text{F}}/X_{\text{Cl}})^{\text{biotite}} - 1000/T(1.22 + 1.65(X_{\text{Mg}})^{\text{biotite}}) + 0.25 \quad (1)$$

$$\log (f_{\text{H}_2\text{O}}/f_{\text{HCl}})^{\text{fluid}} = \log (X_{\text{OH}}/X_{\text{Cl}})^{\text{biotite}} + 1000/T(1.15 + 0.55(X_{\text{Mg}})^{\text{biotite}}) + 0.68 \quad (2)$$

$$\log (f_{\text{H}_2\text{O}}/f_{\text{HF}})^{\text{fluid}} = \log (X_{\text{OH}}/X_{\text{F}})^{\text{biotite}} + 1000/T(2.37 + 1.1(X_{\text{Mg}})^{\text{biotite}}) + 0.43 \quad (3)$$

where T is the equilibrium temperature (expressed in Kelvin) for volatile exchange between biotite and hydrothermal fluids and X_{F} , X_{Cl} and X_{OH} are the mole fractions of the corresponding volatile components in biotite. Detailed information about how to calculate the X_{F} , X_{Cl} and X_{OH} values of biotites is in the appendix. Note that $(X_{\text{Mg}})^{\text{biotite}}$ is defined as (Mg cation numbers/sum octahedral cation numbers), which is different from that of X_{Mg} in the notes of table 3.

For any given biotites, we do not know the final temperature of equilibration with the coexisting fluid(s), so here we provide modeled results for a range of potential temperatures of equilibration. Pan et al. (2009) conducted rehomogenization

experiments on fluid inclusions in Tongchang quartz veins which precipitated from potassic fluid. We have applied their median homogenization temperature (690 K) of the fluid inclusions as one reaction temperature of this alteration stage for the calculations (Fig. 16A, B). The ratios of $\log(f_{\text{HF}}/f_{\text{HCl}})$, $\log(f_{\text{H}_2\text{O}}/f_{\text{HCl}})$ and $\log(f_{\text{H}_2\text{O}}/f_{\text{HF}})$ range from -4.40 to -2.67, 4.43 to 4.67 and 6.29 to 6.90, respectively. Furthermore, in order to determine the relationship between temperature and halogen fugacity ratios, we calculated the related fugacity ratios at a higher temperature of 973K to address a broader temperature range better spanning near but super-solidus to sub-solidus temperatures of this magmatic system. With this increase in the reaction temperature, the $\log(f_{\text{H}_2\text{O}}/f_{\text{HCl}})^{\text{fluid}}$ and $\log(f_{\text{H}_2\text{O}}/f_{\text{HF}})^{\text{fluid}}$ shift to lower values whereas the $\log(f_{\text{HF}}/f_{\text{HCl}})^{\text{fluid}}$ shifts to higher values (Fig. 16A, B). In addition, we also calculated the related fugacity ratios at a lower temperature of 573K., and the $\log(f_{\text{HF}}/f_{\text{HCl}})$, $\log(f_{\text{H}_2\text{O}}/f_{\text{HCl}})$ and $\log(f_{\text{H}_2\text{O}}/f_{\text{HF}})$ values of the fluid range from -5.04 to -3.22, 4.86 to 5.05 and 7.07 to 8.87, respectively. If equilibrium reaction occurred between mica and fluids at 573K, then this is what the fugacity ratios would have been.

It is useful to compare our data with those from other porphyry settings. Based on biotite compositions and measured equilibrium temperatures, Selby and Nesbitt (2000) revisited and recalculated volatile-component fugacity ratios for the hydrothermal fluids coexisting with biotite from potassic alteration zones in porphyry deposits of: Bingham, Utah (Lanier et al., 1978; Parry et al., 1978; Bowman et al., 1987); Santa Rita, New Mexico (Jacobs and Parry, 1979); Los Pelambres, Bakircay (Taylor, 1983) and for porphyry copper mineralization of the Hanover, and Deboullie plutons (Loferski and Ayuso, 1995) for comparison with those of the Casino porphyry deposit of the Yukon (Selby and Nesbitt, 2000). In addition, we compile the relevant fugacity

ratios for the fluids calculated from the biotite of potassic zones of the Miduk (Boomeri et al., 2009) and Sarcheshmeh (Boomeri et al., 2010) porphyry deposits, Iran, and our studied Tongchang biotites which we have projected in Fig. 16C, D. Most samples of the selected deposits are located in the potassic alteration zone, so it is useful and effective to compare them with those of the Tongchang system. The $\log(f\text{H}_2\text{O}/f\text{HF})$ values calculated for the Tongchang deposit are higher than those of other deposits except for those at Bakircay, Los Pelambres and Deboullie, which possess the similar $\log(f\text{H}_2\text{O}/f\text{HF})$ values as most of those results of the Tongchang mine, Dexing deposit. As for $\log(f\text{HF}/f\text{HCl})$, the calculated ratios are, in contrast, lower than other deposits considered above, which may partly stem from the fact that the Tongchang is a Cl-enriched F-deficient system as shown by the MI compositions. The F contents of the studied biotites are always near or below the detection limit of the electron probe microanalyses. The calculated $\log(f\text{H}_2\text{O}/f\text{HCl})$ values for the Tongchang porphyry deposit lie between those of Miduk (include Sarcheshmeh) and other deposits except for Bingham, which covers all the range of this parameter for the Tongchang potassic fluid. As shown in Fig. 16A, B, the differences in $\log(f\text{HF}/f\text{HCl})$ and $\log(f\text{H}_2\text{O}/f\text{HF})$ of the fluids among Tongchang and other deposits decrease because of the influence of temperature on these halogen fugacity ratios if we compute the related ratios at the higher temperature. For comparison, if equilibrium between the biotites and the aqueous fluid occurred at temperatures lower than 690K, the fugacity ratios differences of $\log(f\text{HF}/f\text{HCl})$ and $\log(f\text{H}_2\text{O}/f\text{HF})$ between Tongchang and other major deposits will increase, which also supports our conclusion that the Tongchang fluid system was Cl-enriched and F-deficient. The discrepancies among the various porphyry deposits exist because of diversely varying compositions of the exsolved aqueous fluids in the different plutons, which in turn

rests with other factors such as initial melt composition and the physical parameters during emplacement, crystallization, and degassing (Cline and Bodnar, 1991; Cline, 1995).

5.3.2. Comparison of Tongchang porphyry apatites with apatites of other porphyry deposits

It is also useful to compare the F, OH, Cl and S concentrations of apatites from Tongchang with those of other porphyry deposits. The apatites from Duolong deposit have similar fluorapatite, chlorapatite and hydroxylapatite components as those of Tongchang system (Fig. 17A) (Li et al., 2011). In contrast, the compositions of apatites from the Qulong porphyry Cu-Mo deposit (Xiao et al., 2011) have much higher fluorapatite components in comparison to those of the Tongchang mine. This is important because as proposed in Aiuppa et al. (2009), addition of F to the silicate melt can lower its solidus temperature and lead to greater differentiation of the melt in comparison to that to melts with less F. Extended evolution of F-enriched magmas is advantageous to forming porphyritic Mo deposits that are different from other porphyry Cu-Au deposits (e.g., the Tongchang system) (Westra and Keith, 1981; Adam and Green, 2006). Similarly, apatite from the Yerington (Streck and Dilles, 1998) porphyry system also possesses higher fluorapatite components with respect to those of Tongchang.

As noted, the F, Cl and 10*S numbers of Tongchang apatites define an obvious bimodal distribution (high-S and high-Cl vs. low-S and low- and variable-Cl apatites) (Fig. 17B). The S and Cl contents of Qulong apatites, which coexist with or within magmatic anhydrites, are similar as those of the low-S and low- and variable-Cl Tongchang apatites. This is consistent with the buffering and reduction of the sulfur contents of silicate melts by anhydrite crystallization (Streck and Dilles, 1998) and the

crystallization of low-S and low-Cl apatites from anhydrite-saturated melts. Yerington apatites have distinct S zonation from S-rich cores to abruptly S-poor rims. Streck and Dilles (1998) interpreted this zonation as the result of early crystallization of S-rich apatite from S-rich magma (at high oxidation state) forming the sulfur-enriched core, followed by later crystallization of S-deficient apatite rim from low-S, anhydrite-saturated magma. The Tongchang apatites lack S-rich cores which is interpreted to indicate crystallization of apatite after saturation in magmatic anhydrite. The compositions of the Duolong apatites also vary significantly, especially for S contents (expressed as $10 \times S$ in Fig. 17B). The Duolong apatite with high S and Cl contents that was trapped in a biotite phenocryst, indicates a similarly high oxidation state and high S and Cl contents of the magmatic-hydrothermal system. Two of the empty triangles of Fig. 17B represent two apatites disseminated in the potassic zone of granodiorite porphyry deposit of Duolong deposit that possess lower S in comparison with the former apatite trapped in the biotite phenocryst, manifesting that the oxidation state and S contents of the Duolong potassic fluid were lower than those of the Dulong melt prior to formation of the potassic fluid.

5.4. Estimating F and Cl contents in the melt

Magmatic apatite chemistry can be used to calculate Cl, F and S concentrations in coexisting melt, provided that the apatites and melt (with or without fluids) were in equilibrium, that the P-T conditions of equilibrium are known or can be estimated, and that the experimental partitioning coefficients of these volatile components between the apatite and concomitant melt at the geologically relevant conditions are available. In addition, this also assumes that the halogens and hydroxyl ions in natural magmatic apatite have not re-equilibrated with later, coexisting phases within the magmatic or magmatic-hydrothermal system after the apatites crystallized. In this

regard, the experimental and analytical results of Brennan (1994) indicate that F, Cl and OH in apatite can diffuse, parallel to the crystallographic c-axis, relatively rapidly and form a geochemical compositional gradient for these components if post-magmatic changes in temperature, pressure, and fluid or melt composition occur. In contrast, such fast rates do not apply for F, Cl, or OH diffusion along the a-axis; because the relative diffusion of these volatiles along the a-axis of the apatite can be very slow. Given these diffusion rates, the resistance of apatite to potential, late re-equilibration may only be satisfied when the system cools rapidly (i.e., 1°C /100 years) (Brennan, 1994) at conditions which are likely in eruptive magmas or very shallowly emplaced melts (Piccoli and Candela, 2002). These conditions are always not easy to be obtained in porphyritic magmas emplaced at relatively deeper levels like those of Tongchang system.

Another concern is that the quenched composition of the apatite cannot be changed by reaction with later fluids. Hence, on the other hand, if apatites are trapped in and armoured by other mineral phases, they should be isolated from other coexisting melt- or fluid-medium phases after their entrapment as long as the fluids or melts do not penetrate their host minerals. Thus, it is probable that they will maintain either their early pristine magmatic chemistry, or potentially, their compositions formed immediately before their entrapment. Hence, apatites trapped in other phenocrysts may be an ideal form for studies on volatiles in coexisting melts and fluids. In this study, all the analyzed apatites were trapped in biotite and plagioclase phenocrysts exhibiting variable extents of hydrothermal alteration.

Several previous experimental studies determined the partitioning behavior of S, Cl and/or F in the apatite-fluid(s)-silicate melt system at differing shallow-crustal conditions (Parat and Holtz, 2004, 2005; Mathez and Webster, 2005; Webster et al.,

2009b; Doherty et al., 2014). In order to estimate the Cl concentrations of the melt that equilibrated or last reacted with the Tongchang apatites, we have extracted experimental data from prior publications of Webster et al. (2009b) and Doherty et al. (2014) involving felsic systems to apply to these apatites. These experiments determined the partitioning of Cl between rhyodacitic to rhyolitic melts, apatite and vapor and/or brine and were conducted at 50 and 200 MPa and temperatures of 850 to 950°C. The molar A/CNK and N/NK of the melts range from 0.9 to 1.05 and 0.6 to 0.77, respectively, and are roughly consistent with the Tongchang MI. One can estimate the Cl concentrations of felsic silicate melts with these geochemical properties using the equation:

$$\text{wt.\% Cl in felsic melt} = (\text{wt.\% Cl in apatite}) \times (0.16052) \quad (4)$$

Equation (4) involves a simple weight-based Nernstian partition coefficient approach, which has recently been argued to be less accurate for estimating Cl contents of melts. An alternative approach (Webster et al., 2012; McCubbin et al., 2015) is to apply exchange coefficients like: $K_{\text{exF-Cl}}^{\text{apatite-melt}} = (\text{content of F in apatite}) \times (\text{content of Cl in melt}) / (\text{content of Cl in apatite}) \times (\text{content of F in melt})$ based on equilibrium relations like: $\text{Cl}_{\text{apatite}} + \text{F}_{\text{melt}} = \text{F}_{\text{apatite}} + \text{Cl}_{\text{melt}}$ or $K_{\text{exOH-Cl}}^{\text{apatite-melt}} = (\text{concentration of OH in apatite}) \times (\text{concentration of Cl in melt}) / (\text{concentration of Cl in apatite}) \times (\text{concentration of H}_2\text{O in melt})$ based on equilibrium relations like:

$$\text{Cl}_{\text{apatite}} + \text{H}_2\text{O}_{\text{melt}} = \text{OH}_{\text{apatite}} + \text{Cl}_{\text{melt}} \quad (6)$$

In order to deal with the influence of the 3 primary and essential constituents F, Cl, and OH occupying the hydroxyl site in apatite. For this study, we have measured the F contents of the felsic MI, but we have limited constraints on the F contents of the melts at the time of apatite reaction with melt and no information on the H₂O contents

of this melt, so our use of the exchange coefficient method would be limited by these missing data. Thus, we apply equation (4) because the ranges in these components in the Tongchang apatites are generally similar to those for the experimental apatites of Webster et al. (2009b) and Doherty et al. (2014) (Fig. 18). The overlap between the above two data sets is best for the set of data representing equilibria between felsic melt and S-enriched apatite not buffered by anhydrite. Conversely, the overlap between experimental apatites and the anhydrite-buffered S-poor apatites is not as good. With this approach we assume that majority of apatites included in mica and plagioclase represent magmatic values. Based on the dispersion exhibited by the Cl contents of the experimental apatites, we estimate their one-sigma imprecision for calculated Cl in melt to average about 30 relative %. With these experimental constraints we theoretically estimate that any felsic Tongchang melts which may have equilibrated or reacted with Tongchang apatites would have contained: 0.03 to 0.22 wt.% Cl for the anhydrite-buffered S-poor apatites and from 0.24 to 0.60 wt.% Cl for the S- and Cl-enriched apatites apparently unbuffered by anhydrite crystallization.

5.5. The role of Cl on ore-forming processes for the Tongchang magmatic-hydrothermal system

The studied samples should represent the much larger mass of the Tongchang ore-forming porphyritic granodiorite pluton because of the following reasons: (1) the Tongchang system involved only one intrusive (granodiorite intrusive) event that is related to its ore-forming processes (Fig. 2), which is different from other giant porphyry system that always be involved in multiple stages of ore-formation-related intrusive events (Silitoe, 2010); (2) The sample locations of this study span most of the Tongchang ore-forming pluton; (3) numerous previous studies and this research (Table 5) involved many samples from multiple locations of this ore-forming

porphyritic granodiorite pluton (Wang et al. 2006; Liu et al., 2012; Hou et al., 2013; Zhou et al., 2012; Zhang et al., 2013; Wang et al., 2015). Moreover, all of these collected samples show very similar major- and minor-element compositions. In conclusion, our samples should be representative of the Tongchang system. We also note that these compositions contrast with those of the more-evolved compositions of the silicate MI which reflect fractional crystallization of the granodioritic magma.

Bao et al. (2014) noted that Cl is a highly efficient anion for complexing with and increasing the solubility of geologically common metals in hydrothermal fluids. Other related research shows that a high salinity aqueous fluid can play a significant role in forming hydrothermal deposits (Ulrich et al., 1999; Wilkinson et al., 2009). This was also demonstrated by Yardley (2005) for Fe, Mn, Pb and Zn showing that the molar ratios of chloride/metal in crustal fluids stay relatively constant over a range of varying chlorinities. It follows that a high-salinity aqueous fluid is very important in transporting metals in many hydrothermal systems, especially in porphyry systems, and hence is a key factor for the ore-forming processes of relevant deposits. In addition, the quantity of ore fluid necessary to form a giant deposit will be considerably reduced if the metal content of the high salinity fluid is relatively higher (Bodnar, 2009) due to enhanced ore metal solubilities in more Cl-enriched fluids.

As one advancement to Burnham's (1979) milestone orthomagmatic ore deposit model, it is often proposed that the first aqueous fluid exsolved from silicate melt that is genetically associated with most porphyry copper deposits contains less than 10 wt.% NaCl equivalent (i.e., generally of low salinity) (Bodnar, 1995; Sillitoe, 2010; Yardley and Bodnar, 2014). With the reduction in pressure that results from magma and fluid ascent in the crust, this single fluid unmixes into a Cl-poor vapor phase and a Cl-enriched brine (hydrosaline) phase which thus generates the more Cl-enriched

saline fluid phase (Burnham, 1979; Bodnar et al., 2014).

Experimental (Webster, 2004) and other research (Cline and Bodnar, 1994), however, show that a high-salinity fluid can also exsolve directly from some silicate melts. The definition of Cl solubility in a melt at particular pressure and temperature conditions, given by Webster (2004) and Webster and De Vivo (2002), is the Cl content of the silicate melt when the melt is saturated and in equilibrium with hydrosaline liquid (definition in Halter and Webster, 2004) with or without a coexisting vapor. Hence, when a magmatic system attains its Cl solubility level via fractional crystallization and/or pressure reduction, a hydrosaline liquid (or brine) directly exsolves from the melt with or without the vapor phase. The measured Cl contents of several of the Tongchang MI (e.g., 0.3 to 0.43 wt%) are at or very near the computed chloride saturation levels for the specific MI compositions at the chosen conditions of 850°C and 50 MPa (e.g., computed Cl solubilities of 0.36 to 0.46 wt.%) and also at 850°C and 200 MPa (e.g., computed Cl solubilities of 0.42 to 0.54 wt.%). These findings signify that hydrosaline liquid, with or without an aqueous vapor, could have exsolved directly from the late-stage granitic melts of the Tongchang magmas at pressures $\leq$ 200 MPa. This interpretation is consistent with and also supported by the considerably high Cl contents in apatite, biotite and amphibole in this study (Table 1, 3, 4). The combination of this evidence with the breadth and representivity of our porphyritic granodiorite sampling indicates that a significant portion of the granodioritic Tongchang ore-forming magma was very enriched in and actually saturated in Cl. This interpretation is very similar to the evidence for immiscibility between silicate melt and hydrous salt melt in porphyry copper deposits of Romania documented by Pintea (2014). Such elevated Cl contents in a magmatic-hydrothermal system must be highly efficient at dissolving and transporting

large quantities of ore metals given the high concentrations of Cl in the hydrosaline liquids with or without vapor. The significant difference between this aspect of the orthomagmatic model and that of the Tongchang magmatic system (i.e., extreme Cl enrichments) may partly explain why the Tongchang porphyry deposit is such a giant one. Giant porphyry ore deposits can be formed by combinations of just "common" geological processes (Richards, 2003, 2005, 2013). But, all of these processes should be optimized for forming a giant deposit. Thus, we propose that the direct exsolution of high-salinity fluid may be an advantageous criterion for forming giant porphyry deposits because of the optimization of ore metal transport in such Cl-enriched fluids. This observation, however, does not rule out a similarly important role for magmatic sulfur (Zajacz et al., 2011), which requires further investigation at this important porphyry deposit.

Conclusions

(1) The occurrence of secondary biotite, magnetite, and potassium feldspar filling interstices and replacing primary mineral phases and the presence of anhydrite, potassium feldspar, and quartz in hydrothermal veinlets show that the main-stage metasomatism of that part of the Tongchang magma represented by our samples occurred through potassic alteration.

(2) In this study, Tongchang biotites exist as altered magmatic biotite, secondary biotite and as microinclusions in plagioclase and quartz phenocrysts. All examples are Mg-rich micas and represent phlogopite-annite. The mole fractions of phlogopite of secondary biotites (0.55 to 0.63) are equivalent to or slightly higher than those of altered magmatic biotites (0.53 to 0.59). Most of the studied biotites represent re-equilibrated micas. The Fe, Ti, and Ba numbers (per formula unit) of the altered magmatic biotites are higher than those of the secondary biotites. In contrast, the Mg

numbers tend to increase from altered magmatic to secondary biotites. The X_{Mg} values of the secondary biotites vary from 0.63 to 0.68 while those of the altered magmatic biotite range from 0.60 to 0.65. The BaO content of these biotite also serves as a proxy for discriminating between re-equilibrated magmatic and secondary biotite. In addition, the X_{Mg} values of biotites correlate negatively with the concentrations of (K_2O+Na_2O+BaO) , FeO and TiO_2 for the biotites.

(3) The alteration characteristics of primary amphibole and biotite and the lack of zoning in representative biotite phenocrysts show that the potassic fluid apparently obtained equilibrium with these biotites. The calculated $\log(fH_2O/fHCl)$ values for the Tongchang porphyry deposit lie between those of other major porphyry deposits. The $\log(fHF/fHCl)$ and $\log(fH_2O/fHF)$ of the potassic fluids of Tongchang deposit are significant lower and higher, respectively, than those of these other deposits, and suggest that Tongchang is a Cl-enriched and F-deficient system.

(4) The F, Cl, OH and S contents of the Tongchang apatites define two groups. Many apatites show subequal proportions of Cl, F, and OH; whereas others are fluorapatite rich. The apatite compositions shown in ternary F-Cl-10*S plots define two groups; one represents very low-S and variable but lower-Cl apatite and the second expresses significantly greater and highly variable S and Cl contents. These compositional differences apparently are a result of magmatic anhydrite saturation from the melt and anhydrite dissolution by variably Cl-enriched fluid.

(5) The calculated Cl concentrations in the melt, based on experimental Cl partitioning between apatite and melt and on the compositions of the high-S and high-Cl apatites, are 0.24 to 0.60 wt.%. The Cl contents of most of the glassy MI range from 0.3 to 0.43 wt.%, which are very near or actually at the chloride saturation level in the specific melt compositions at pressure-temperature conditions of 200 MPa

and 850°C and 50 MPa and 850°C. This evidence shows that hydrosaline liquid has the potential to exsolve from the evolved granitic melt directly.

Table 1

Compositions (wt.% averages $\pm$ 1 σ standard deviations) of representative potassium feldspar and altered amphibole in samples of ore-forming granodiorites of the Tongchang mine, Dexing deposit.

Sample	TC-6-2	TC-21	
Mineral types	Potassium feldspar	Potassium feldspar	Amphibole
Analysis numbers ^a	n=2	n=15	n=6
SiO ₂	63.77 $\pm$ 0.43	64.72 $\pm$ 0.63	44.71 $\pm$ 0.89
TiO ₂	0.01 $\pm$ 0.02	0.00 $\pm$ 0.00	1.56 $\pm$ 0.19
Al ₂ O ₃	18.46 $\pm$ 0.20	18.50 $\pm$ 0.21	8.85 $\pm$ 0.40
FeO ^b	0.05 $\pm$ 0.06	0.07 $\pm$ 0.07	14.89 $\pm$ 0.93
MnO	0.01 $\pm$ 0.01	0.00 $\pm$ 0.00	0.42 $\pm$ 0.03
MgO	0.00 $\pm$ 0.00	0.00 $\pm$ 0.00	12.63 $\pm$ 0.53
CaO	0.06 $\pm$ 0.07	0.03 $\pm$ 0.02	11.95 $\pm$ 0.03
Na ₂ O	0.62 $\pm$ 0.32	0.84 $\pm$ 0.34	1.29 $\pm$ 0.06
K ₂ O	15.75 $\pm$ 0.48	15.45 $\pm$ 0.47	0.99 $\pm$ 0.13
BaO	0.20 $\pm$ 0.08	^c	0.03 $\pm$ 0.01
Cr ₂ O ₃	^c	^c	0.04 $\pm$ 0.01
F	^c	^c	0.03 $\pm$ 0.03
Cl	^c	^c	0.25 $\pm$ 0.05
Total	98.93 $\pm$ 0.46	99.69 $\pm$ 0.74	97.63 $\pm$ 0.47

^a Denotes the number of minerals analyzed. For each mineral, we conducted several spot analyses and calculated the mean values. This procedure was also used when the mineral (plagioclase, biotite and apatite) compositions in the following tables were obtained.

^b Total iron expressed as FeO.

^c Denotes undetermined values.

Table 2

Compositions (wt.% averages $\pm 1\sigma$ standard deviations) of representative plagioclase in samples of ore-forming granodiorites of the Tongchang mine, Dexing deposit.

Sample	TC-3	TC-4	TC-6-1	TC-6-2	TC-21
Analysis numbers	n=3	n=4	n=2	n=1	n=16
SiO ₂	59.63 $\pm$ 1.04	59.58 $\pm$ 0.50	58.95 $\pm$ 0.59	60.20 $\pm$ 0.34	58.97 $\pm$ 0.87
TiO ₂	0.01 $\pm$ 0.01	0.01 $\pm$ 0.01	0.01 $\pm$ 0.01	0.00 $\pm$ 0.00	0.01 $\pm$ 0.01
Al ₂ O ₃	25.50 $\pm$ 0.63	25.29 $\pm$ 0.31	25.23 $\pm$ 0.34	24.72 $\pm$ 0.24	24.97 $\pm$ 0.50
FeO ^a	0.22 $\pm$ 0.03	0.21 $\pm$ 0.03	0.22 $\pm$ 0.04	0.21 $\pm$ 0.02	0.22 $\pm$ 0.03
MnO	0.01 $\pm$ 0.01	0.01 $\pm$ 0.02	0.01 $\pm$ 0.01	0.01 $\pm$ 0.01	0.01 $\pm$ 0.01
MgO	0.01 $\pm$ 0.01	0.01 $\pm$ 0.01	0.01 $\pm$ 0.01	0.01 $\pm$ 0.00	0.01 $\pm$ 0.01
CaO	7.04 $\pm$ 0.80	6.93 $\pm$ 0.37	7.05 $\pm$ 0.42	6.39 $\pm$ 0.31	7.16 $\pm$ 0.48
Na ₂ O	7.14 $\pm$ 0.43	7.32 $\pm$ 0.14	7.31 $\pm$ 0.18	7.67 $\pm$ 0.18	7.27 $\pm$ 0.24
K ₂ O	0.61 $\pm$ 0.15	0.70 $\pm$ 0.08	0.52 $\pm$ 0.07	0.64 $\pm$ 0.07	0.55 $\pm$ 0.09
BaO	0.05 $\pm$ 0.03	0.06 $\pm$ 0.03	0.07 $\pm$ 0.03	0.07 $\pm$ 0.02	0.07 $\pm$ 0.03
Total	100.22 $\pm$ 0.25	100.15 $\pm$ 0.38	99.41 $\pm$ 0.36	99.93 $\pm$ 0.17	99.28 $\pm$ 0.65
An	0.35 $\pm$ 0.04	0.34 $\pm$ 0.02	0.35 $\pm$ 0.02	0.32 $\pm$ 0.02	0.36 $\pm$ 0.02

^a Total iron expressed as FeO.

976 **Table 3**

977 EPMA analyses (wt.% averages $\pm 1\sigma$ standard deviations), structural formulas and related
 978 chemical parameters of biotites in samples of ore-forming granodiorites of the Tongchang mine,
 979 Dexing porphyry deposit.

Sample	TC-3	TC-4	TC-6-1	TC-6-2	TC-21			
Biotite type ^a	□	□	□	□	□	□	□	□
Analysis numbers	n=6	n=8	n=6	n=7	n=47	n=1	n=1	n=18
SiO ₂	36.39±0.40	36.47±0.65	36.69±0.06	36.20±0.05	36.71±0.41	36.70	37.93	37.67±1.05
TiO ₂	4.73±0.14	4.61±0.52	4.71±0.18	4.82±0.19	4.64±0.22	4.62	2.02	2.83±0.58
Al ₂ O ₃	14.20±0.10	14.18±0.17	14.02±0.16	14.04±0.15	13.67±0.23	13.88	13.94	14.26±0.56
FeO ^b	15.48±0.38	15.34±0.45	15.85±0.20	15.93±0.38	15.41±0.40	15.60	14.69	14.82±0.51
MnO	0.07±0.02	0.06±0.02	0.15±0.05	0.17±0.04	0.14±0.03	0.12	0.12	0.14±0.03
MgO	14.12±0.14	14.43±0.25	13.95±0.12	13.84±0.12	14.10±0.36	13.73	16.21	15.50±0.74
CaO	0.01±0.01	0.03±0.02	0.02±0.03	0.02±0.02	0.03±0.02	0.07	0.02	0.10±0.20
Na ₂ O	0.19±0.01	0.19±0.01	0.18±0.02	0.18±0.01	0.16±0.02	0.12	0.14	0.17±0.17
K ₂ O	8.79±0.14	8.78±0.16	8.79±0.33	8.69±0.44	9.02±0.18	9.40	8.83	8.58±0.57
BaO	0.89±0.06	0.89±0.08	0.83±0.03	0.85±0.06	0.64±0.20	0.39	0.07	0.09±0.03
F	0.02±0.01	0.01±0.01	0.14±0.09	0.10±0.05	0.12±0.04	0.00	0.13	0.11±0.06
Cl	0.33±0.01	0.33±0.01	0.28±0.01	0.28±0.01	0.27±0.02	0.31	0.26	0.26±0.02
Total	99.02±0.69	99.13±1.04	99.34±0.40	98.85±0.53	98.64±0.62	98.77	98.13	98.31±1.79
Atom numbers calculated based on 22 (O)								
Si	5.51±0.04	5.51±0.04	5.55±0.02	5.51±0.05	5.58±0.04	5.57	5.72	5.67±0.06
Ti	0.54±0.02	0.52±0.06	0.54±0.02	0.55±0.02	0.53±0.02	0.53	0.23	0.32±0.06
Al(IV) ^c	2.49±0.04	2.49±0.04	2.45±0.02	2.49±0.05	2.42±0.04	2.43	2.28	2.33±0.06
Al(VI) ^d	0.05±0.04	0.04±0.05	0.04±0.02	0.02±0.03	0.03±0.04	0.06	0.20	0.20±0.08
Fe	1.96±0.05	1.94±0.05	2.00±0.02	2.03±0.06	1.96±0.05	1.98	1.85	1.87±0.06
Mn	0.01±0.00	0.01±0.00	0.02±0.01	0.02±0.01	0.02±0.00	0.02	0.02	0.02±0.00
Mg	3.19±0.03	3.25±0.06	3.14±0.02	3.14±0.03	3.19±0.08	3.11	3.64	3.48±0.19
Ca	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.01±0.00	0.01	0.00	0.02±0.03
Na	0.06±0.00	0.06±0.00	0.05±0.01	0.05±0.00	0.05±0.00	0.04	0.04	0.05±0.05
K	1.70±0.02	1.69±0.04	1.70±0.06	1.69±0.08	1.75±0.03	1.82	1.70	1.65±0.11
Ba	0.05±0.00	0.05±0.00	0.05±0.00	0.05±0.00	0.04±0.01	0.02	0.00	0.01±0.00
OH	3.91±0.01	3.91±0.01	3.86±0.04	3.88±0.03	3.87±0.02	3.92	3.87	3.88±0.03
F	0.01±0.01	0.00±0.00	0.07±0.04	0.05±0.03	0.06±0.02	0.00	0.06	0.05±0.03
Cl	0.09±0.00	0.08±0.00	0.07±0.00	0.07±0.00	0.07±0.00	0.08	0.07	0.07±0.01
Parameters								
X _{Fe} ^e	0.39±0.01	0.38±0.01	0.39±0.01	0.40±0.01	0.38±0.01	0.40	0.36	0.37±0.02
X _{Mg} ^f	0.62±0.01	0.63±0.01	0.61±0.01	0.61±0.01	0.62±0.01	0.61	0.66	0.65±0.02
X(phlogopite) ^g	0.55±0.00	0.56±0.01	0.55±0.00	0.54±0.01	0.56±0.01	0.55	0.61	0.59±0.02
X(siderophyllite) ^g	0.21±0.01	0.20±0.01	0.20±0.01	0.21±0.01	0.18±0.01	0.20	0.15	0.18±0.02
X(annite) ^g	0.24±0.01	0.23±0.01	0.25±0.01	0.24±0.01	0.26±0.01	0.26	0.23	0.23±0.03
log(fH ₂ O/fHF) ^h	7.39±0.18	7.64±0.25	6.53±0.25	6.71±0.28	6.60±0.17	/ ⁱ	6.64	6.83±0.51
log(fH ₂ O/fHCl) ^h	4.45±0.01	4.46±0.02	4.51±0.01	4.51±0.01	4.54±0.03	4.47	4.60	4.58±0.04
log(fHF/fHCl) ^h	-3.82±0.17	-4.07±0.24	-2.90±0.24	-3.07±0.28	-2.95±0.16	/ ⁱ	-3.02	-3.19±0.50

^a I, II, III and IV represent altered magmatic biotite, biotite enclosed in plagioclase, biotite in quartz and secondary biotite, respectively.

^b Total iron expressed as FeO.

^c Al numbers residing in the tetrahedral site of the biotite.

^d Al numbers occupying the octahedral site of the biotite.

^e $X_{Fe} = (Fe + Al(VI)) / (Fe + Al(VI) + Mg)$.

^f $X_{Mg} = Mg / (Mg + Fe)$; The elements in the equations represent the corresponding cation numbers.

^g Mole fractions of different biotite solid solution components.

^h The fugacity ratios were calculated with equations (1, 2 and 3) in the text for a temperature of 690K.

ⁱ Undetermined values.

1011 **Table 4**
1012 EPMA analyses (wt.% averages $\pm$ 1 σ standard deviations or ranges), structural formulas and
1013 related chemical parameters of apatite inclusions in samples of ore-forming granodiorites of the
1014 Tongchang mine, Dexing porphyry deposit.

Sample	TC-3	TC-4	TC-6-1	TC-6-2	TC-21
Host mineral	Biotite	Biotite	Plagioclase	Biotite	Plagioclase
Analysis numbers	n=13	n=11	n=2	n=3	n=1
SiO ₂	0.04±0.03	0.19±0.06	0.24±0.06	0.31±0.03	0.21
TiO ₂	0.04±0.02	0.04±0.04	0.00±0.00	0.03±0.02	0.02
Al ₂ O ₃	0.00±0.00	0.00±0.01	0.00±0.00	0.00±0.00	0.00
Ce ₂ O ₃	0.18±0.10	0.28±0.12	0.38±0.05	0.44±0.03	0.37
FeO ^a	0.41±0.13	0.52±0.12	0.08±0.02	0.52±0.05	0.74
MnO	0.08±0.05	0.06±0.04	0.16±0.01	0.25±0.05	0.17
MgO	0.01±0.01	0.02±0.01	0.02±0.00	0.05±0.01	0.02
CaO	55.05±0.45	54.46±0.49	54.04±0.42	53.80±0.24	54.30
SrO	0.05±0.02	0.07±0.02	0.12±0.02	0.06±0.01	0.07
Na ₂ O	0.07±0.03	0.09±0.05	0.10±0.01	0.23±0.03	0.15
K ₂ O	0.03±0.03	0.10±0.06	0.00±0.00	0.03±0.02	0.05
BaO	0.02±0.02	0.01±0.01	0.02±0.01	0.01±0.03	0.02
P ₂ O ₅	41.04±0.41	40.38±0.50	40.72±0.11	40.31±0.30	40.66
SO ₃ ^b	0.01-0.06	0.00-0.64	0.16-0.23	0.24-0.31	1.54
F ^b	1.79-2.35	0.75-2.45	1.32-1.43	1.60-1.79	2.69
Cl ^b	0.66-1.32	0.65-3.73	2.10-2.24	1.96-2.14	0.49
Total	98.91±0.52	98.56±0.66	98.51±0.43	98.80±0.45	99.93
Atom numbers on the basis of 25 (O)					
Si	0.01±0.00	0.03±0.01	0.04±0.01	0.05±0.00	0.03
Ti	0.01±0.00	0.01±0.00	0.00±0.00	0.00±0.00	0.00
Al	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00
Ce	0.01±0.01	0.02±0.01	0.02±0.00	0.03±0.00	0.02
Fe	0.06±0.02	0.07±0.02	0.01±0.00	0.07±0.01	0.10
Mn	0.01±0.01	0.01±0.01	0.02±0.00	0.04±0.01	0.02
Mg	0.00±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01
Ca	9.78±0.07	9.76±0.06	9.68±0.04	9.63±0.04	9.51
Sr	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01
Na	0.02±0.00	0.03±0.00	0.03±0.00	0.07±0.00	0.05
K	0.03±0.02	0.19±0.25	0.25±0.03	0.32±0.04	1.89
P	5.76±0.03	5.72±0.04	5.77±0.02	5.70±0.01	5.63
S	0.00±0.00	0.02±0.02	0.02±0.00	0.03±0.00	0.19
F	1.09±0.08	0.94±0.28	0.72±0.03	0.88±0.04	1.39
Cl	0.24±0.05	0.43±0.31	0.61±0.02	0.57±0.03	0.14
Parameters					
X _F ^c	0.55±0.04	0.47±0.14	0.36±0.02	0.44±0.02	0.71
X _{Cl} ^c	0.12±0.02	0.22±0.16	0.32±0.01	0.30±0.01	0.07
X _{OH} ^c	0.32±0.04	0.31±0.04	0.32±0.01	0.26±0.02	0.21

^a Total iron expressed as FeO.

^b We list the whole ranges for the magmatic volatiles (SO₂, F and Cl) in apatites.

^c X_F, X_{Cl}, X_{OH} represent mole fractions of corresponding volatile components in apatites (calculated with methods of Piccoli and Candela, 2002).

1059 **Table 5**

1060 Compositions (wt.%) of Tongchang granodiorite sample TC-21 and homogenized glassy melt
 1061 inclusions showing the solubility of Cl (850 °C) for the given melt compositions.

Wt.%	Melt inclusions						Whole rock ^a
Sample	Q2 M1	Q2 M2	Q2 M3	Q3 M1	Q4 M1-1	Q4 M1-2	TC-21
SiO ₂	77.23	77.42	72.55	75.69	78.84	77.33	65.28
TiO ₂	0.05	0.08	0.12	0.10	0.12	0.19	0.45
Al ₂ O ₃	11.79	13.74	15.88	14.65	11.41	11.34	15.22
FeO ^b	0.37	0.25	0.45	0.26	1.35	0.56	2.52
Fe ₂ O ₃	/ ^c	/ ^c	/ ^c	/ ^c	/ ^c	/ ^c	2.25
MnO	0.00	0.01	0.04	0.03	0.02	0.05	0.04
MgO	0.07	0.06	0.07	0.06	0.09	0.09	2.42
CaO	0.71	1.20	1.57	0.88	0.76	0.57	3.82
Na ₂ O	4.69	5.76	5.65	4.78	4.32	4.44	3.53
K ₂ O	2.96	1.33	1.39	4.15	2.52	2.94	2.79
P ₂ O ₅	0.00	0.02	0.07	0.00	0.01	0.00	0.23
SO ₂	0.01	0.02	0.00	0.00	0.03	0.01	/ ^c
F	0.00	0.00	0.00	0.00	0.04	0.05	/ ^c
Cl	0.15	0.35	0.44	0.24	0.43	0.33	/ ^c
Total	98.02	100.25	98.24	100.83	99.93	97.90	99.80
(A/CNK) ^d	0.97	1.05	1.16	1.05	1.02	0.98	0.96
(N/NK) ^e	0.71	0.87	0.86	0.64	0.72	0.70	0.66
Chlorine solubility (50MPa) ^f	0.37	0.46	0.53	0.40	0.42	0.36	/ ^c
Chlorine solubility (200MPa) ^f	0.43	0.54	0.62	0.47	0.50	0.42	/ ^c
LOI ^g	/ ^c	/ ^c	/ ^c	/ ^c	/ ^c	/ ^c	5.74

1062

1063 ^a The rock is analyzed by X-ray fluorescence spectrometry (XRF).

1064 ^b total iron is expressed as FeO for melt inclusions.

1065 ^c denotes undetermined values.

1066 ^d denotes molar (Al₂O₃/(Na₂O+K₂O+CaO)).

1067 ^e denotes molar (Na₂O/(Na₂O+K₂O)).

1068 ^f Cl solubilities calculated via Webster et al. (2015); see text for details.

1069 ^g loss on ignition

Figure captions

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