

Composition of biotite within the Wushan granodiorite, Jiangxi Province, China: Petrogenetic and metallogenetic implications

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ABSTRACT

The Wushan skarn copper deposit is genetically associated with the Wushan granodiorite. In this study, we investigate the petrography and mineralogy of biotites within the Wushan granodiorite. We also determine the formation conditions of these biotites and discuss the significance of these minerals in terms of petrogenesis and mineralization. Electron microprobe analysis shows that biotites within the Wushan granodiorite are Magnesian-biotites that contain relatively high Mg and Ti concentrations and low Fe and Al concentrations. The ionic coefficient of Al^{VI} in these biotites ranges from 0.03 to 0.19, with $\sum\text{FeO}/(\sum\text{FeO} + \text{MgO})$ ratios that range from 0.531–0.567 and MgO concentrations that range from 12.80–14.06 wt%. These results indicate that the Wushan granodiorite is an I-type granite. The Wushan biotites crystallized at temperatures (T) of 720°C–750°C, with oxygen fugacity (fO₂) conditions of –11.6 to –12.5 and pressures (P) of 0.86–1.03 kb. These conditions are indicative of a crystallization depth (H) of 2.84–3.39 km. These data also indicate that the Wushan granodiorite developed under conditions of high temperature and high oxygen fugacity, suggesting that the Wushan granodiorite is prospective for magma-hydrothermal mineralization and that this granodiorite probably contributed to the formation of the Wushan skarn copper deposit.

Key words: biotite, granodiorite, mineral chemistry, petrogenesis and mineralization, Wushan skarn copper deposit

RESUMEN

El depósito de skarn cuprífero de Wushan está asociado genéticamente con la granodiorita de Wushan. En este estudio se investiga la petrografía y mineralogía de biotitas de la granodiorita de Wushan. Se determinan también las condiciones de formación de estas biotitas y se discute la significación de estos minerales en términos de petrogénesis y mineralización. Un análisis de microsonda a electrones muestra que las biotitas de la granodiorita de Wushan son biotitas de magnesio que contienen altas concentraciones relativas de Mg y Ti y bajas de Fe y Al. El coeficiente iónico de Al^{VI} en estas biotitas oscila entre 0,03 y 0,19, con índices SFeO/(SFeO + MgO) que oscilan entre 0,531-0,567 y concentraciones de MgO que van desde 12,80 a 14,06 wt%. Estos resultados indican que la granodiorita de Wushan es de granito tipo I. Las biotitas de Wushan se cristalizaron a temperaturas (T) de 720°C–750°C, con condiciones de fugacidad del oxígeno (fO₂) de -11,6 a -12,5 y presión (P) de 0,86 a 1,03 kb. Estas condiciones indican una profundidad de cristalización (H) de 2,84-3,39 kilómetros. Los datos también indican que la granodiorita de Wushan se desarrolló bajo condiciones de alta temperatura y alta fugacidad de oxígeno, lo que sugiere que la granodiorita de Wushan tiene potencial para la mineralización magmática-hidrotérmica y que esta granodiorita probablemente contribuyó a la formación del depósito de skarn cuprífero de Wushan.

Palabras clave: biotita; granodiorita; química mineral; petrogénesis y mineralización; depósito cobrizo de Wushan.

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1. Introduction

A number of previous studies (Wones and Eugeter, 1965; Burhard, 1991; Barrière and Cotten, 1991; Sheshtawi et al., 1993; Lalonde and Bernard, 1993; Abdel-Rahman, 1994; Hecht, 1995; Abdel-Rahman, 1996; Zhang et al., 2014) have shown that the composition of fluids associated with skarn mineralization is closely related to the physical and chemical conditions that are present during magma cooling and crystallization. Previous studies also indicate that the chemical composition of biotites in granites is controlled by conditions of

magma cooling and crystallization; these conditions include oxygen fugacity, temperature, and pressure. Therefore, biotite is an effective indicator that can be used to establish the physical and chemical conditions that were present during the cooling and crystallization of magma.

The Wushan skarn copper deposit is located in the central part of the Jiujiang–Ruichang district in the Middle–Lower Yangtze River metallogenic belt (Figure 1a). The deposit is genetically associated with the formation of the Wushan granodiorite (Figure 1b). A number of studies on the Wushan granodiorite

have determined that the magmas that formed this body contained a very high proportion of mantle component material (Jiang et al., 2008). These studies also indicate that these magmas were produced by late Yanshanian magmatism (145 ± 3.9 Ma), which is associated with significant crust–mantle interaction (Gu, 1987; Bao et al., 2002; Ding et al., 2006; Yang et al., 2011). These studies have also determined that the Wushan granodiorite is genetically related to the Wushan skarn copper deposit (Kong et al., 2012; Jiang et al., 2008; Ji et al., 1989; Huang et

al., 1990; Cui et al., 2002). Nevertheless, the magmatic conditions of the Wushan granodiorite have not been considered by these studies.

In this study, we focus on the composition of biotite within the Wushan granodiorite to estimate the magmatic conditions that were present and to determine the petrogenetic and metallogenic significance of this formation. This research has also led to an increase in understanding about the metallogenic processes that led to the formation of the Wushan skarn copper deposit.

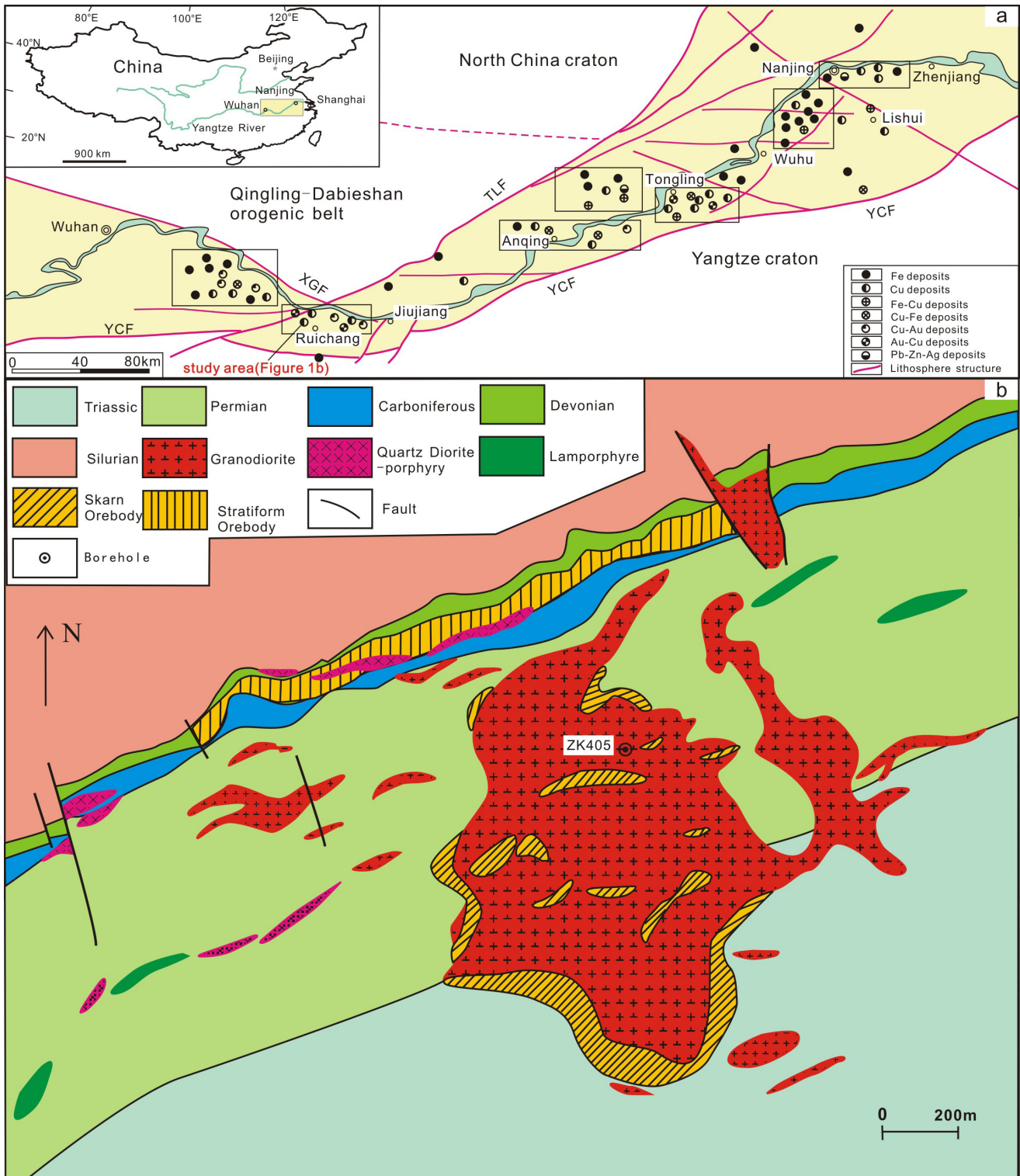


Figure 1. Geological map of the Wushan skarn copper deposit (after Yang et al., 2011).

2. Geological background

The Wushan skarn copper deposit is located 8 km north of the city of Ruichang, in Jiangxi Province, China (Figure 1a). Most of the ore bodies that make up the deposit are hosted by Upper Carboniferous to Middle Triassic carbonates, with igneous units in the area that is dominated by granodiorites, quartz diorites, quartz porphyries, and lamprophyres. Faulting is widespread throughout the deposit, and the deposit is dominated by NEE-striking inter-laminar fractures and NE- and NW-striking faults. The Wushan granodiorite is located within the southern Wushan ore belt, and it consists of a stock that intruded into Permian to Carboniferous carbonates. The stock is oval-shaped in the planar view (Figure 1b) and trumpet-shaped in the cross-sectional view (Cui et al., 2002).

3. Samples and analytical techniques

Samples were obtained from a number of underground tunnels and stopes located in the southern Wushan ore belt. These tunnels and stopes were originally used for underground prospecting, mining, and other underground activities. For this study, granodiorite samples were collected from the underground in the -260 m N2 stope and from borehole ZK405. These hand-collected samples have a porphyritic structure, and they contain quartz (28%–30%), plagioclase (38%–40%), potassium feldspar (18%–20%), biotite (7%–8%), and hornblende (1%–3%), with accessory minerals including titanite, apatite, zircon, and magnetite. Biotites are widespread in the Wushan granodiorite. They are also euhedral to subhedral, tabular, fresh, dark brown to light yellow, well-cleaved, and 1–5 mm in size. These crystals also contain earlier crystallized inclusions of magnetite, apatite, zircon, and other accessory minerals (Figure 2a–b).

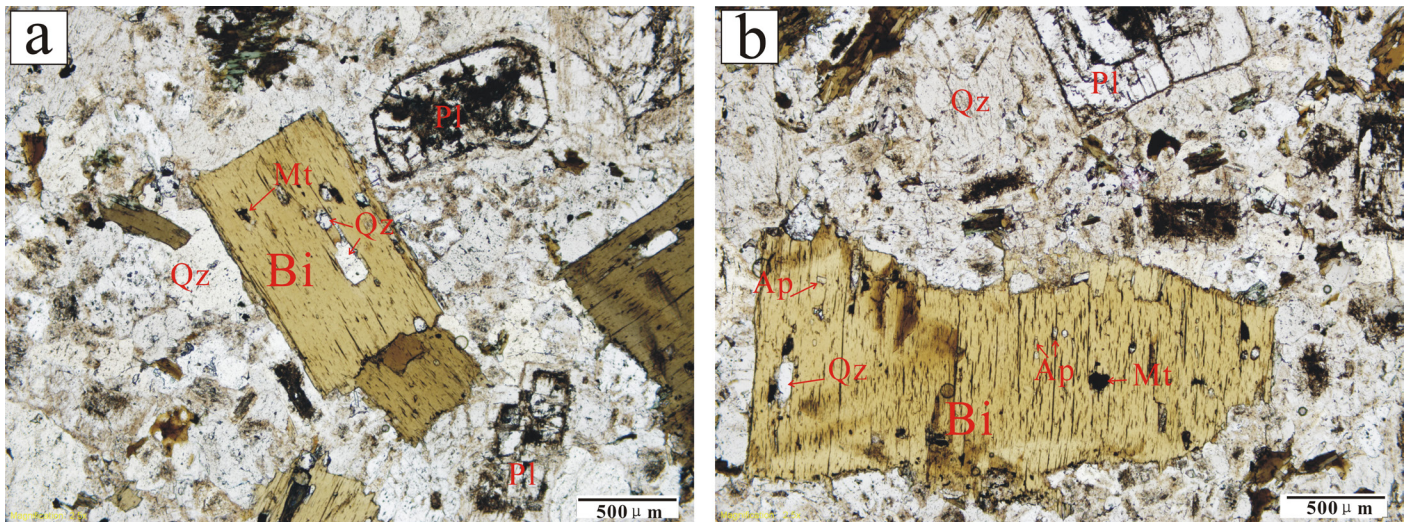


Figure 2. Photomicrographs of biotites from the Wushan granodiorite. a. Euhedral tabular biotite containing magnetite inclusions; b. Subhedral tabular biotite containing magnetite and apatite inclusions. Bi = Biotite; Qz = Quartz; Pl = Plagioclase; Mt = Magnetite; Ap = Apatite.

An electron microprobe analysis (EPMA) was conducted at the Beijing Research Institute of Uranium Geology, Beijing, China employing a JXA-8100 instrument that was operated using a 20 kV accelerating voltage, a 10 nA beam current, and a 10 mm beam diameter. The detection limit was 0.002 wt%. For this analysis, the instrument was calibrated using albite (Na), sanidine

(Si, Al, and K), diopside (Ca, Mg), almandine (Fe), rutile (Ti), fluorapatite (P), and rhodonite (Mn) standards. A calculation method developed by Lin and Peng (1994) was used to adjust the Fe^{2+} and Fe^{3+} concentrations, and we used the electrovalency balance principle to calculate the crystal formulae. The correlation calculation results are shown in Table 1.

Table 1. Representative electron microprobe analyses (wt %) and the structural formulae of biotite collected from the Wushan granodiorite.

No.	1	2	3	4	5	6	7	8	9	10
SiO ₂	37.724	37.512	38.078	37.089	37.433	38.007	37.186	37.737	37.564	37.354
TiO ₂	3.280	3.814	3.800	3.523	3.756	3.680	4.037	3.351	3.910	3.766
Al ₂ O ₃	13.704	13.610	13.933	13.562	13.626	13.836	13.991	13.878	13.841	13.740
FeO	16.356	16.455	17.276	16.102	16.271	15.947	16.785	15.304	16.737	16.897
MnO	0.048	0.066	0.109	0.072	0.034	0.029	0.105	0.095	0.057	0.042
MgO	14.055	12.821	13.180	12.802	13.637	13.925	13.359	13.521	13.598	13.822
CaO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.053	0.000	0.000
Na ₂ O	0.322	0.238	0.121	0.979	0.147	0.101	0.202	0.145	0.139	0.139
K ₂ O	9.483	9.281	9.532	9.304	9.606	9.631	9.419	9.542	9.498	9.531
P ₂ O ₅	0.027	0.034	0.000	0.000	0.000	0.000	0.000	0.082	0.055	0.000
Total	94.999	93.831	96.029	93.433	94.510	95.156	95.084	93.708	95.399	95.291

Structural formulae on the basis of 22 (O)

Si	5.661	5.691	5.660	5.673	5.646	5.672	5.585	5.710	5.620	5.603
Al ^{IV}	2.339	2.309	2.340	2.327	2.354	2.328	2.415	2.290	2.380	2.397
Z	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Al ^{VI}	0.085	0.125	0.101	0.118	0.068	0.105	0.062	0.185	0.061	0.033
Fe ³⁺	0.289	0.335	0.332	0.270	0.308	0.313	0.316	0.312	0.317	0.303
Fe ²⁺	1.764	1.753	1.815	1.789	1.744	1.677	1.792	1.624	1.777	1.816
Ti	0.370	0.435	0.425	0.405	0.426	0.413	0.456	0.381	0.440	0.425
Mn	0.006	0.008	0.014	0.009	0.004	0.004	0.013	0.012	0.007	0.005
Mg	3.144	2.900	2.921	2.919	3.066	3.098	2.991	3.050	3.033	3.091
Y	5.658	5.556	5.607	5.511	5.617	5.610	5.631	5.565	5.635	5.673
Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.009	0.000	0.000
Na	0.094	0.070	0.035	0.290	0.043	0.029	0.059	0.043	0.040	0.040
K	1.815	1.796	1.807	1.815	1.848	1.833	1.805	1.842	1.813	1.824
X	1.909	1.866	1.842	2.106	1.891	1.863	1.863	1.893	1.853	1.864
Sum	15.567	15.422	15.450	15.617	15.508	15.473	15.494	15.457	15.488	15.538
$\Sigma\text{FeO}/(\Sigma\text{FeO}+\text{MgO})$	0.538	0.562	0.567	0.557	0.544	0.534	0.557	0.531	0.552	0.550
$\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg})$	0.359	0.377	0.383	0.380	0.363	0.351	0.375	0.347	0.369	0.370
$\text{Mg}/(\text{Fe}^{2+}+\text{Mg})$	0.641	0.623	0.617	0.620	0.637	0.649	0.625	0.653	0.631	0.630
^T Al	2.440	2.452	2.459	2.460	2.439	2.451	2.494	2.492	2.458	2.446
P(Kb)	0.862	0.900	0.922	0.923	0.861	0.896	1.028	1.022	0.918	0.881
H(Km)	2.845	2.970	3.042	3.047	2.840	2.957	3.393	3.372	3.030	2.908

P.S.: 1. See text for assignment of ferrous and ferric iron;

2. X, Y, Z, respectively represent the sum of the T, O, L cations in the structural formulae;

3. $P = \rho gH$, where $\rho = 2700 \text{ kg/m}^3$, $g = 9.8 \text{ m/s}^2$.

4. Componential characteristics

The EPMA results listed in Table 1 show that the Wushan biotites contain high concentrations of MgO (12.80–14.06 wt%) and low concentrations of Al_2O_3 (13.56–13.99 wt%), with $\text{Mg}/(\text{Fe}^{2+} + \text{Mg})$ ratios that range between 0.62 and 0.65. Using a $\text{Mg}-(\text{Fe}^{2+} + \text{Mn})-(\text{Fe}^{3+} + \text{Al}^{\text{VI}} + \text{Ti})$ biotite classification diagram (Figure 3), all of the biotites from the Wushan granodiorite were classified as Magnesian-biotites.

The Wushan biotites also contain low concentrations of FeO (15.30–17.28 wt%), with all samples falling within a narrow range of $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ ratios. All of these characteristics show that the biotites within the Wushan granodiorite are primary and crystallized directly from magma (Stone, 2000).

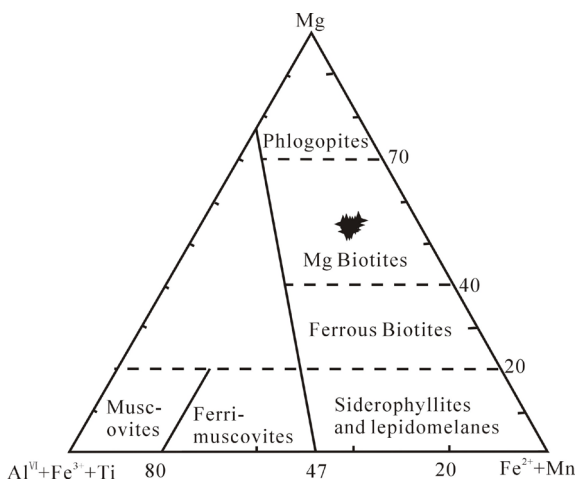


Figure 3. Variations in Mg vs. $(\text{Fe}^{2+} + \text{Mn})$ vs. $(\text{Fe}^{3+} + \text{Al}^{\text{VI}} + \text{Ti})$ in biotites collected from the Wushan granodiorite; diagram after Foster, 1960.

5. Crystallization conditions

5.1 Temperature and oxygen fugacity

The data in Table 1 indicate that the Si within the biotite structures can be replaced by Al^{VI} , but not by Al^{VI} or Ti. These results indicate that the biotites crystallized at high temperatures (Deer et al., 1966), estimated to be between 720°C and 750°C (Figure 4).

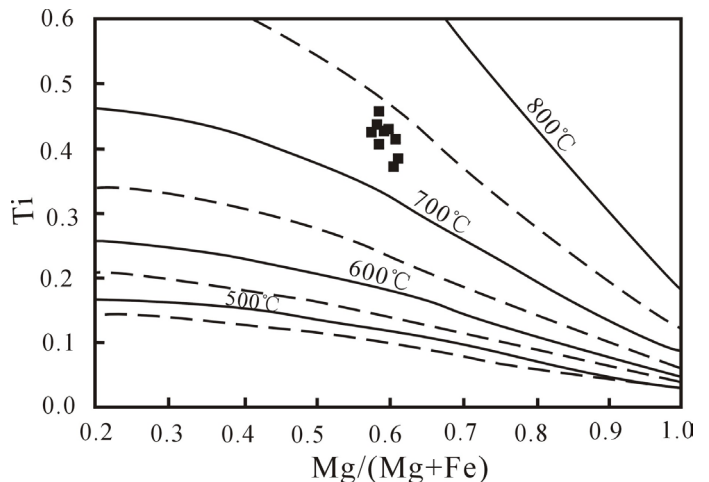


Figure 4. Variations in the Ti vs. $\text{Mg}/(\text{Mg} + \text{Fe})$ ratio of biotite collected from the Wushan granodiorite; diagram after Henry et al., 2005.

Previous research (Wones and Eugeter, 1965; Barrière and Cotten, 1991; Albuquerque, 1973; Noyes et al., 1983) indicates that the atomic abundances of

Fe^{3+} , Fe^{2+} , and Mg^{2+} in biotite collected from a cogenetic biotite–magnetite–K-feldspar assemblage can be used to calculate the oxygen fugacity conditions that were present during crystallization. As determined by petrographic microscopy, biotite within the Wushan granodiorite is present within a hornblende + biotite + K-feldspar + magnetite + quartz assemblage indicating that the oxygen fugacity conditions of crystallization can be calculated. In the Fe^{3+} – Fe^{2+} – Mg biotite diagram shown in Figure 5, all of the biotites that were analyzed in this study fell between the Ni–NiO and Fe_2O_3 – Fe_3O_4 buffers, indicating that they crystallized under conditions of high oxygen fugacity (Wones, 1989).

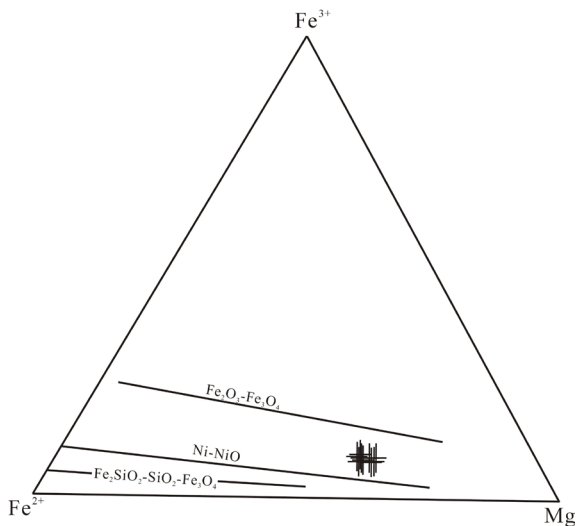


Figure 5. Variations in Fe^{3+} – Fe^{2+} – Mg in biotite collected from the Wushan granodiorite; diagram after Wones and Eugster, 1965.

In addition, Figures 4 and 5, and the $\log f\text{O}_2$ – T diagram for biotites (Figure 6) at $P_{\text{H}_2\text{O}} = 207.0$ MPa (Wones and Eugster, 1965), suggest that these biotites were crystallized at $\log f\text{O}_2$ values between -11.6 and -12.5 . This result is consistent with our previous discussion.

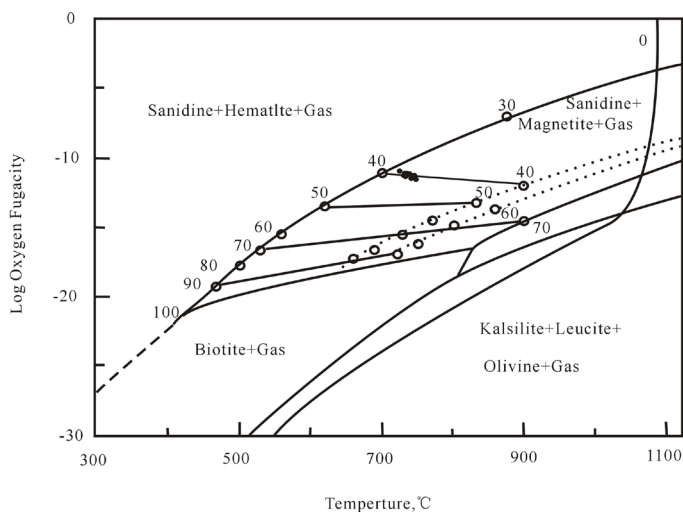


Figure 6. Variations in $\log f\text{O}_2$ – T conditions during biotite crystallization in the Wushan granodiorite; diagram after Wones & Eugster (1965), with the numbers 0–100 representing biotite stability as a function of $(100 \times \text{Fe}/(\text{Fe} + \text{Mg}))$.

5.2 Pressure and depth

The Wushan granodiorite has been significantly altered, with mafic minerals (e.g., hornblende) undergoing variable chloritization. As a result, this mineral cannot be used as a geo-barometer (Jiang et al., 2008). However, the biotites within the Wushan granodiorite are unaltered (Figure 2), and Etsuo et al. (2007) documented a strong positive correlation between the total Al ($^{\text{T}}\text{Al}$) content of a biotite sample and the solidification pressure (P) of the granitic host rocks, as determined using sphalerite and hornblende geo-barometers and mineral assemblages within the surrounding rocks. These results lead to the following empirical equation:

$$P (\text{kb}) = 3.03 \times ^{\text{T}}\text{Al} - 6.53 (\pm 0.33),$$

Where $^{\text{T}}\text{Al}$ is the total Al content of the biotite (calculated using 22 oxygens).

Therefore, this biotite geo-barometer allows us to constrain the pressures that were present during crystallization of the Wushan granodiorite to 0.86–1.03 kb, equating to depths of 2.84–3.39 km.

6. Petrogenesis and metallogenic significance

Biotite compositions enable researchers to determine the type and mineralization potential of a host granite as well as the source of magma from which these biotites formed.

As previously determined, the Al^{VI} abundances of biotite permit discrimination between I- and S-type granites, with Whalen (1988) reporting that I-type granites are associated with biotites with low Al^{VI} abundances (0.144–0.224), whereas S-type granites are associated with biotites with higher Al^{VI} abundances (0.353–0.561). The Al^{VI} abundances in biotites from the Wushan granodiorite ranged from 0.03 to 0.19 (Table 1), indicating that the Wushan granodiorite is an I-type granite. Abdel-Rahman (1994) found that biotites that are present within I-type granites are relatively enriched in magnesium, whereas S-type granite biotites are relatively enriched in aluminum. In addition, Wushan granodiorite biotites are magnesian, which also supports an I-type granite classification for this intrusion.

Zhou (1986) suggested that a $w(\Sigma\text{FeO})/w(\Sigma\text{FeO} + \text{MgO})$ vs. $w(\text{MgO})$ diagram using biotite compositions could be used to discriminate between granites of differing origins. Using such a diagram, biotites from the Wushan granodiorite plot within the mixed mantle–crust source (MC) area (Figure 7). These results are consistent with isotopic analyses showing an $\text{eHf} (t)$ that ranged between -2.1 and -7.0 (Ding et al., 2006) and an $\text{eNd} (t)$ that ranged between -4.08 and -4.44 (Jiang et al., 2008).

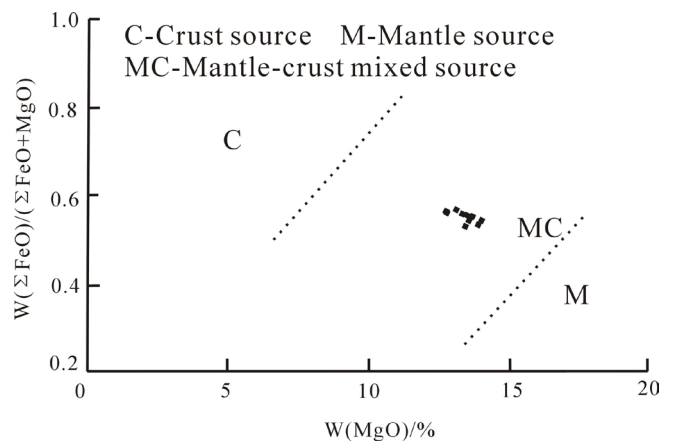


Figure 7. Variations in the $(\Sigma\text{FeO})/(\Sigma\text{FeO} + \text{MgO})$ ratio vs. MgO in biotites from the Wushan granodiorite; diagram after Zhou, 1986.

Wyborn et al. (1994) and Sun et al. (2004) determined that high oxygen-fugacity environments are prospective for the precipitation and mineralization of economic metals such as Cu and Au. This result suggests that intrusive rocks that form in high oxygen-fugacity environments should be considered highly prospective in terms of mineralization. As described above, the crystallization temperatures of biotites from the Wushan granodiorite ranged from 720°C to

750°C, with log f_{O_2} values ranging from -11.6 to -12.5. These results suggest that the Wushan granodiorite formed at pressures of 0.86–1.03 kb, equating to depths of 2.84–3.39 km. These crystallization conditions also indicate that the Wushan granodiorite formed at high temperatures, shallow depths, and under conditions of very high oxygen fugacity. In addition, these results suggest the Wushan granodiorite is highly prospective for mineral exploration and that it contributed to the formation of the Wushan skarn copper deposit.

7. Conclusions

Analyses of biotites from the Wushan granodiorite allowed us to reach the following conclusions.

Biotites within the Wushan granodiorite are Mg- and Ti-rich and Fe-poor. They are classified as magnesio-biotites.

The crystallization temperatures of Wushan biotites ranged from 720°C to 750°C, with crystallization under log f_{O_2} values of -11.6 to -12.5. The Wushan granodiorite was formed at pressures of 0.86–1.03 kb, equating to depths of 2.84–3.39 km. These conditions indicate that the Wushan granodiorite developed at high temperatures, shallow depths, and at a very high oxygen fugacity. As a result, the Wushan granodiorite should be considered highly prospective, and it probably contributed to the formation of the Wushan skarn copper deposit.

The Wushan granodiorite is an I-type granite, which was sourced from the melting of a mixed mantle–crust source.

Acknowledgments

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