Halogen Chemistry of Hydrothermal Micas: a Possible Geochemical Tool in Vectoring to Ore for Porphyry Copper-Gold Deposit

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Abstract

Porphyry copper-gold deposit commonly exhibits an extensive alteration zone of hydrothermal micas particularly biotite and sericite. This study is aimed to analyze and utilize the chemistry of halogen fluorine and chlorine of biotite and sericite to be a possible tool in vectoring to ore for copper porphyry deposits. To achieve the objectives, several selected altered rock samples were taken crossing the Batu Hijau copper-gold mine from inner to outer of the deposit, and hydrothermal micas contained by the rocks were analyzed petrographically and chemically. Mineral chemistry was detected by electron microprobe analyzer, whilst biotite is petrographically classified as either magmatic or hydrothermal types. Sericite replacing plagioclase occurred as fine-grained mineral and predominantly associated with argillic-related alteration types. Biotites in the Batu Hijau deposit are classified as phlogopite with a relatively low mole fraction magnesium (X_{Mg}) (~0.75) compared to the "typical" copper porphyry deposit (~0.82). The relationship between the X_{Mg} and halogen contents are generally consistent with "Fe-F and Mg-Cl avoidance rules". F content in biotite and sericite decrease systematically from inner part of the deposit which is represented by early biotite (potassic) zone where the main copper-gold hosted, to the outer part of the deposit. However, chlorine in both biotite and sericite from each of the alteration zones shows a relative similar concentration, which suggests that it is not suitable to be used in identification of the alteration zones associated with strong copper-gold mineralization. H_2O content of the biotite and sericite also exhibits a systematic increase outward which may also provide a possible geochemical vector to ore for the copper porphyry deposits. This is well correlated with fluorine content of biotite in rocks and bulk concentration of copper from the corresponding rocks.

Keywords: Biotite, Sericite, Halogen Chemistry, Vector to Ore, Porphyry Copper-Gold Deposit

1. Introduction

A number of researchers have suggested that fluorine and chlorine are intimately involved in the hydrothermal transport of metals (Zhu and Sverjersky, 1991; Shinohara, 1994; Gammons and Williams-Jones, 1997; Selby and Nesbitt, 2000). The halogen contents, therefore, may have potential as pathfinder elements in geochemical prospecting for many different types of ore mineral deposits. In the rock forming minerals, F and Cl generally occupy the hydroxyl sites of hydroxysilicate minerals, including micas such as biotite and sericite (Parry et al., 1984; Selby and Nesbitt, 2000; Sarjoughian et al., 2015; Zhang et al., 2016). This paper is aimed to investigate the halogen (F and Cl) chemistry of biotite and sericite as well as the use of halogens for geochemical vector ore, where the Batu Hijau copper-gold porphyry deposit as a case study. The Batu Hijau deposit is located in southwest corner of Sumbawa Island, Indonesia (Fig 1). It contains 914 million metric tons of ore at an average grade of 0.53 % Cu and 0.40 g/t Au (Clode et al., 1999).

The Batu Hijau deposit occurs in steeply incised terrain, with the highest point on the deposit at 555 m above sea level. In general, the pre-mineralisation rock units consist of interbedded andesitic lithic breccia, and fine-grained volcaniclastic sandstones and mudstones, porphyritic andesite intrusive and at least two texturally distinct quartz diorite intrusive bodies. These rocks are intruded by multiple phases of tonalite porphyries, which acted as ore mineralization-bearing intrusions (Clode et al., 1999; Garwin, 2002) (Fig 2). The emplacement of tonalite porphyries and mineralisation are spatially and temporally associated with north-south (N-S) and northeast-southwest (NE-SW) trending structures (Priowarsono and Maryono, 2002).

Hydrothermal alteration and mineralization developed in four temporally and spatially overlapping stages consists of the early alteration stage is divided into biotite (potassic), actinolite (inner propylitic) and chlorite-epidote (outer propylitic) zones (Idrus, 2005). The transitional alteration stage is typified by a chlorite-sericite (intermediate argillic) zone (Idrus, 2005). The late

alteration stage is characterized by destruction of feldspar and the formation of pyrophyllite-andalusite (advanced argillic) and sericite-paragonite (argillic) zones (Idrus, 2005). The very late alteration stage is characterized by illite and sericite replacement of feldspar. Alteration zones of the Batu Hijau porphyry copper-gold deposit can be seen in Fig 3.

Biotite is observed in the biotite, chlorite-sericite and actinolite alteration zones, while sericite occurs intensively in the biotite and chlorite-sericite zones as well as in the pyrophyllite-andalusite and sericite-paragonite alteration zones. Fluorine and chlorine contents were analyzed in both hydrothermal micas (biotite and sericite) from these alteration zones.
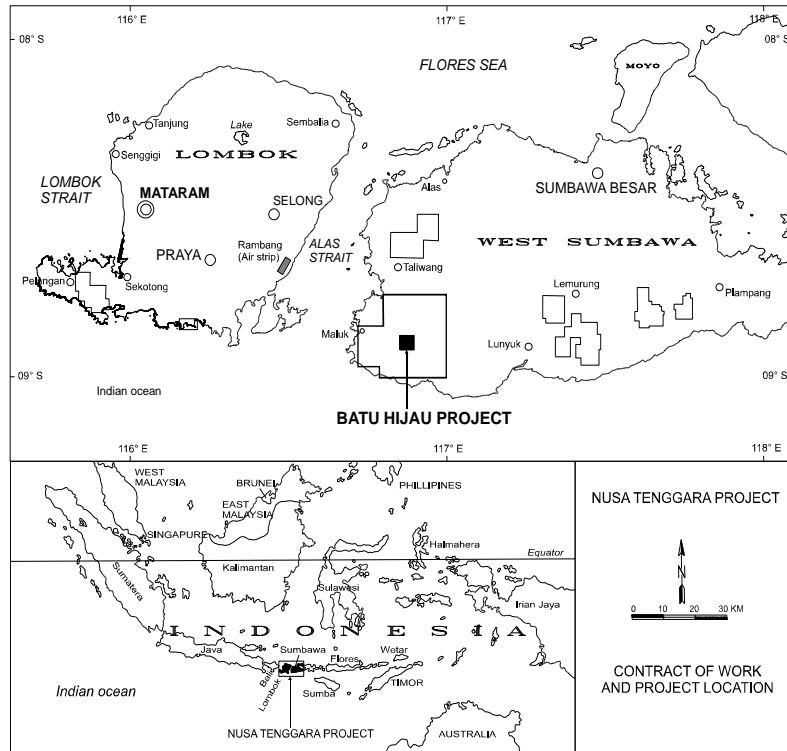

Fig 1. The Batu Hijau porphyry copper-gold mine site in Sumbawa Island, Indonesia, and study area location (black box).
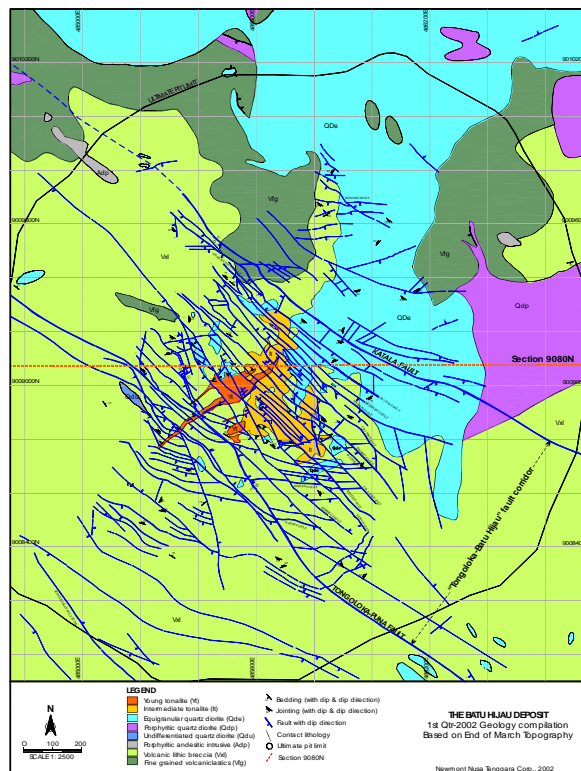

Fig 2. Geological map of the Batu Hijau deposit (Newmont Nusa Tenggara Corp., 2002).
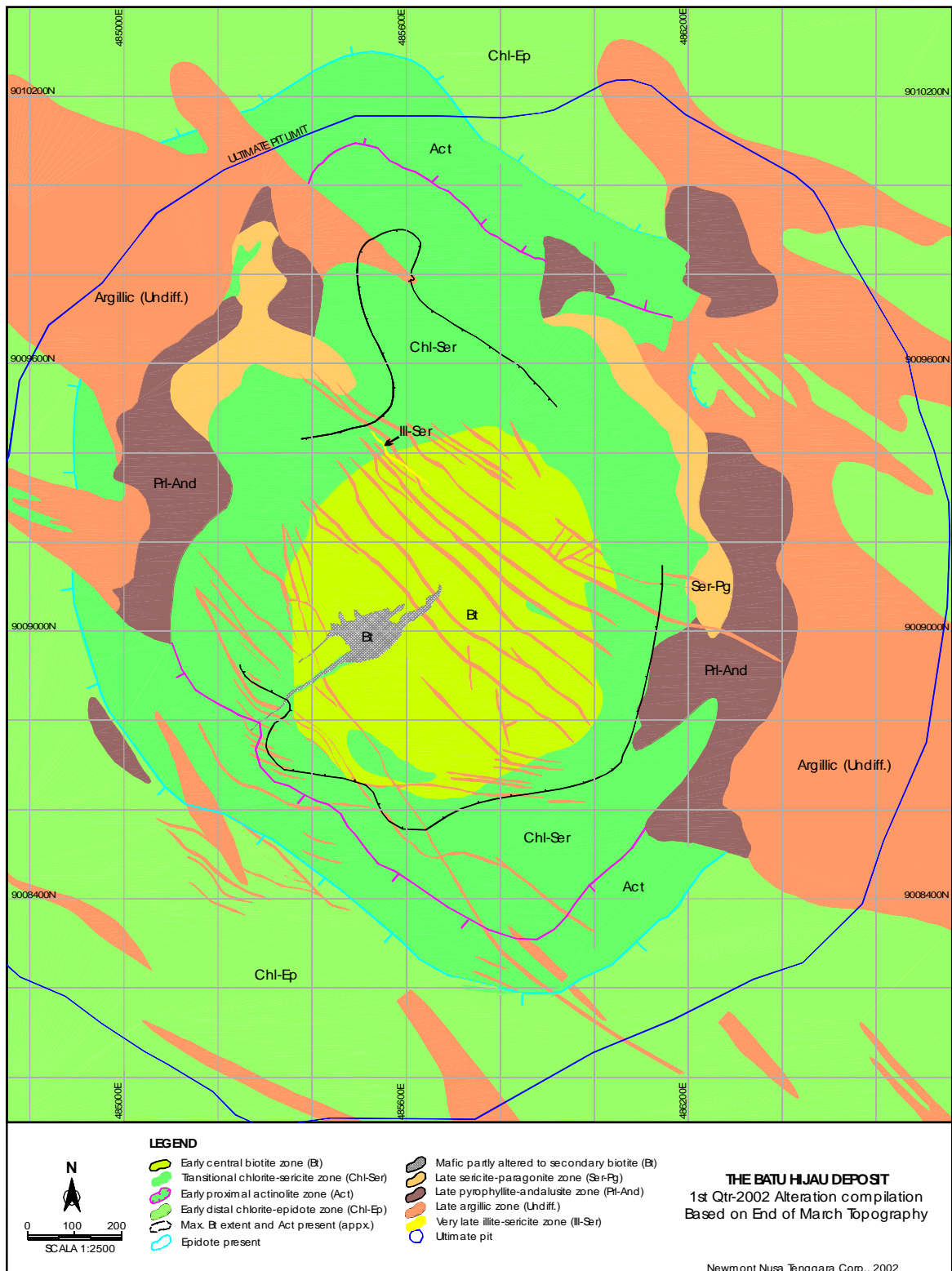
Fig 3. Hydrothermal alteration map of the Batu Hijau deposit (Newmont Nusa Tenggara Corp., 2002; Idrus, 2005).

2. Analytical Methods

A suite of representative altered samples was systematically taken crossing from inner to outer part of the Batu Hijau porphyry copper-gold mine in SW Sumbawa Island, Indonesia. Several selected rock samples were analyzed petrographically and mineral-chemically. Petrographic methods include the analyses of thin and polished thin sections under a polarized-light microscope, to identify primary and hydrothermal minerals, their textures and occurrences. Mineral chemistry analysis utilizes electron probe micro analyzer (EPMA) JEOL

JXA-8900R to determine the chemical composition of the biotite and sericite in each of their related alteration zones from the inner to outer part of the deposit.

Element determinations (Si, Al, Fe$_{Total}$, Mg, Ti, Mn, Na, K, F and Cl) were carried out using a beam size 3 μm, an accelerating potential voltage of 15 kV, a probe current of 2.35 nA, and a counting time of 20 second for each element analyzed. Natural apatite, jadeite, rutile, tugtupite, fayalite, spinel, orthoclase, and plagioclase standards were used in the analytical procedure for F, Na, Ti, Cl, Mn, Fe, Mg, Al, K, Ca and Si. Matrix effects were corrected using the ZAF software provided by JEOL. The accuracy of the reported values for the analyses is 1-5 % (1σ) depending on the abundance of the elements. A microprobe analysis is defined as the arithmetic mean of 1- 10 spot analyses of the biotite and sericite depending on mineral grain size. The OH values are calculated on the basis of 24 oxygens.

A computer software program MINPET 2.02 was primarily used to calculate the structural formula of the analysed minerals. All analyses were carried out at the Institute for Mineralogy and Economic Geology, RWTH Aachen University, Germany.

3. Results and Discussion

3.1 Biotite petrography

Biotites are petrographically classified as either magmatic or hydrothermal types (Fig 4). The term "magmatic" denotes biotite inferred to have crystallized directly from silicate melt. Magmatic biotite grain is further subdivided into least-altered and altered varieties (Selby and Nesbitt, 2000). The term "least-altered" is used for biotites from least-altered rock types, and "altered" is used to biotites present in hydrothermal assemblages (e.g. potassic, phyllic and propylitic). The magmatic biotites of Batu Hijau is only observed as altered magmatic biotite in few intermediate and young tonalite samples. Magmatic biotite occurs characteristically as euhedral to subhedral phenocrysts and microphenocrysts and euhedral to subhedral flakes. Some magmatic biotite is ragged, splintery or frayed. The term "hydrothermal" describes biotite inferred to have precipitated from the

hydrothermal fluid. Hydrothermal biotite is petrographically distinct from magmatic biotite, occurring as aggregates of fine grained flakes. Biotite that has partially or completely replaced igneous hornblende and occurring as biotite veinlet are also termed "hydrothermal".

3.2 Sericite petrography

Hydrothermal sericite is a common alteration product in many hydrothermal deposits. The Batu Hijau porphyry copper-gold deposit exhibits extensive argillic alteration styles, in which sericite becomes a major constituent surrounding or superimposed on the central biotite alteration. The argillic alteration styles include the transitional chlorite-sericite (intermediate argillic), late pyrophyllite-andalusite (advanced argillic) and late sericite-paragonite (argillic) alteration zones. However, very minor sericite occurs in the central biotite (potassic) alteration zone. The sericite associated with the central biotite alteration zone partially replaces plagioclase phenocrysts in the tonalite porphyries. A complete replacement is locally observed in the young tonalite. The replacements mostly occur in the cores, rather than in the rims of the zoned plagioclase grains. In comparison to the intermediate tonalite, the plagioclase in the young tonalite is more intensely dusted by the sericite. The sericites are present in a small portion (≤ 1 %), and commonly occur as an aggregate of fine to medium-grained flakes (up to 0.8 mm in length).

The transitional chlorite-sericite alteration zone occupies a temporal position between the central biotite and late argillic alteration styles (pyrophyllite-andalusite and sericite-paragonite zone). This alteration zone is characterized by weak-moderate chloritization and sericitization (Fig 5A). The plagioclase grains are partially to completely replaced by sericite. The replacement is more conspicuously in the equigranular quartz diorite than in the andesitic volcaniclastic rocks. The hydrothermal sericite is present in variable portion (5-25 %) of the rock volume. The mineral occurs mostly as fine-grained flakes, with length of up to 0.4 mm (commonly < 0.04 mm).
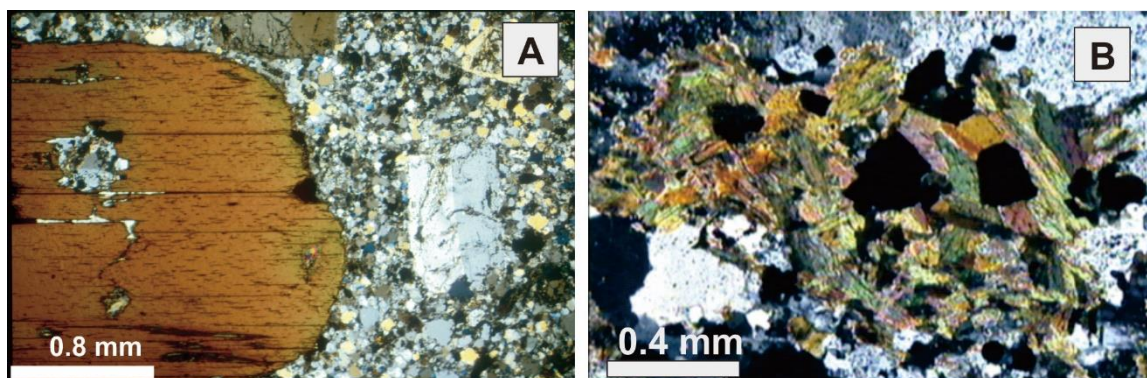

Fig 4. Petrographic images of biotite types in rocks from Batu Hijau deposit: (A) euhedral-subhedral altered magmatic biotite contained by tonalite porphyries, and (B) fine-grained hydrothermal biotites replacing hornblende in equigranular quartz diorite.
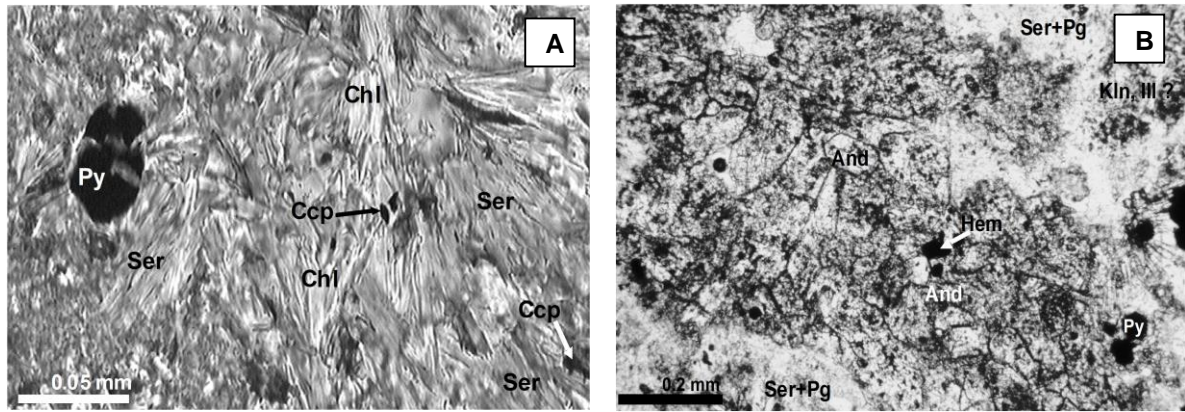
Fig 5. Grey-petrographic images of sericite: (A) intergrowth of chlorite replacing ferromagnesian minerals and sericite replacing plagioclase) of transitional chlorite-sericite-altered volcaniclastic rocks, (B) Euhedral-subhedral andalusite (high relief) after sericite-paragonite replacing plagioclase of late andalusite-pyropyllite (advanced argillic)-altered quartz diorite. Mineral abbreviations: Ser = sericite, Chl = chlorite, Pg = paragonite, And = andalusite, Kln/Ill = kaolinite/illite, Ccp = chalcopyrite, and Py = pyrite.

The sericite in the late pyrophyllite-andalusite alteration zone occurs in a relatively minor to moderate amounts (2-20 %) (Fig 5B), and is associated with pyrophyllite, andalusite, kaolinite, diaspore and dickite. The sericite replaces the plagioclase grains completely. They occur as very fine-grained flakes, with a length mostly < 0.04 mm. In comparison to those in the pyrophyllite-andalusite alteration zone, the sericites related to the late sericite-paragonite alteration zone are characterized by relatively fine to medium-grained flakes (up to 0.8 mm). The XRD data indicates that the white-mica solid solutions are predominantly composed of sericite and paragonite end-members. The Rietveld program quantifies the phases as the major components (30-60 % of the rock) (Idrus, 2005).

3.3 Biotite and sericite chemistry

Biotite, a *trioctahedral mica* with the generalized formula $(K, Na, Ca, Ba) (Fe^{+2}, Fe^{+3}, Mg, Ti,$ $Mn, Al)_3 (Al, Si)_4O_{10}(OH, F, Cl)_2$ is a common constituent in many copper porphyry deposits. The previous studies of biotite chemical composition in copper porphyry deposits have mostly concentrated on the determination of F and Cl contents, with the objective of distinguishing between mineralized and barren plutons. Biotites in the Batu Hijau deposit are classified as phlogopite $K_2Mg_6[Si_6Al_2O_{20}](OH)$ with a relatively low mole fraction magnesium (XMg) (~0.75) compared to the "typical" copper porphyry deposit (~0.82) (Mitchell et al., 1998). Representative composition of the Batu Hijau biotites is given in Table 1. Some elements show a systematic compositional variation in the central biotite (Bt) and partly chloritized (Partly Chl'd), through transitional chlorite-sericite (Chl-Ser) to the outer actinolite (Act) alteration zones. The relationship between the XMg and halogen contents is generally consistent with "Fe-F and Mg-Cl avoidance rules" (Munoz, 1984; Idrus, 2005).

Table 1. Representative microprobe data of major oxides and halogen chemistry of biotite in various altered rocks taken from the inner (central) to the outer part (peripheral) of the deposit

Elements	Alteration zone (inner → outer deposit)			
	Bt	Partly Chl'd	Chl-Ser	Act
SiO_2	41.08	39.85	39.52	38.85
TiO_2	2.38	1.69	2.15	4.92
Al_2O_3	13.12	14.18	15.20	13.37
FeO	10.49	10.66	11.17	13.68
MnO	0.05	0.11	0.12	0.35
MgO	19.92	19.59	17.78	15.31
CaO	bd	0.03	0.03	0.02
Na_2O	0.16	0.15	0.15	0.17
K_2O	8.74	8.92	9.38	9.18
F	0.99	0.98	0.64	0.38
Cl	0.19	0.22	0.25	0.31
H_2O	3.66	3.48	3.75	3.81
Total	100.78	99.86	100.13	100.32
Si	5.90	5.79	5.75	5.72
Al^{IV}	2.10	2.21	2.25	2.28
Al^{VI}	0.12	0.22	0.35	0.04
Ti	0.26	0.19	0,24	0.55
Fe^{+2}	1.26	1.30	1.36	1.69

Elements	Alteration zone (inner → outer deposit)			
	Bt	Partly Chl'd	Chl-Ser	Act
Mn	0.01	0.01	0.01	0.04
Mg	4.27	4.24	3.86	3.36
Ca	0.00	0.01	0.00	0.00
Na	0.04	0.04	0.04	0.05
K	1.60	1.65	1.74	1.73
F	0.90	1.14	0.59	0.35
Cl	0.09	0.11	0.13	0.15
OH	3.51	3.37	3.64	3.75
X_{Fe}	0.77	0.77	0.74	0.67
X_{Mg}	0.24	0.26	0.31	0.34
X_{Phl}	0.72	0.71	0.66	0.59

Note: Bt = biotitic (potassic); Partly Chl'd = partly chloritized; Chl-Ser = chlorite-sericite (phyllic); and Act = actinolitic (inner propylitic) alterations.

Table 2. Representative microprobe data of major oxides and halogen chemistry of sericite in various altered rocks taken from the inner (central) to the outer part (peripheral) of the deposit

Elements	Alteration zone (inner → outer deposit)				
	Bt	Partly Chl'd	Chl-Ser	Prl-And	Ser-Pg
SiO_2	47.07	47.65	47.00	45.90	46.9
TiO_2	0.18	0.21	0.14	0.19	0.09
Al_2O_3	33.01	30.13	32.70	37.26	36.25
FeO	1.83	2.97	2.03	0.74	1.29
MnO	bd	0.07	0.02	bd	bd
MgO	1.97	3.30	1.96	0.19	0.55
CaO	0.03	0.05	0.01	bd	bd
Na_2O	0.52	0.08	0.37	2.01	1.36
K_2O	10.32	9.93	10.43	8.37	9.09
F	0.39	0.37	0.24	0.11	0.l5
Cl	0.04	0.04	0.01	0.01	0.02
H_2O	4.29	4.26	4.34	4.47	4.48
Total	99.64	99.05	99.26	99.25	100.21
Si	6.30	6.44	6.32	6.08	6.18
Al^{IV}	1.70	1.56	1.68	1.92	1.82
Al^{VI}	3.50	3.23	3.49	3.89	3.80
Ti	0.02	0.02	0.01	0.02	0.01
Fe	0.20	0.34	0.23	0.08	0.14
Mn	0.00	0.01	0.00	0.00	0.00
Mg	0.39	0.66	0.39	0.04	0.11
Ca	0.00	0.01	0.00	0.00	0.00
Na	0.14	0.02	0.10	0.52	0.35
K	1.76	1.71	1.79	1.41	1.53
F	0.33	0.31	0.21	0.09	0.12
Cl	0.02	0.02	0.01	0.00	0.01
OH	3.83	3.84	3.89	3.95	3.93
X_{Ser}	0.93	0.99	0.95	0.73	0.81
X_{Pg}	0.07	0.01	0.05	0.27	0.19

Note: Bt = biotitic (potassic); Partly Chl'd = partly chloritized; Chl-Ser = chlorite-sericite (phyllic) alteration; Prl-And = pyrophyllite-andalusite (advanced argillic); and Ser-Pg = Sericite-Paragonite (intermediate argillic) alterations.

Sericite, is a term given to fine grained, white mica including muscovite, phengite, illite, and other solid solution end members. Sericite often occurred in mineral aggregates in which chlorite, sericite or albite may be intermixed and therefore not distinguishable with the microprobe optics. Batu Hijau sericites show an inhomogeneity degree in the chemical composition, it may contain unit-thick layers of smectite and chlorite, and/or submicrometerized patches of kaolinite, quartz, and other minerals. Representative composition of the Batu Hijau sericites is shown in Table 2. Mole fractions of sericite (Xser) decrease relative to those in the late alteration zones including pyrophyllite-andalusite (Prl-And) and sericite-paragonite (Ser-Pg) as a decrease of their forming temperatures. In general, sericite chemistry exhibits insignificant variation in the composition (Table 2). However, Si and F decrease as well as Al and Mg increase to the late alteration zones.

3.4 F-OH exchange of biotite-sericite pairs

The F and OH contents of biotite, sericite, and hydrothermal fluids in natural systems allow an evaluation of exchange equilibrium between the biotite, sericite and hydrothermal fluids in natural systems allow an evaluation of exchange equilibrium between the biotite, sericite and the fluids (Parry et al., 1984; Selby and Nesbitt, 2000; Siahcheshm et al., 2011; Sarjoughian et al., 2015; Zhang et al., 2016). The F content of sericites from early biotite alteration zone has a positive correlation with the X_{Mg} as shown in Fig 6, whereas those from transitional Chl-Ser as well as late Prl-

And and Ser-Pg alteration zones show a scatter relationship. The positive correlation of the X_{Mg} and F suggest that Mg controls the F-OH exchange (Munoz, 1984; Selby and Nesbitt, 2000; Zhang et al., 2016).
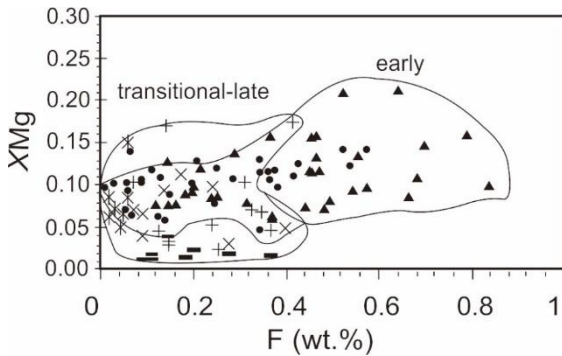

Fig 6. A positive correlation of X_{Mg} and F in sericite from the early biotite (potassic) and transitional-late alteration zones.

The experimentally calibrated F-OH exchange relations of Munoz et al. (1974) and computational techniques of Gunow et al. (1980) have been used to evaluate exchange equilibrium between biotite and sericite at the Batu Hijau deposit. A generalized reaction for F-OH exchange of biotite or sericite with hydrothermal fluid can be written as:

$$OH_{(mica)} + HF_{(fluid)} = F_{(mica)} + H_2O_{(fluid)} \qquad (1)$$
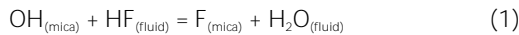
If the F and OH mix ideally on the hydroxyl sites, the equilibrium expression is:

$$\log K = \log (X_F/X_{OH})_{mica} + \log (fH_2O/fHF)_{fluid} \qquad (2)$$

where X denotes mole fraction and f is fugacity.

Experimental equilibrium constants for exchange reactions have been applied to natural micas of variable composition by Parry et al. (1984) and Gunow et al. (1980) using the following constants:

$$\text{Log } K_{biotite} = 2100/T + 1.523(X_{phlogopite}) + 0.416(X_{annite}) + 0.079(X_{siderite}) \qquad (3)$$

and

$$\log K_{sericite} = 2100/T + 1.523(X_{Mg}) + 0.4l6(X_{Fe}) - 0.1 \, l(X_{Al}) \qquad (4)$$

Combination of exchange reactions and equilibrium constants for these two micas produces a relationship between the mica independent of temperature and fluid composition. which can be used to evaluate exchange equilibria between the hydrothermal mica pairs.

$$OH_{biotite} + F_{sericite} = F_{biotite} + OH_{sericite} \qquad (5)$$
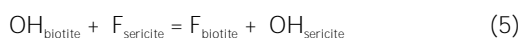
$$\log K_{(biotite+sericite)} = 1.523 (X_{phlogopite} - X_{Mg} + 0.416(X_{annite} - X_{Fe}) + 0.079 (X_{sericite} - 0.11 X_{Al}) \qquad (6)$$

$$\log K = \log (X_F/X_{OH})_{biotite} + \log (X_{OH}/X_F)_{sericite} \qquad (7)$$

Equilibrium constants calculated from F-OH content of the sericite-biotite pairs (equation 7) produce values ranging between 0.61-1.12 and an average of 0.82 (Idrus, 2005).

3.5 Variation in halogen fugacity ratios

The fugacity ratios of [H_2O] and [HF] as well as [H_2O] and [HCl] of hydrothermal fluids were calculated using the equations from (Munoz, 1992) which are based on the revised coefficients for F-Cl-OH exchanges between the biotite and the fluid (Zhu and Sverjersky, 1991, 1992). Our results suggest that the ratios increase systematically to the outer alteration zones. By using the same equations (Zhu and Sverjersky, 1991, 1992), the halogen fugacity ratios of fluids based on the sericite chemistry have also been computed and show an increase towards the outer (late) alteration zones (Fig 7).
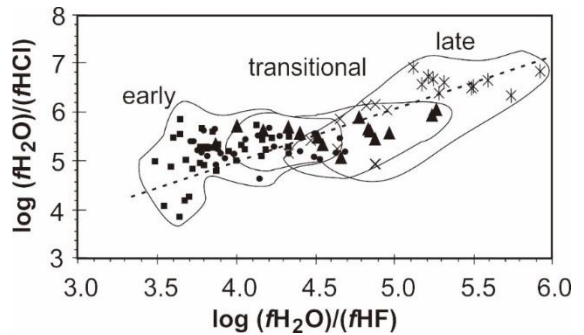

Fig 7. Fugacity ratios of sericite increasing from inner to outer part of alteration zones. Calculation based on forming temperatures at 510, 475, 360 and 250°C for the early, transitional and late alteration zones, respectively (Temperature data from Idrus, 2005).

3.6 Halogen chemistry used for vector to ore

The concentration of halogen fluorine and chlorine in rocks might provide an indication of mineralization and thus find utility as an exploration tool. The F and Cl used in exploration has limited to lithogeochemical studies. Due to availability of EPMA analysis, nowadays, the F and Cl studies are more concentrated on hydrous minerals, including biotite and sericite in the rocks, both barren and mineralized rocks. A strong correlation between the F and Cu contents of biotites in mineralized plutons from Basin and Range Province, USA has been described by (Parry and Jacobs, 1975). The high content of F in biotites at Casino Cu-Au-Mo porphyry deposit (Canada) and Lar Cu-Mo porphyry deposit (Iran), respectively is strongly associated with potassic and phyllic alterations, in which high copper-gold mineralization occurred (Selby and Nesbitt, 2000; Moradi et al., 2016).
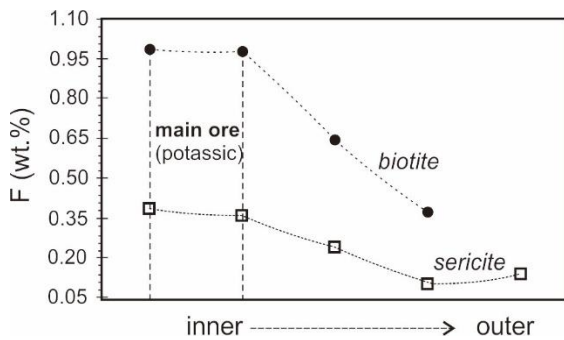
Fig 8. The fluorine content of biotite and sericite regularly increase toward central deposit (potassic).
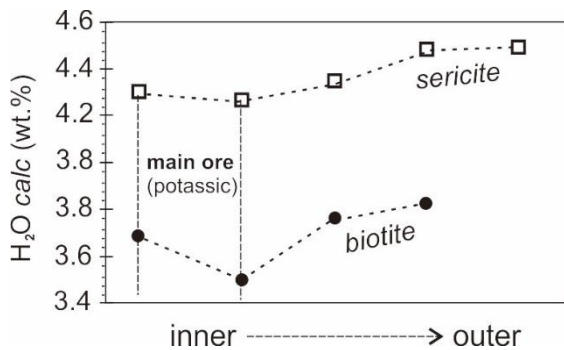

Fig 9. Water content of both biotite and sericite decreased toward central deposit
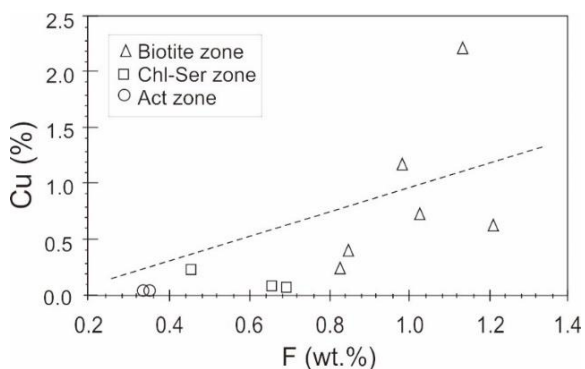

Fig 10. A positive correlation between fluorine (F) content in biotite and bulk concentration of copper (Cu) in corresponding altered rocks (Idrus, 2005).

Fig 8 shows a compositional variation of fluorine in biotite and sericite at the Batu Hijau deposit. The F content decrease systematically from inner part of the deposit which is represented by early biotite (potassic) zone where the main copper-gold is hosted, to the outer part of the deposit. However, chlorine in both sericite and biotite from each of the alteration zones shows a relative similar concentration, which suggests that it is not suitable to be used in identification of the alteration zones associated with strong copper-gold mineralization. The latest result has also been observed at other deposits worldwide, for instance, the Casino porphyry deposit, Canada (Selby and Nesbitt, 2000), Dalli porphyry deposit (Ayati et al., 2008), Kahang porphyry deposit, Iran (Afshooni et al., 2013) and Dexing porphyry deposit, SE-China (Bao et al., 2016). In addition, H_2O content of the

biotite and sericite also exhibits a systematic increase outward which may suggest an increase the role of meteoric water in alteration toward outer part of the deposit (Fig 9). The variation of water content may also provide a possible geochemical exploration tool in vectoring to ore for the copper porphyry deposits.

The fluorine content of biotite in rocks and bulk concentration of copper from the corresponding rocks indicates a positive correlation (Fig 10). Copper concentration of the altered-rocks increases with an increase of fluorine content of the biotite in the rocks. The highest fluorine and copper contents occur in the central early biotite (potassic) alteration zone and decrease to the outer alteration zones of the porphyry deposit. The central biotite zone contains relative higher copper (Fig 10) compared to average grade of copper in SW Pacific porphyry deposits (~0.52%) (Titley and Beane, 1981; Cooke et al., 1998; Cooke et al., 2005).

4. Conclusions

The high concentration of halogen, particularly fluorine in hydrothermal micas (biotite and sericite) is strongly associated with central ore-bearing biotite (potassic) alteration zones in copper porphyry systems. This may imply the important role of halogen particularly fluorine and chlorine in hydrothermal transportation of copper and gold in form of halogen copper and gold complexes.

The fluorine content decreases systematically toward the outer part of the deposit. However, the chlorine content of biotite and sericite shows unsystematic variations crossing those alteration zones, suggesting it is not suitable to be used for vector to ore in exploration. The systematic compositional variation of fluorine and H_2O contents in the hydrothermal micas might provide a possible geochemical tool in vector to ore for porphyry copper-gold deposits.

5. Acknowledgements

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