

Ore-forming fluid constraints on illite crystallinity (IC) at Dexing porphyry copper deposit, Jiangxi Province

JIN Zhangdong (金章东)^{1, 2}, ZHU Jinchu (朱金初)¹, JI Junfeng (季峻峰)¹,
LU Xinwei (卢新卫)¹ & LI Fuchun (李福春)¹

1. State Key Laboratory for Research of Mineral Deposits, Nanjing University, Nanjing 210093, China;

2. Lake Sediment and Environment Laboratory, Nanjing Institute of Geography & Limnology, Chinese Academy of Sciences, Nanjing 210008, China

Correspondence should be addressed to Jin Zhangdong (email: zhdjin@niglas.ac.cn)

Received January 25, 2000

Abstract Illite, a distinctive kind of clay minerals of potassium alteration within the hydrothermal alteration zone, frequently occurs at the Tongchang porphyry copper deposit ore field. The illite crystallinity (IC) value and expandability are mainly affected by water/rock ratio or fluid flux. It was formed by illitization of plagioclase and micas during hydrothermal fluid-rock interaction within the porphyry body and near the contact zone with wall rocks. Moreover, the negative correlation between illite index (IC) and copper grade indicates that within the alteration zone, the smaller the illite crystallinity value, the higher the alteration degree, and the higher the copper grade due to higher water/rock ratio. At lower levels of the porphyry body, however, the illite crystallinity (IC) values are mainly controlled by temperature and time duration.

Keywords: illite, kübler index, ore-forming fluid, porphyry copper deposit.

Illite, as a clay mineral, commonly occurs both in middle-low temperature hydrothermal alteration environment, and during burial diagenesis and low-grade metamorphism. Much progress has been made in the study of illite related to sedimentary basins, modern geothermal fields, kinetic hydrothermal experiments and independent geothermometer^[1-5], but still, there is a weakness in study of illite related to hydrothermal alteration and mineralization system for ore deposit. Recent researches indicate that besides temperature and time duration, as a water-rock kinetic reaction process, illite formation is also controlled by the water/rock ratio, fluid nature and fluid flux, as well as by petrochemical composition of the system^[1, 6-8]. Sometimes, as in low permeability and active fluid environment, either fluid flux or water/rock ratio is more important for the illite growth than temperature and/or time duration. On the other hand, unlike other easily weathered clay minerals such as chlorite, mixed layer illite/smectite, kaolinite, as long as there is no intense late-stage metamorphism, illite formed in the hydrothermal alteration environment is always stable, even in epigenetic environment^[5, 9]. Consequently in some hydrothermal systems, especially in the magmatic hydrothermal environment such as porphyry copper deposit, illite could be used to understand the forming condition of the environment and to serve as an indicator of fluid nature, water/rock ratio, mineralization and alteration degree.

According to previous studies^[10], there occur illitization and hydromuscovitization within the hydrothermal alteration zones at Tongchang giant porphyry copper deposit, Dexing County, Jiangxi Province. What is called hydromuscovitization by the former lies within the Tongchang porphyry body and the periphery of hydrothermal illitization zone. By composition, though the hydromuscovite includes illite, micrograined muscovite and sericitic, most of them are illite, and micrograined muscovite and sericitic could be a series of altered minerals of sericitic alteration. As a new exploration, we have gained some further knowledge by illite through scientific comparison between 24 samples from two drill holes at the Tongchang copper deposit.

1 Materials and analytical methods

By comparison, 24 samples analyzed in this study are taken from drill holes No. SC211 and No. SC804 at the Tongchang porphyry copper deposit. The former hole is located in the central part of porphyry body and the latter in the endocontact zone with wall rocks. The carbonate, ferruginous cement and organic matter in each sample were removed by HCl, H₂O₂. Afterwards, the <2 μm fraction in the first order and then the <1 μm fraction in the second order of each sample were isolated by centrifugation respectively. The oriented clay specimens were prepared by dropping the suspension on the glass slide and drying them in the air (air-dried, AD). In order to avoid effect of thickness during X-ray diffraction (XRD) examination^[11], a thickness of 3 mg/cm² was made for each specimen. After the AD-oriented specimens examined by XRD, three <2 μm oriented specimens among them (804-28, 211-2, 211-12) were saturated with glycolate liquid (GL) using an atomizer and then examined immediately by XRD again. Both air-dried (AD) and glycolated (GL) oriented specimens were studied twice by XRD, and the error was <5%.

All air-dried (AD) and glycolated (GL) oriented specimens (<2 μm) were examined by D/Max-Rb type XRD, at the Center of Materials Analysis, Nanjing University. Each sample was scanned at 1°2 θ/min with Cu-K-Alpha radiation, 40 kV, 80 mA, 0.01°2θ steps and scanning range of 2—36°2θ. For <2 μm fraction, the air-dried (AD) oriented specimens were examined by XRD and then glycolated (GL) oriented specimens. We also examined the <1 μm fraction air-dried (AD) oriented specimens from each sample by XRD, indicating that illite crystallinity (IC) in <1 μm fraction is almost the same as that in the <2 μm fraction (see table 1).

Illite crystallinity (IC) is the Kübler index by °Δ2θ, which is the width, at half-height, of the illite (001) XRD reflection obtained from each oriented clay specimen. The smaller the Kübler index, the higher the degree of illite crystallinity^[12]. The expandability (%) of illite in the sample was determined by comparing the measured result with model value calculated by the NewMod (R.C.Reynolds, 1985) computer program.

Table 1 The crystallinity index of illite and chlorite, expandability of illite and copper grade at different depths for drill holes (SC211, SC804) at the Tongchang porphyry copper deposit

Sample no.	Lithology symbol ^{a)}	Elevation (m)	Illite crystallinity ($^{\circ}\Delta 2\theta$)		Expandability (%)	Chlorite crystallinity ($^{\circ}\Delta 2\theta$)	Copper grade (%)
			<2 μm	<1 μm			
804-2	γ_1	183.4	0.63	—	2	0.32	0.0045
804-5	γ_2	162.5	0.74	0.73	5	0.32	0.1125
804-9	H ₂	144.6	0.84	0.85	1	0.26	0.0795
804-10	γ_2	138.9	0.53	0.58	1	0.43	0.0660
804-12	H ₂	128.6	0.42	0.42	1	0.32	0.7816
804-13	H ₂	103.1	0.32	0.26	1.5	0.47	0.8227
804-16	γ_1	87.3	0.21	0.21	0	0.21	0.3147
804-19	γ_1	66.0	0.45	—	1	0.16	0.0758
804-21	H ₂	40.7	0.42	0.40	0.5	0.21	0.1194
804-24	H ₁	-12.8	0.40	0.40	1	0.27	0.2290
804-25	γ_1	-44.0	0.74	0.82	5	0.47	0.0659
804-28	γ_1	-50.1	0.63	—	4	0.21	0.0309
804-30	H ₁	-64.4	0.48	0.62	2	0.16	0.0042
211-7	γ_2	128.4	0.53	0.53	1.5	0.21	0.0457
211-19	γ_2	120.1	0.69	0.67	2	0.21	0.0562
211-21	γ_2	93.6	0.65	0.65	1	0.20	0.0205
211-16	γ_2	79.3	0.63	0.63	2	0.20	0.0114
211-13	γ_2	69.0	0.65	0.65	1.5	0.38	0.0020
211-23	γ_1	50.8	0.63	0.63	2	0.42	0.0645
211-12	γ_1	40.9	0.80	0.82	8	0.44	0.1539
211-2	γ_1	32.2	1.37	1.37	8	0.42	0.0094
211-6	γ_1	17.8	1.03	1.01	6	—	0.0219
211-10	γ_0	8.0	0.95	—	6	0.42	0.0521
211-9	γ_0	7.0	0.53	—	1	0.42	0.2783

a) Symbols γ and H represent granodiorite porphyry and metamorphic tuffaceous phyllitic at Dexing ore field, respectively. The subscripts 0, 1 and 2 denote fresh unaltered, weakly-altered and moderately-altered rocks, respectively. The copper concentrations were analyzed by X-fluorescence method at the Center of Materials Analysis, Nanjing University (Nov. 1998).

2 Results and discussion

Table 1 lists the crystallinity index of illite and chlorite, expandability (in percent) of illite (<2 μm , <1 μm fraction respectively) and copper grade at different depths for two drill holes SC211 and SC804 at the Tongchang porphyry copper deposit. Fig. 1 shows XRD pattern of No. 804-30 air-dried specimen after HCl-treatment. It illustrates the characteristic peaks which were used to distinguish and quantify illite and other altered clay minerals in this work.

Many works on clay minerals in the active geothermal fields and sedimentary basins have indicated that illite crystallinity (IC) value is not only related to temperature and time duration, but also constrained by other parameters such as water/rock ratio, fluid nature, fluid flux and petrochemical composition^[1,2,5,6,13,14]. Especially under poor permeability and intense interaction environment, water/rock ratio and fluid flux are more important for the illite formation than temperature and time duration. Through hydrothermal experiments, G. Whitney (1990) found that the

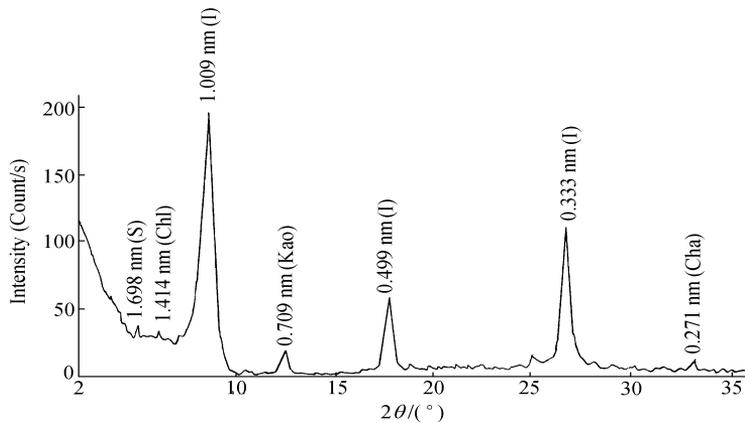


Fig. 1. XRD pattern of clay minerals from sample 804-30 (HCl-treated). S, smectite; Chl, chlorite; I, illite; Kao, kaolinite; Cha, chamoisite.

crystallinity rate of illite was restrained distinctly under poor fluid system^[7]. Subsequent investigations made by M. Buatier (1992) and A. Inoue et al. (1994) further verified that smectite illitization rate increased while illite crystallinity (IC) value became smaller under high water/rock ratio condition^[11]. The clay minerals studies of C. C. Harvey and P. R. L. Browne (1991) in the Wairakei geothermal field, New Zealand, demonstrate that in poorly-permeable sediments, where diffuse fluid flow prevails, a clearly-defined sequence of mixed-layer clays occurs, but it is absent where channel flow dominates and the discrete illite and chlorite precipitate directly from solution^[6]. These studies show the strong control of fluid flow type on the clay mineral formation. Under condition of poor permeability and diffuse fluid flow, a well-defined sequence of mixed-layer clays such as illite-smectite with different percentage of illite layers commonly develops. Because solute migration is slow and the water-rock interaction is too weak to achieve equilibrium, illite layers occur as metasomatic after feldspar and/or mica *in situ*, or as interlayer/surface of smectite. However, in zones or environment where water/rock ratio is very high and channel flow is dominant, illite and chlorite with no/or little swelling layers deposit directly from solution away from the *loci* of thermal regime because solutes migrate easily along fluid flow in channel. The knowledge, on the other hand, of chlorite formation is poorly understood because its process is more complicated^[15]. Generally, under high permeability and high water/rock ratio, chlorite can be formed by direct precipitation from fluid at a temperature above 220°C.

The IC values from the drill holes SC211 and SC804 for the two size fractions are in the range of 0.53—1.37° $\Delta 2\theta$ (averaging 0.76° $\Delta 2\theta$) and 0.21—0.84° $\Delta 2\theta$ (averaging 0.42° $\Delta 2\theta$), respectively (table 1). It is mentioned above that IC value is controlled by fluid flux and water/rock ratio under hydrothermal condition, so is the degree of metal mineralization. But, is there an in-

herent relationship between IC and mineralization degree? For comparison, fig. 2 illustrates the illite crystallinity (IC) index and copper grade at different depths from two drill holes. As shown in fig. 2, there is a negative correlation between the IC values and copper grades for each drill hole separately. Namely, at depths with small IC values (high degree of illite crystallinity), Cu grades are high and vice versa. Compared with the SC804 (located in endocontact zone with wall rocks), in general, for the SC211 (located in the central part of porphyry body) the IC values are higher and the Cu grades are lower. Nevertheless, at elevation from 130 m to 50 m, IC values in both drill holes are smaller (higher degree of illite crystallinity), being coincident with intense disseminated mineralization^[10] (fig. 2). Moreover, with increasing depth, IC values increase immediately below 50 m in SC211 while IC values in SC804 drill hole begin to increase till -12.4 m, being identical with the fact that mineralization and Cu grade at the contact with wall rocks are stronger and higher than that at the central part of porphyry body. These relationships indicate that IC values are closely spatially associated with Cu mineralization degree, i.e. in the portion of high degree of illite crystallinity, mineralization is dense; otherwise is weak. The expandability of illite varied between 0.5% and 8% with most of the values less than 5%, illustrating a positive relationship with IC value (table 1). At the same time, for chlorite, as another commonly altered mineral, its crystallinity values have a narrower range of $0.16\text{--}0.47^\circ\Delta 2\theta$ than that of illite (AD oriented specimens). In the same sample, chlorite crystallinity value is smaller than that of IC values, indicating that chlorite has higher crystallinity degree than illite.

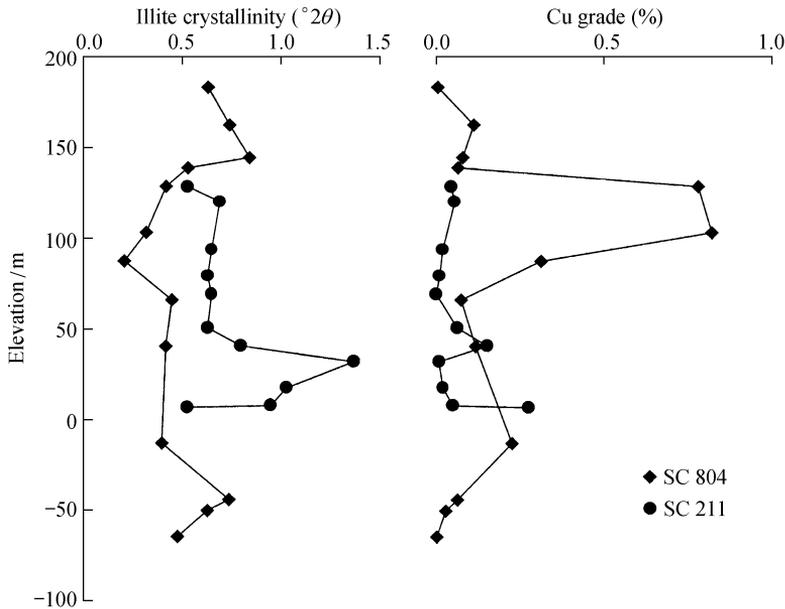


Fig. 2. Comparison between illite crystallinity (IC) index and copper grade at different depths from two drill holes (SC804 and SC211).

Like in the modern active geothermal system, for the intermediate-acidic magmatic system closely related to porphyry copper deposit, the heat originates from deep magma chamber; the late-stage hydrothermal fluid intensely circulates upwards and laterally at the portion of the contact, and forms upwelling vapor plumes after boiling (might interact with ground water); and finally mineralization along with hydrothermal alteration takes place. Consequently, as a common clay mineral by hydrothermal fluid alteration, crystallinity and variation of illite can be used as an indicator for ore fluid action, hydrothermal alteration and mineralization intensity within a magmatic hydrothermal system, and even can provide composition data for mineral-fluid equilibrium modeling^[2,3,6,13]. By comparison of IC values, Cu grades and expandabilities (fig. 2, table 1), combined with mineralization features of the Tongchang porphyry body^[10], we found that at the elevations between 130 m and 50 m where IC values are small and expandabilities are low, strong disseminated mineralization and alteration occur, and Cu grade is up to 0.8% via intense fluid circulation and water-rock exchange through upwelling transportation of hydrothermal fluid with ore materials. At shallower depths (above elevation of 130 m), the occurrence of illite with larger IC value is due to short-term water-fluid interaction where veinlet mineralization takes place^[10]. It further certifies that the illite crystallization depends on fluid flux in the geothermal systems. Relatively, upward movement of the ore-forming fluid causes decrease of water/rock ratio resulting increase of IC values at low portion of Tongchang porphyry body (fig. 2). However, with further increasing depth and temperature, IC values become smaller again and the ordering degree of illite texture also increases. Here IC values are mainly dependent on time duration and temperature while the water/rock ratio becomes less important^[5,16]. Smaller IC value suggests relative higher temperature at the similar geological setting, consequently the illite can serve as an independent geothermometer. The fluid flux and mineralization intensity in the contact zone with wall rocks are stronger than those in the central part of porphyry body due to upward and lateral transportation of ore-forming hydrothermal fluid. The discrepancy of IC values between two drill holes is, however, mainly attributed to water/rock ratio. This opinion is consistent with the hydrogen and oxygen isotope evolution in Tongchang porphyry copper system. Zhang Ligang et al (1996)^[17] showed that the water-rock interaction took place while the late-stage magmatic fluids migrated upward and diffused outward from five low $\delta^{18}\text{O}$ value centers within the porphyry body.

IC value is chiefly a function of domain size, swelling layer content, crystal defect and chemical difference^[12], among which the domain size mainly depends upon temperature, whereas the swelling layer content (expandability, in percent) reflects the degree of the interparticle swelling. The latter can be further judged by the J. Srodon intensity ratio (Ir) which is very sensitive to the presence of swelling layers in illite^[13]: if Ir = 1, the illite has no detectable tendency to swell; if Ir > 1, the illite has swelled to some degree. In our study, three samples (804-28, 211-12 and 211-2) were selected for XRD on GL oriented specimens treated by glycolate liquid. The J. Srodon inten-

sity ratio (Ir) was obtained from the formula defined as
$$Ir = \frac{I_{(001)}/I_{(003)(AD)}}{I_{(001)}/I_{(003)(GL)}}$$
, where the maximum illite XRD peak (001) and (003) intensities are used^[13]. The results show that the Ir values of three samples are all more than 1 (2.28, 6.18 and 1.89, respectively). This suggests that the illites are formed by illitization of plagioclase and micas during hydrothermal fluid-rock interaction^[2,6,7,13].

Actually, illite formation is a K fixation process and the K concentration in a system directly influences the speed and degree of plagioclase and micas illitization during ore-forming fluid and rock interaction^[18, 19]. Under low K concentration and low water/rock ratio, the conversion rate of mixed layer illite/smectite illitization significantly decreases^[7,16]. However, in the porphyry copper system characterized by K-feldspar and biotite hydrothermal alteration, fortunately plenty of K is available to provide a perfect chance for illite formation. Extensive development of illitization in the porphyry copper system gives us a good opportunity to define the range of hydrothermal fluid interaction and alteration, the water/rock ratio and the mineralization intensity by illite study in the paper.

3 Conclusions

Based on the above discussion, we can draw the following conclusions:

(1) Illite is one of the characteristic altered clay minerals during potassium hydrothermal alteration occurring within the Tongchang porphyry copper deposit. The average IC values (Kübler index) for two drill holes are $0.76^\circ\Delta 2\theta$ and $0.42^\circ\Delta 2\theta$, respectively, and their expandability is low (1—5%). It indicates that these illites were formed by plagioclase and micas illitization during late-stage magmatic hydrothermal ore-forming fluid-rock interaction.

(2) The difference of illite crystallinity (IC) values in two drill holes is related to hydrothermal fluid flux. During upward and lateral transportation of the hydrothermal fluid, the ore-forming fluid intensely circulated at the middle-upper portions of the contact zone between the porphyry and wall rocks, creating a high water/rock ratio environment at which the illites with lower IC values (SC804) were formed. On the contrary, in the central portion of porphyry body (SC211), the water/rock ratios were lower, and the illites with higher IC values were formed.

(3) Our IC value data are well correlated with both expandability (positively) and copper grade (negatively). The correlation between them, with increasing depth, is controlled either by water/rock ratio caused by upward transportation of ore-forming fluids at the middle-upper portion of the porphyry body, or by time duration and temperature at its low portion.

(4) Furthermore, IC value is closely related to mineralization type and intensity. The higher the degree of illite crystallinity, the stronger the pervasive disseminated mineralization. By contrast, the lower the degree of illite crystallinity, the weaker the sulfide mineralization.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Nos. 49733120 and 49873026) and by the National Post-Doctor Foundation of China.

References

1. Buatier, M. D., Peacor, D. R., O'Neil, J. R., Smectite-illite transition in Barbados accretionary wedge sediments: TEM and AEM evidence for dissolution/crystallization at low temperature, *Clays and Clay Minerals*, 1992, 40(1): 65.
2. Eberl, D., Hower, J., Kinetics of illite formation, *Geological Society of America Bulletin*, 1976, 9: 1326.
3. Elliott, W. C., Matisoff, G., Evaluation of kinetic models for smectite to illite transformation, *Clays and Clay Minerals*, 1996, 44(1): 77.
4. Ji Junfeng, Browne, P. R. L., Liu Yingjun et al., Kinetic model for the smectite to illite transformation in active geothermal system, *Chinese Science Bulletin (in Chinese)*, 1997, 42 (21): 2313.
5. Pollastro, R. M., Considerations and applications of the illite/smectite geothermometer in hydrocarbonbearing rocks of Miocene to Mississippian age. *Clays and Clay Minerals*, 1993, 41(1): 119.
6. Harvey, C. C., Browne, P. R. L., Mixed-layer clay geothermometry in the Wairakei geothermal field, New Zealand, *Clays and Clay Minerals*, 1991, 39(3): 614.
7. Whitney, G., Role of water in the smectite-to-illite reaction, *Clays and Clay Minerals*, 1990, 38 (2): 343.
8. Inoue, A., Kitagawa, R., Morphological characteristics of illitic clay minerals from a hydrothermal system, *American Mineralogist*, 1994, 79: 700.
9. Velde, B., Vasseur, G., Estimation of the diagenetic smectite to illite in time-temperature space, *American Mineralogist*, 1992, 77: 967.
10. Zhu Xun, Huang Chongke, Rui Zongyao et al., *Dexing Porphyry Copper Deposit (in Chinese)*, Beijing: Geological Publishing House, 1983.
11. Kisch, H. J., Illite crystallinity: recommendation on sample preparation, X-ray diffraction settings and interlaboratory samples, *Journal of Metamorphic Geology*, 1991, 9: 665.
12. Eberl, D. D., Velde, B., Beyond the Kübler Index, *Clay Minerals*, 1989, 24(3): 571.
13. Srodon, J., Eberl, D. D., Illite. Micas, *Reviews in Mineralogy* (ed. Bailey, S. W.), 1984, 13: 495.
14. Yao, Y. C., Peacor, D. R., McDowell, S. D., Smectite-to-illite reactions in Salton Sea shales: a transmission and analytical electron microscopy study, *Jour. Sed. Petrology*, 1987, 57(2): 335.
15. Schiffman, P., Staudigel, H., The smectite to chlorite transition in a fossil seamount hydrothermal system: the basement complex of La Palma, Canary Islands, *JMG*, 1995, 13: 487.
16. Huang, W. L., Longo, J. M., Pevear, D. R., An experimentally derived kinetic model for smectite-to-illite conversion and its use as a geothermometer, *Clays and Clay Minerals*, 1993, 41(2): 162.
17. Zhang Ligang, Liu Jingxiu, Chen Zhensheng et al., Hydrogen and oxygen evolution for water-rock system in super-huge Tongchang copper deposit, Jiangxi Province, *Scientia Geologica Sinica (in Chinese)*, 1996, 31(3): 250.
18. Bell, T. E., Microstructure in mixed-layer illite/smectite and its relationship to the reaction of smectite to illite, *Clays and Clay Minerals*, 1986, 34(1): 146.
19. Rask, J. H., Bryndzia, L. T., Braunsdorf, N. R. et al., Smectite illitization in Pliocene-age gulf of Mexico mudrocks, *Clays and Clay Minerals*, 1997, 45(1): 99.