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Regional variations in ore composition and fluid features of massive sulphide deposits in South China: Implications for genetic modelling

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Upper Palaeozoic intracontinental massive sulphide deposits occur in both the Lower Yangtze River and the Nanling Mountain regions of South China. However, sulphide ores of these two regions are remarkably different in composition. Ores of the Lower Yangtze region are copper-rich with minor Pb and Zn and recoverable Au, Ag, Co and Mo; they usually have low concentrations of radiogenic lead and have tight $\delta^{34}\text{S}$ distribution patterns close to zero. Fluid inclusions are highly saline and sodium-rich. Ores of the Nanling Mountain region mainly comprise Pb, Zn, Sn and W as well as Cu with recoverable Ag, Sb, Hg, U, Bi, Tl and Mo; they usually have higher concentrations of radiogenic lead and wide-ranging $\delta^{34}\text{S}$ values. Their fluid inclusions have low salinities and are potassium-rich.

There is evidence to indicate that the Upper Palaeozoic continental crust in the Lower Yangtze region has lower maturity than that of the Nanling Mountain region. The compositional contrasts between these two regions are suggested to have been controlled by differences in their basin basements and thus reflect the difference in crustal maturity during ore formation.

Introduction

It has long been recognized that the composition and geological features of massive sulphide deposits were substantially affected by the nature of the crust upon which they were formed (Ishihara and Terashima, 1974; Sawkins, 1976; Hutchinson, 1980), as well as by the composition of basin basement (Russell, 1968; Ishihara and Terashima, 1974). The three major types of massive sulphides, i.e. the Cyprus-, Kuroko- and Sullivan-types were considered by Sawkins (1976) to represent products on ocean ridges, island arcs and intracontinental basins, respectively. Fouquet et al. (1993) noted that variations in composition of modern massive sulphide deposits are related to their formation in back-arc systems of different maturity. However, discussions on regional variations of massive sulphides and their relationships to the continental crust are rare. The present contribution aims to discuss the differences between massive sulphides in the Lower Yangtze River and the Nanling Mountain regions and to connect their genesis with continental evolution and crustal maturity.

Geological setting

There exist more than 20 major massive sulphide base-metal deposits (Figure 1) in the Upper Palaeozoic marine fault-bounded depression troughs developed on post-Caledonian continental crust.

According to Guo and co-workers (1980), the triangular Dabie craton which is located to the north of the Yangtze River and belongs to the south part of the North China plate (Figure 1) is composed of Late Archaean to Early Proterozoic metamorphic rocks. During the Mid-Proterozoic the South China oceanic plate was subducted northwards beneath the North China plate, resulting in the northeast-trending island arc system, i.e., the Changsha- Qianyang belt. This belt is represented by a thick sequence of calc-alkalic and spilite-keratophyric volcanites and flysch sediments with fragments of ophiolites. The Lower Palaeozoic subduction zone is marked by the northeast-trending fault that passes through Zhenghe and Dapu in Fujian Province (Figure 1). The Late Proterozoic to Early Palaeozoic flysch with spilite-keratophyric intercalations northwest of that fault were formed in an arc-trench-basin environments.

A northeast-trending Mesozoic volcanic belt (Figure 1), which is part of the circum-Pacific magmatic zone, extends along the southeastern coast of China. There has been heated debate regarding the tectonics of the basement beneath the volcanic cover. Guo and co-workers (1980) suggested that the basement rocks, which have suffered greenschist- to amphibolite-facies metamorphism, may represent an active Hercynian-Indosinian continental margin. In contrast, an exotic Precambrian terrane is inferred by others based mainly on U-Pb isotope dates between 1.0 and 2.0 Ga (Ma and Sun, 1985; Shui, 1987; Zhang, 1991; Li, 1997).

Towards the end of the Early Palaeozoic (Caledonian orogeny), the continental crust of South China stabilized (Gu and Xu, 1987). Subsidence of the crust during the Late Palaeozoic resulted in marine transgression from the southwest to the northeast. Based upon their relationships to the basements on which they were initiated, Shi et al. (1963) distinguished two types of fault-bounded sedimentary basins: inherited and superimposed. The Xinjiang, Pingxiang-Leping, West Fujian, North Guangxi and North Guangdong basins (Figure 1) are of the superimposed type where Upper Palaeozoic sediments are separated by a sharp unconformity either from the folded Lower Palaeozoic sequences or directly from the metamorphosed Mid-Proterozoic basement. The Lower Yangtze basin (Figure 1), on the other hand, is of the inherited type, which was formed by continued development of a pre-existing Caledonian basin. In this case there is no angular unconformity between the Lower and the Upper Palaeozoic sequences (Xu and Zhu, 1978). During the Hercynian-Indosinian cycle, both the superimposed and inherited basins generally received several thousand metres of sediments, predominantly carbonates and clastic rocks (Xu and Zhu, 1978). Most of the massive sulphide ore layers occur 50 ~ 200 m above the base of the upper Palaeozoic successions. Volcanic intercalations, mainly of basalts, dacites and rhyolites, have been identified within these sequences in many places

Figure 1 Locations of major Upper Palaeozoic massive sulphide deposits in South China. Hercynian-Indosinian Basins: F-West Fujian; G-North Guangdong; N-North Guangxi; P-Pingxiang-Leping; X-Xinjiang; Y-Lower Yangtze; S-Sihui-Wuchuan. Massive Sulphide Deposits: 1-Qixiashan; 2-Magushan (East Tongshan); 3-Xinqiao; 4-Tongguanshan; 5-Dongguashan; 6-Mashan; 7-West Tongshan; 8-Chengmenshan; 9-Wushan; 10-Yinshan; 11-Linghou; 12-Yongping; 13-Dongxiang; 14-Lehua; 15-Qibaoshan; 16-Fankou; 17-Dabaoshan; 18-Yangliutang; 19-Xiniu; 20-Hongyan; 21-Dajiangping; 22-Longfengchang; 23-Yushui; 24-Shiding; 25-Dachang.

(Gu et al., 1993), Andesitic volcanites are not important in these basins, and the petrological association is bimodal. Hence, these basins may represent the initial stage of continental rifting (Sawkins, 1976; Gu and Yang, 1989).

The Upper Palaeozoic sediments in these basins are largely unmetamorphosed although folding took place during the Late Triassic (Indosinian) compression. During the Mesozoic time, extensive volcanism and granite intrusion occurred all over SE China.

General features of the massive sulphide deposits in South China

The geology and genesis of the massive sulphide deposits in South China have been described by many authors (Xu and Zhu, 1978; Hsu et al. 1980; Wang et al., 1986; Gu et al., 1993; Yue et al., 1993). These deposits mainly occur in the transitional horizons from clastic to carbonatic sequences which represent Upper Palaeozoic marine transgression of the fault-bounded basins (Gu and Xu, 1987; Hu et al., 1994). Since basin subsidence occurred progressively later towards the north, occurrences of massive sulphides are found at progressively higher positions in the sedimentary columns in that direction with predominantly Devonian in the Nanling Mountain region, lower Carboniferous in the Xinjiang River region and middle Carboniferous along the Yangtze River (Gu et al., 1993). Volcanites, basaltic, dacitic and rhyolitic in composition have been reported in the ore-hosting horizons (Fu, 1977; Zhu and Zhang, 1981; Gu and Xu, 1984). Compositionally, the South China deposits have considerable reserves of tin and tungsten as well as copper, lead, zinc, gold

and silver (Gu et al., 1993). The distribution of metals and ore minerals in these deposits exhibits stratigraphically vertical and lateral zonations (Gu, 1984): The general trend of metal zonation from the base upwards is Fe (sulphides) — Cu—(Cu, W)—Pb, Zn—Fe, Mn (carbonates and/or oxides) (W). Laterally from the feeders, they show a trend of Cu, S (W)—Pb, Zn, Ag—Fe, Mn. These zonations are thought to be produced by a combination of sedimentation, diagenesis, remobilization, and late stage superimposition (Gu et al., 1993). Underlying the stratiform ores in some of the deposits are fissure-filling, breccia-cementing and impregnated mineralizations representing the submarine hydrothermal feeders. Alterations genetically related to footwall mineralizations include silicification, sericitization and K-feldspathization, which were interpreted to reflect the silica- and potassium-rich nature of the continental crust (Gu and Yang, 1989), and which might have been prompted by the nuclei in the footwall quartzofeldspathic clastic sediments. Being formed contemporaneously with the sulphide deposits, stratiform iron and manganese ores occur in relatively oxidizing environments within the same basins. Locally, such iron and manganese ores are underlain by cross-cutting lead-zinc veins that may represent the hydrothermal feeders (Gu, 1987a).

Contrasting ore composition and fluid features of two regions

Although the Upper Palaeozoic massive sulphide deposits in South China share many common features, there are strong contrasts in ore composition and fluid features between those in the Nanling Mountain and the Lower Yangtze River regions.

Metal components

The ore deposits in the Lower Yangtze region are characterized by massive copper sulphide ores (Figures 1, 2 and Table 1), such as those at Wushan (1.3 Mt Cu, avg. 1.3%) and Dongguashan (0.94 Mt Cu, avg. 1.0%). Gold is an important by-product in these deposits (0.1 to 1 ppm, e.g., at Wushan, Chengmenshan, Tongguanshan, Xinqiao, Dongguashan and Qixiashan). Locally, gold is economically much more important than base metals, and has formed a separate gold deposit at Mashan (6 tons Au, avg. 9.6g/t). The deposit at Qixiashan also has significant reserves of gold. Cobalt and molybdenum are also recoverable in some of the deposits (Table 1). However, none of these deposits have significant concentration of fluorine, boron, uranium, mercury, bismuth, antimony, thallium and tin. Only a small mine at Longjiaoshan to the southeast of Wushan is reported to have recoverable tungsten.

By contrast, massive sulphide ores in the Nanling Mountain region (Figure 1) have lead, zinc and silver reserves economically more important than copper and gold (Table 1). Examples include Fankou (3.4 Mt Zn and 1.7 Mt Pb), Yangliutang, Siding and Dachang. The ores are usually also enriched in fluorine, boron, uranium, mercury, bismuth, antimony and thallium. The fluorine concentration is normally higher than 280 ppm in the ores of the region and even reaches 1.65% in the low-grade sulphur ores from the Jingtang deposit in the North Guangdong basin. The Dachang tin-poly-metallic deposit is characterised by boron enrichment. Tourmaline is a common constituent in the stratiform sulphide ores and their host siliceous rocks with banded tourmalinites containing >20 vol.% tourmaline being present locally (Han et al., 1997; Jiang et al., 1999). Uranium is considerably higher in the Fankou and Siding deposits of the Nanling Mountain region (Tu et al., 1984). Mercury is of high enough grade to be economic in the massive lead-zinc ore (avg. 135 ppm) of Fankou mine (Huang, 1989). Analyses of various

Table 1. Comparison between the Lower Yangtze and the Nanling Mountain regions in ore metals in massive sulphide deposits.

Region	Deposit	Principal metals	Associating metals
Lower Yang-tze	Mashan	Au	Cu, Co
	Dongguashan	Cu	Au, Ag, Co
	Tongguanshan	Cu	Au, Co, Mo
	Tongshan	Cu	Au, Mo
	Xinqiao	Cu	Au
	Magushan	Cu	Au
	Wushan	Cu, Zn, Pb	Au, Ag
	Chengmenshan	Cu, Mo	
	Qixiashan	Zn, Pb, Mn	Au, Ag, Cu, Co
Nanling	Dabaoshan	Cu, W, Zn, Pb	Mo, Bi
	Yangliutang	Zn, Pb	Sb
	Fankou	Zn, Pb	Hg, Ag, Sb,
	Shiding	Zn, Pb	Ag, U
	Hongyan	Fe(S)	Tl
	Dajiangping	Fe(S)	Tl
	Xiniu	Fe(S)	Tl
	Dachang	Sn, Zn, Pb	Sb, Ag, U

Table 2 Comparison in fluid composition (x 10⁻⁶) between massive sulphide deposits in the Lower Yangtze and Nanling Mountain regions.

Region	Deposit	Mineral	Sample Number	K ⁺	Na ⁺	K ⁺ /Na ⁺
Lower Yangtze	Tongguanshan	siderite	3	7.13	16.4	0.43
		pyrite	1	0.51	2.00	0.26
		quartz	1	0.42	1.48	0.28
	Qixiashan	galena	2	2.15	2.80	0.77
		pyrite	4	1.10	2.37	0.46
	Wushan	pyrite	6	1.09	3.17	0.34
	Tongshan	siderite		7.50	17.6	0.43
	Magushan	siderite		3.40	6.80	0.50
Nanling	Dabaoshan	pyrite	3	2.30	1.80	1.28
		sphalerite		2.84	0.10	28.4
	Fankou	galena	2	1.80	1.70	1.06
		sphalerite	19	2.73	0.50	5.48
		pyrite	3	6.82	0.33	20.7
	Hongyan	pyrite	3	0.38	0.29	1.31

Data sources: Tongguanshan: This research and Wang (1987); Qixiashan: This research and East China Geoexploration Bureau (1990); Wushan: This research; Tongshan and Magushan: Wang (1987); Dabaoshan and Fankou: This research and Nin (1991). Hongyan: Institute of Geology, Metallurgical Ministry (1982).

mineral separates indicate that 91% of the mercury in the deposit is hosted in sphalerite, which has an average Hg content of 790 ppm. Most of the mercury is suggested to be scattered in the lattice of this mineral, although minute cinnabar grains (<2µm) have also been found in the ores of the deposit (Tu,1984; Huang, 1989).

Ores in the Dabaoshan mine of the Nanling Mountain region have an average of 0.04% Bi, but values up to 0.4% Bi have been recorded. Bismuthinite has been found in the ores. Massive lead-zinc ores in the Fankou mine contain an average of 0.016% Sb. Stibnite crystals 1 to 2 cm in length have been found locally in the deposit. The powder-like pyrite ore in the Tianliao mine near Xiniu has an

Figure 2 Cu:Zn:Pb ratios of massive sulphide deposits in South China. 1-Tongguanshan; 2-Xinqiao; 3-Fankou; 4-Magushan; 5-Longjiaoshan; 6-Qixiashan; 7-Linghou; 8-Dongxiang; 9-Yongping; 10-Lehua; 11-Dabaoshan. 12-Yangliutang; 13-Dongguashan; 14-Qibaoshan.

antimony content of 0.04%. Ores from the Dachang tin mine of Guangxi Province and the Yangliutang lead-zinc deposit near Dabaoshan in North Guangdong also have remarkable concentrations of antimony. Pyrite ores from the Xiniu mine have recoverable thallium with an average concentration of 0.0019%, and the average concentration in ore body No.5-1 reaches up to 0.0027%. The thallium content is also high (up to 0.0046%) in the sulphide ores at Dajiangping. Fifteen samples of pyrite separates from the Hongyan mine show an average of thallium content of 0.005% with a maximum of 0.015%.

Several stratiform barite deposits with n to 10n Mt BaSO₄ and tens of smaller ones are distributed in the Devonian sequence of the Nanling region (Li and Yu, 1991), although no significant barite accumulations have so far been reported in mining areas of the massive sulphides. Barite layers or lenses in these deposits are often accompanied by siliceous sediments, and contains various quantities of pyrite, sphalerite and galena, and occasionally chalcopyrite. Fracture-filling barite mineralizations with alterations of silicification, baritization, carbonatization and pyritization are found cutting the footwall rocks in some of the deposits (Li and Yu, 1991; Lei, 1998). δ³⁴S of barite and sulphide minerals varies in the ranges of +10 ~ +27‰ and 0.2 ~ +35‰, respectively. Homogenization temperatures of fluid inclusions within barite ranges from 105°C to 276°C. These deposits have been recognized as products of Devonian submarine exhalation coeval with that for the massive sulphides in the same region (Li and Yu, 1991; Lei, 1998).

Tungsten and tin are also typical components of the massive sulphide ores in the Nanling Mountain region. The Dabaoshan mine has a WO₃ reserve of 0.1 million tonnes at grades averaging 0.12%. The stratiform pyrrhotite ores at Yindingge, Fujian Province, usually contain 0.02–0.1% W. Scheelite is an important ore mineral in the Qianfeng mine of Fujian Province (Li, 1989). The Dongxiang and Yongping deposits in the Xinjiang basin, which is geographically situated between the Nanling Mountain and the Yangtze regions (Figure 1), contain averages of 0.11% and 0.13% WO₃, respectively, in their sulphide ores (Ren et al., 1993). The WO₃ content of hematite ores at Dongxiang reaches 0.4–0.6% and has a positive correlation with the iron content of the ores.

The Dachang mine, Guangxi Province, is one of the largest polymetallic tin mines in the world with a total reserve of more than 1 million tons Sn and the richest ore averaging 0.71% Sn (Han et al., 1997; Fu et al., 1993; Jiang et al., 1999). Recent research has suggested that the deposit was originally a Devonian massive sulphide deposit (Zhou et al., 1987; Han and Hutchinson, 1989; Jiang et al., 1999). A considerable amount of tin in this deposit is also thought to

Figure 3 Histogram of $\delta^{34}\text{S}\text{‰}$ of sulphides from massive sulphide deposits in the Lower Yangtze and the Nanling Mountain regions.

have been introduced by submarine exhalation (Han and Hutchinson, 1989; Zhang and Chai, 1987). Recently, we examined thin sections of the drill cores from the Changpo ore-zone at Dachang. Cassiterite grains 0.05–0.2 mm across have been found in a siliceous rock with intricate sedimentary layering. Cassiterite occurs only in one layer about 2 mm thick. The microcrystalline nature of the quartz grains of the host rock, which never exceed 0.02 mm across, appears unaffected by subsequent hydrothermal events. This observation indicates that the cassiterite in that layer should have been formed no later than diagenesis.

At the same stratigraphical levels as the massive sulphides in the Nanling Mountain region there are exhalative iron and manganese deposits, which are considered by the authors to be equivalents to the massive sulphides but to have been precipitated in more oxidising environments (Gu, 1987a). These deposits can also have high contents of tungsten and/or tin. For example, the iron-manganese ores in the Houjiangqiao mine of Hunan Province contain 450 ppm WO_3 and 120 ppm Sn. The tin content of iron-manganese ores from the Manaoshan mine, Hunan Province, averages 370 ppm (Tang, 1985). The iron ores at Makeng, Fujian Province was reported to contain 0.3–1.0% Sn (Zhou, 1987). Interestingly, some of the Middle Devonian carbonate-hosted exhalative barite deposit also contain scheelite in their ore layers (Li and Yu, 1991).

Tungsten usually occurs as scheelite in sulphide ores and as wolframites in iron-oxide ores (Gu et al., 1993). In the Dongxiang, Yongping and Dabaoshan mines, scheelite occurs both as impregnations and in veinlets. Wolframites at Dongxiang can be identified by the naked eye as subhedral to euhedral grains less than 1 mm in size. Compositionally they are end members of the FeWO_4 – MnWO_4 series with ferberite predominating and less hubnerite (Hua and Hu, 1980).

Isotope compositions

Massive sulphide ores in the Lower Yangtze and the Nanling Mountain regions also differ in their sulphur and lead isotope compositions.

As indicated in Figure 3, the sulphur isotope compositions of sulphides in most deposits of the Lower Yangtze region are characterized by a tight distribution pattern. The $\delta^{34}\text{S}$ values have very limited variations with the histograms peak at several parts per thousand greater than zero (Gu and Xu, 1986; Gu et al., 1993). Such a distribution of sulphur isotopes could imply more or less homogenized, deep sources for sulphur in these deposits. The only exception is the Qixiashan lead-zinc deposit, which has pronounced negative $\delta^{34}\text{S}$ values, indicating significant involvement of biogenic sulphur. By contrast, the sulphides in the Nanling Mountain region show large variations in $\delta^{34}\text{S}$ values from very positive around 20‰, such as those at Fankou and Xiniu, to very negative between -10 and -20‰, such as those at Dajiangping and Siding. Such a wide $\delta^{34}\text{S}$ distribution suggests that plenty of the sulphur in the Nanling Mountain deposits might have been produced via bacteriogenic reduction of seawater sulphate as is in the Irish Zn-Pb deposits (Anderson et al., 1998). The positive $\delta^{34}\text{S}$ values around 20‰, which approach that of upper Palaeozoic seawater sulphate (Claypool et al., 1980), might indicate reduction in relatively closed systems (Ohmoto and Goldhaber, 1997), whereas the negative values between -10 and -20‰ may represent reduction in relatively open systems (Ohmoto and Goldhaber, 1997) with a H_2S – SO_4^{2-} fractionation around -30 to -

Figure 4 Plot of average ore lead isotopes for massive sulphide deposits in the Lower Yangtze and the Nanling Mountain districts. Growth curves: A-mantle; B-orogenic; C-upper crust; D-lower crust (after Doe et al., 1979).

Figure 5 Comparison of ore-forming temperature (°C) and fluid salinity (equiv. wt% NaCl) between massive sulphide deposits in the Lower Yangtze and Nanling Mountain regions.

45‰. The moderately positive $\delta^{34}\text{S}$ values between 0 and +15‰ may have been derived by reduction of seawater sulphate in the convection system. Experimental evidence indicates that sulphate can be reduced in high temperature hydrothermal systems by oxidation of Fe^{2+} . This results in a fractionation between 0 and 25‰ lower than the starting sulphate, depending on the degree of reduction (Rhy and Ohmoto, 1974).

The lead isotope ratios of the sulphide ores from the Nanling Mountain region are more radiogenic than those of the lower Yangtze region. The Nanling samples are characterised by $^{206}\text{Pb}/^{204}\text{Pb} > 18.34$, $^{207}\text{Pb}/^{204}\text{Pb} > 15.64$ and $^{208}\text{Pb}/^{204}\text{Pb} > 38.74$ (Figure 4). This highly radiogenic feature of the leads is comparable with those of the sediments in intracontinental basins elsewhere in the world (Doe and Zartman, 1979). Lead in the Nanling Mountain region is presumably ultimately derived from the basement rocks which sourced the metasedimentary package, though to date there are no isotopic analyses of the putative source rocks.

In the light of the fractionation between the $^{238}\text{U}/^{204}\text{Pb}$ and the $^{232}\text{Th}/^{204}\text{Pb}$ ratios during the evolution of continental crust (Doe and Zartman, 1979), the less radiogenic lead in the Lower Yangtze region, particularly the strong depletion of uranogenic with less depletion of thorogenic lead of the Qixiashan mine (Figure 4), may indicate that a significant portion of the lead in that region was derived from the Precambrian basement to the Palaeozoic basin or from a much deeper source in the continental crust. Thus it is not surprising that the single-stage model ages (Gu et al., 1993) are much older than the host strata of the ores.

If it were the case, as seems likely, that the leads in the ores were derived from various sources besides the mantle, the single-stage model ages may represent the youngest limit of their separation time from the U-Th-Pb system. It follows that the leads might have been separated from their radiogenic source earlier than is indicated by their model ages. If so, the concordant model ages as well as the older-than-mineralization ages (Gu et al., 1993) may be taken to imply that considerable proportions of the leads (normal and B-type leads) in both the Lower Yangtze and the Nanling Mountain regions were derived from the rocks beneath the Upper Palaeozoic sedimentary horizons that host the ores in the basins. In particular, the B-type ages of the Qixiashan mine

indicate a principal source region deep in the Precambrian basement. The J-type lead which gives younger-than-mineralization ages (Gu et al., 1993) might have been transferred to the ores either during the sedimentary/diagenetic processes or by post-diagenetic fluids from more radiogenic sources.

Fluid features

Analyses of fluid inclusions in sulphides and other associated minerals (Table 2 and Figure 5) show a low K^+/Na^+ ratio (<1) but higher temperature and salinity for the samples from the Lower Yangtze region than those from the Nanling region ($\text{K}^+/\text{Na}^+ > 1$). Although fluid inclusions could have been formed during diagenesis and hence may not indicate the exact physico-chemical parameters of either the ascending sub-seafloor fluids or the submarine brines, it may still reflect the differences of fluid property and ore-forming environment in the two regions. The potassium-rich nature of inclusion fluids in the Nanling Mountain region is reminiscent of those from the modern sulphide deposit in the Okinawa Trough, which were interpreted by Urabe and Marumo (1991) to have been formed by the reaction of the fluids with underlying potassium-rich volcanic rocks.

The higher K^+ contents in fluid inclusions of the Nanling Mountain region are consistent with the chemistry of the orebodies at least in one case. For example, Han and Hutchinson (1989) reported a thin layer of orthoclase as an exhalative product in the tin-bearing massive sulphide deposit at Dachang, Guangxi Province.

Table 3 presents a general comparison of the features for massive sulphide deposits between the Lower Yangtze and the Nanling Mountain regions.

Crustal maturity of the two regions

We have demonstrated above that contrasts exist in ore metals, isotope compositions, ore-forming temperatures and fluid properties between the Upper Palaeozoic massive sulphide deposits of the Yangtze and the Nanling Mountain regions. These contrasts can be well elucidated in terms of variations in maturity of the continental crust upon which deposits of these two regions were formed, although the Nanling deposits show a stronger bacteria activity during their formation.

Crustal maturity is defined by He and co-workers (1989) as the extent to which the crust approaches its final product—stable continental crust during its course of formation and evolution.

The deformed and metamorphosed basements underlying the sedimentary basins in which the massive sulphide ores in the Lower Yangtze and the Nanling Mountain regions were formed comprise the Proterozoic and the Caledonian successions, respectively. Geological features of the basements show that these two regions were different in crustal maturity during the Upper Palaeozoic time.

Table 3 Comparison of the features between massive sulphide deposits in the Lower Yangtze and the Nanling Mountain regions.

Region	Lower Yangtze	Nanling
Ore-hosting strata	M. Carboniferous	Mainly M. & U. Devonian
Basin basement	M. & L. Precambrian	Caledonian
Crustal maturity	lower	higher
Major economic metals	Cu, Zn, Pb	Zn, Pb, Cu, Sn
Associated metals	Au, Ag, Co, Mo	Ag, Sb, Hg, W, U, Bi, Tl, Mo
Ore-forming temperature	Higher	lower
Fluid salinity	Higher	lower
Fluid composition	sodium-rich	potassium-rich
$\delta^{34}\text{S}\text{‰}$	close to zero	close to zero, very positive or negative,
Sulphur source	from basement	from basement $\pm$ bacteriogenic sulphur
Radiogenic lead	lower	higher

Figure 6 Contrasting genetic models for the Lower Yangtze (upper) and the Nanling Mountain (lower) basins.

An essential indication of crustal maturity is given by the characteristics of igneous activity, especially by the $K_2O/(CaO+Na_2O)$ ratios of intrusive rocks (Brown et al., 1984; He et al., 1989). The basement for the Lower-Upper Palaeozoic ore-hosting marine basin of the Lower Yangtze region is composed of a succession of Middle and Late Proterozoic eugeosynclinal flysch with significant amount of spilitic-keratophytic volcanic rocks. These basement rocks crop out in the Zhangbaling area to the north of the Lower Yangtze basin and are thought to have been formed in a back-arc environment (Guo et al., 1980). Some Late Proterozoic intrusives have also been found in the Feidong area, which are dioritic and quartz dioritic in composition (Chang et al., 1991). All these igneous rocks are characterized by $K_2O/Na_2O < 1$. No Caledonian granitic intrusions have been found in the Lower Yangtze region. These features can be regarded as evidence of lower maturity of the continental crust beneath the Upper Palaeozoic Lower Yangtze basin. In contrast, the Caledonian geosynclinal successions of the Nanling Mountain region are composed of greywackes, flysches and flyschoids with a total thickness of more than 10 km. Only insignificant occurrences of volcanic intercalations have been reported in this region (DGNU, 1981). Of these, the andesites, dacites and rhyolites at Mashan in the Guangdong Province have $K_2O/Na_2O > 1$ (Yang, 1987). Caledonian deformation, metamorphism, migmatization and granite intrusion are widespread in the Nanling Mountain region. Late Caledonian granites have average contents of K_2O and Na_2O totaling 7.10 wt%, and an average K_2O/Na_2O ratio of 1.5. Together they comprise a suite evolving towards two-mica granites (DGNU, 1981). These features suggest that the Caledonian basement underlying the Upper Palaeozoic basins of the Nanling Mountain region had higher maturity than that beneath the Lower Yangtze region. He et al., (1989) suggested that the present crustal thickness is also an indicator of crustal maturity. The present crust thickness in the Nanling Mountain region is 34–37 km (Guo et al., 1982; Huang, 1992), whereas in the Lower Yangtze region it is only about 25 km (Yun et al., 1983). Based on the fact that these two regions have similar geological histories since Upper Palaeozoic time, we suggest that the crustal thickness and hence crustal maturity in the Nanling Mountain region was greater than those in the Lower Yangtze region during the development of the ore-forming Upper Palaeozoic basins.

Although no systematic data are available on trace element abundances of the two crustal segments, preliminary research revealed a higher uranium content of the upper crust in the Nanling Mountain region than that in the Lower Yangtze region (Zhang et al., 1993). This would also imply a higher crustal maturity in the Nanling Mountain region and is comparable with the trace element model proposed by Brown and co-workers (1984).

Xu and his colleagues (1982) classified the Mesozoic granites in South China into the syntaxis- and the transformation-types, which are loose equivalents to the I- and S-types of Chappell and White (1974). Large numbers of granite bodies of the Lower Yangtze and the Nanling Mountain regions are typical I- and S-types, respectively, implying that these two regions might have inherited and even intensified their Upper Palaeozoic differences in crustal maturity during the Mesozoic time.

Discussion and conclusions

According to the contrasting metal and isotope compositions and fluid features of the ores in the two regions, we would suggest that they may have different metal-fluid sources and genetic models. A considerable amount of the ore metals and fluids in the massive sulphide deposits of the Lower Yangtze region could have been derived from the Precambrian basement. The ore-forming fluids were driven up along deep faults to the seafloor without significant contamination from cool and low-salinity sea water during their ascent (Figure 6). In contrast, metals and sulphur in the massive sulphides of the Nanling Mountain region could have been leached mostly from the Caledonian basement. The ore-forming fluids may largely originate from geothermally driven convecting sea-water of low temperature and salinity (Figure 6). Recent research (Lewis et al., 1995; Russell et al., 1995) has suggested that hydrothermal convection is a process that may readily occur throughout the upper crust in which cells form with or without specific structural control. A calculation (cf. Russell, 1968) has been made to estimate the volume of the source rocks in the Caledonian basement that supposedly supplied metals during leaching for the 1.7 Mt Pb and 3.4 Mt Zn of the Fankou deposit. Based on the average concentrations of 20 ppm Pb and 90 ppm Zn for the basement of the Nanling region (Yu et al., 1987), and assuming that the basement rocks had special gravity of 2.6 g/cm³ and that 10% of the lead was leached from the source, the result shows that a source volume of some 320 km³ should have been involved in the convection cell. Further calculation suggests that 4.4% of the zinc might have been leached from the same source for the formation of the ore in that deposit.

As basement composition is an essential indication for crustal maturity, we will be able to establish the connections between the features of massive sulphides and the maturity of the continental crust during ore formation, and thereby account for the compositional contrasts of the ores between these two regions:

Copper, gold and cobalt appear to have higher concentrations in more mafic rocks (Graf, 1977; Hutchinson, 1990), and hence, these metals are enriched in lower-maturity crust such as in the Lower Yangtze region. The Precambrian chlorite schists of the Pichen group, which is locally exposed about 70 km east to Nanjing and is thought to represent the basement under the Lower Yangtze Palaeozoic basin, have average contents of 106 ppm Cu and 6.2 ppb gold (Li et al., 1997). Based on the analyses of residual enclaves of Precambrian amphibolites and schists inside a granite body at Tongling, Du (1999) suggested that the basement metamorphic rocks have an average content of 373 ppm Cu. Therefore, the basement rocks of the Lower Yangtze region were likely sources of these metals and sulphur.

By contrast, lead, zinc, silver, uranium, bismuth, antimony, mercury, fluorine and boron are relatively enriched in more felsic rocks (Hutchinson, 1990; Liu et al., 1984) and hence in the higher-maturity crust such as in the Nanling Mountain region. The Lower Cambrian carbonaceous sediments in South China commonly have

anomalously high uranium contents up to several ppm (Zhang et al., 1993). Yu et al., (1987) have reported that the average bismuth contents in the Sinian, Cambrian and Ordovician strata in the Nanling Mountain region are 2.2, 1.9 and 2.9 times, respectively, the values given by Taylor (1964) for the continental crust. The Sinian, Cambrian and Ordovician-Silurian sediments in central Hunan Province have average antimony contents of 214, 72 and 23 ppm, respectively (Tu et al., 1984). Mercury contents of the Cambrian sediments are generally higher than 0.2 ppm in the Wanshan area of East Guizhou Province (Tu et al., 1984).

The hydrothermal convection through the potassium-rich Caledonian basement in the Nanling Mountain region produced ore-forming fluids with higher potassium content than those in the Lower Yangtze region (Table 5). Thallium and barium, like lead, have similar geochemical features to potassium, therefore they tend to enter the lattice of K-feldspar. As a result, thallium and barium are also apparently enriched in the matured crust that has high potassium content. This is in accord with the high thallium contents of the sulphide ores and the widespread exhalative barite deposits in the Nanling Mountain region. The large influx of seawater into the sub-seafloor convecting systems of the Nanling Mountain region resulted in high concentrations of sulphate sulphur and lower temperature (<250°C) and salinity of the circulating fluids, as is suggested from the isotope and fluid inclusion data of their ores. Bacteria are likely to have played an important role in the reduction of seawater sulphate and, to some extent, in the fixation of some metals. The close association of silver, uranium, antimony and mercury with lead and zinc can be accounted for not only by their higher abundances in sedimentary successions of the Caledonian basement, but also by their relatively higher stability in medium to low temperature ore-forming fluids in the Nanling Mountain region.

Tungsten and tin are two characteristic elements enriched in the continental crust in South China (Gu et al., 1990, 1992; Hutchison and Chakraborty, 1979). It was reported that some argillaceous and clastic horizons of the Lower Palaeozoic successions in the basement of this region have primary enrichment of 50-500 ppm tungsten (Liu and Ma, 1987) and 10-40 ppm tin (Xian, 1984). Consequently, it is not surprising that these two metals are strongly enriched in the massive sulphide deposits associated with matured continental crust such as in the Nanling Mountain region. The higher contents of radiogenic lead in the Nanling Mountain massive sulphide deposits are consistent with the common knowledge that matured continental crust is usually higher in radiogenic lead (Doe and Zartman, 1979).

In addition to sub-seafloor leaching by the convecting fluids of terrigenous sediments fed from the surrounding post-Caledonian lands, the characteristic elements of the continental crust could have been transported to the massive sulphide ore bodies by later-stage magmatism and relevant hydrothermal activities (cf. Gu et al., 1993). Many of the Upper Palaeozoic massive sulphide layers were intruded by Mesozoic granites of the syntaxis-type in the Lower Yangtze region and the transformation-type in the Nanling Mountain region (Xu et al., 1982; Gu, 1987b; Zhou et al., 1987). Since the localisation of the massive sulphides and the granites were controlled by the same regional faults, the magmas are thought to have intruded through the same tectonic pathways as the earlier sub-seafloor hydrothermal systems. Crustal materials could have been involved in Mesozoic magmas during partial melting or assimilation and then superimposed on to the massive sulphide layers during post-magmatic processes (Gu et al., 1993). Magmatic hydrothermal mineralisations on the contact zones between granites and the Upper Palaeozoic ore layers are dominated by copper in the Lower Yangtze region, such as those at Wushan, Tongguanshan and Dongguashan (Gu, 1984; Gu et al., 1993), but in the Nanling region the magmatic hydrothermal mineralizations are characterized by tungsten and tin, such as those at Dabaoshan and Dachang (Liu and Zhou, 1985; Han et al., 1997; Lei, 1998). These overprinted mineralisations have resulted in the intensification of the compositional contrasts between massive sulphide ores of the two regions.

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