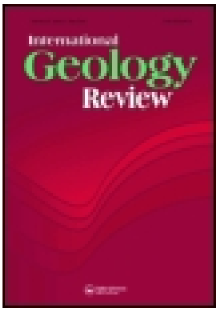

International Geology Review
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tigr20

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Version of record first published: 16 Jul 2010.

To cite this article: Christina Yan Wang, Mie-Fu Zhou, Liang Qi, Shuguang Hou, Hongguang Gao, Zhengwei Zhang & John Malpas (2006): The Zhaotong Native Copper Deposit Associated with the Permian Emeishan Flood Basalts, Yunnan, Southwest China, International Geology Review, 48:8, 742-753

To link to this article: http://dx.doi.org/10.2747/0020-6814.48.8.742

International Geology Review, Vol. 48, 2006, p. 742–753.

The Zhaotong Native Copper Deposit Associated with the Permian Emeishan Flood Basalts, Yunnan, Southwest China

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Abstract

The Zhaotong native copper deposit in Yunnan, Southwest China, is associated with the upper Middle Permian Emeishan flood basalts and is mainly hosted in the upper part of the Emeishan volcanic succession. Native copper mainly appears as disseminations in basaltic tuffs, and vesicular and brecciated tops of subaerial lava flows. Sheets of native copper up to 30 × 10 × 0.2 cm have also been found along fractures within the volcanic breccias. The native copper is associated with bitumen, zeolite, quartz, and calcite, typical of a low-temperature (100–150°C) hydrothermal alteration assemblage. The ore grades vary from ~0.1 to 20 wt% Cu. Copper was likely a result of organic-inorganic interactions under conditions of the paucity of reduced S.

Introduction

DEPOSITS DOMINATED by native copper are rare because reduced-S poor hydrothermal environments are not common. The best documented example is in the Keweenaw Peninsula, Michigan, USA (Butler and Burbank, 1929; White, 1968). The 1060–1047 Ma Keweenaw native copper deposit is hosted by the 1109–1085 Ma flood basalts of the Mid-Continental rift system (Bornhorst, 1997; Davis and Paces, 1990; Bornhorst et al., 1988; Ernst and Buchan, 2004). The native copper deposit in the Zhaotong area, Yunnan Province, Southwest China, is spatially associated with the late middle Permian Emeishan continental flood basalts (Fig. 1) and provides another example of native copper hosted by flood basalts. This paper presents the field relationships and petrographic observations of the Zhaotong native copper deposit in order to place some constraints on its origin.

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Geological Background

The geology of Southwest China consists of the Yangtze Block to the east and the Tibetan Plateau to the west. The Yangtze Block is composed of a crystalline basement known as the Kangding Complex (YBGMR, 1990). The oldest strata are the Proterozoic Kunyang Group, which host stratabound copper deposits (Ran, 1989), such as the Dongchuan and Yimen deposits in Yunnan Province (inset in Fig. 1). These two deposits have mineralization ages of 780–640 Ma (Ar–Ar) and 879 Ma (Pb–Pb), respectively (Zhu et al., 2000). The mineralization is considered to be related to 900–800 Ma mafic magmas that intruded into the Kunyang Group (Zhu et al., 2000).

A thick sequence of Sinian (Neoproterozoic) to Mesozoic strata lies above the basement of the Yangtze Block. The Sinian, Paleozoic, and lower Mesozoic strata are of shallow-marine origin. Permian strata include carbonate-rich rocks and the Emeishan continental flood basalts. Triassic strata include both continental and marine sedimentary rocks. Jurassic to Cretaceous strata are entirely

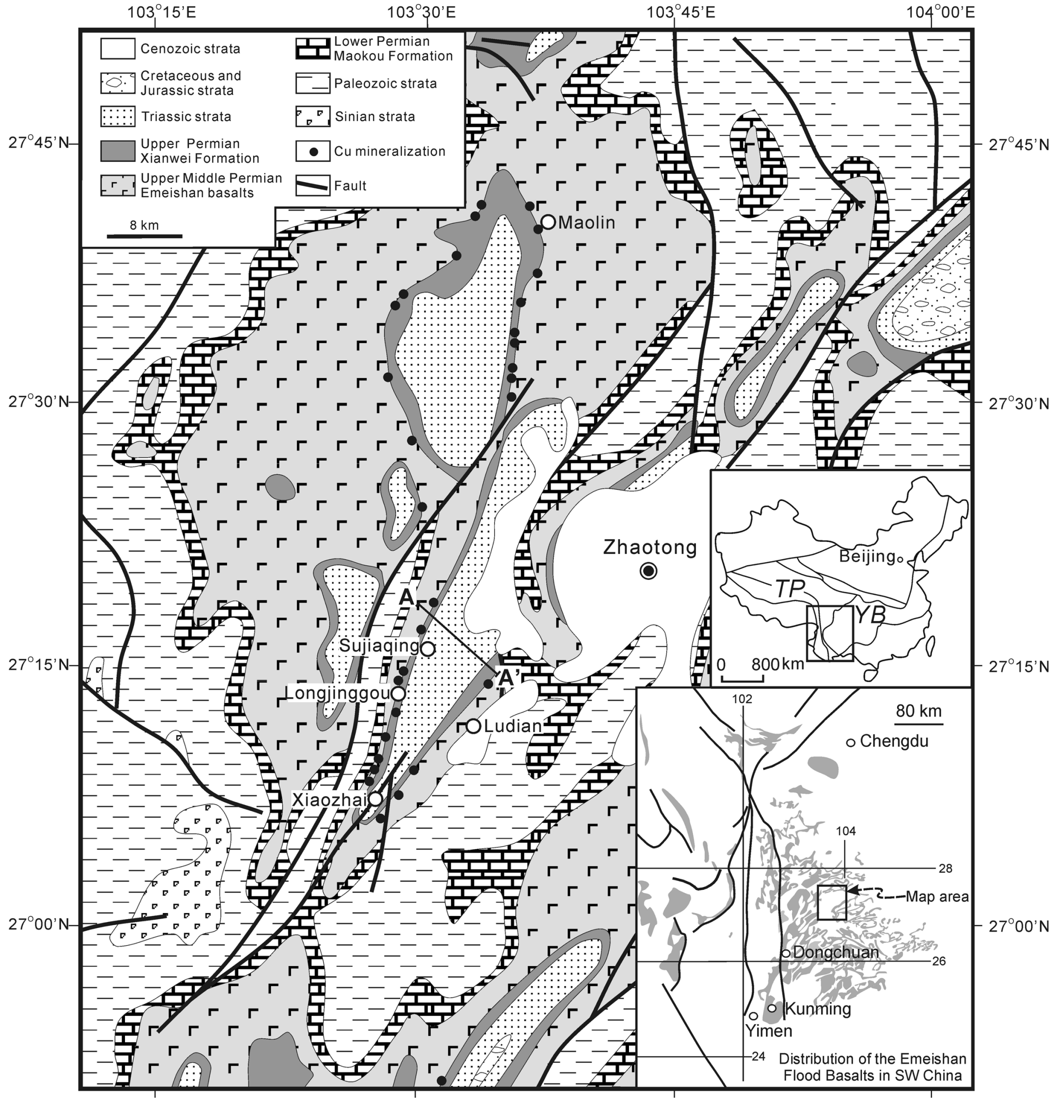

FIG. 1. Geologic map of the Zhaotong area, Yunnan Province, Southwest China, showing the distribution of copper mineralization areas. Abbreviations in the inset: TP = Tibetan Plateau; YB = Yangtze Block.

continental sedimentary rocks. All these rocks are deformed by a late Mesozoic northwest-directed overthrust system (Yan et al., 2003). Triassic (250–230 Ma) and Cretaceous (120–80 Ma) magmatic activity is widespread in the Yangtze Block (YBGMR, 1990).

The Emeishan flood basalts crop out over an area of more than 5×10^5 km^2 in Southwest China and northern Vietnam (e.g., Chung and Jahn, 1995) (inset in Fig.1), and are located in the western part of the Yangtze Block and the eastern margin of the Tibetan Plateau. The volcanic sequence ranges in thickness from several hundred meters up to 5 km, and contains mainly both high-Ti and low-Ti basalts.

In the Zhaotong region, northeastern Yunnan Province, the >1,000 m thick flood-basalt sequence consists of four mappable units separated by thin layers (<50 cm) of carbonaceous-tuffaceous sedimentary rocks. Each unit is basically composed of massive basaltic volcanic flows overlain by volcanic breccias and basaltic tuffs. The flood basalts are unconformably underlain by limestones of the Lower Permian Maokou Formation, and are conformably overlain by the Upper Permian Xuanwei Formation composed of sandstone, mudstone and conglomerate with interbedded coal seams. The coal seams indicate a fresh or saltwater lake with a coal-bearing swamp depositional environment. The Xuanwei Formation, in turn, is overlain by the sandstone and mudstone of the Triassic Feixianguan Formation. Above the Feixianguan Formation, the Yongningzhen Formation is composed of limestone interbedded with mudstone and sandstone.

A series of synclines with NE-striking axes is present in the Zhaotong area (Fig. 1). These synclines are part of the Mesozoic overthrust fault system within the Yangtze Block (Yan et al., 2003), and consist of Triassic strata in the cores and Permian strata in the limbs.

Field Relationship of the Zhaotong Native Copper Deposit

There are more than 30 native copper occurrences in the Zhaotong area, occurring in the limbs of the Xiaozhai and Maolin synclines (Fig. 1). These folds consist of Triassic sedimentary rocks in the core and the Permian Xuanwei Formation and Emeishan flood basalts in the limbs. A cross section of the Xiaozhai syncline is illustrated in Figure 2. The northwest limb of the syncline dips 30–48°S, whereas the southeast limb dips 20–37°N. Copper mineralization occurs in Unit 4 of the Emeishan flood basalts as shown in the stratigraphic column in Figure 3. Five subunits can be recognized in Unit 4; from bottom to top, they are: lower basaltic tuffs (8 to 10 m in thickness), multiple basalt flows (50 to 130 m), middle basaltic tuffs (2 to 11 m), massive basalts (37 to 70 m), and upper basaltic tuffs (0.5 to 9 m). The multiple basalt flow subunit includes five to seven subaerial lava flows, each of which, from bottom to top, consists of massive, vesicular, and brecciated basalts.

The uppermost part of the lower basaltic tuffs is mineralized, with a 0.2 to 3.3 m thick layer in which mineralization is associated with carbonaceous mudstone. Each lava flow top in the multiple basalt flow subunit is mineralized. Cu mineralization in the middle basaltic tuffs also occurs in the uppermost 5 m. Rare Cu mineralization occurs in the massive basalts and the upper basaltic tuffs.

Detailed exploration is currently being carried out for two of the native copper occurrences in the Xiaozhai syncline. One occurrence, hosted in the vesicular lavas of multiple basalt flow units, is about 1500 m in strike length, with an average thickness of 4 m. Its estimated Cu reserve is 18,000 tonnes of Cu mineralization at an average grade of 2 wt% Cu. The other occurrence is hosted in the lower basaltic tuff unit and is about 500 m in strike length, with an average thickness of 10 m. Its estimated reserve is 16,000 tons of Cu mineralization at an average grade of 1.5 wt% Cu (Zhu et al., 2003). Mineral resources have not yet been estimated for other native copper occurrences in this region.

Petrography

Native copper appears in various shapes in the Zhaotong deposit. Network-like native copper is spatially associated with chalcocite in carbonaceous mudstones and silicified wood in the uppermost part of the lower and middle basaltic tuffs (Figs. 4A and B). Sheets of native copper are associated with quartz and bitumen in fractures within volcanic breccias (Figs. 4C–4E). The largest sheet that has been found to date is about 30 × 10 × 0.2 cm.

Abundant native copper occurs in vesicular basaltic lavas (Figs. 4F–4H). Native copper occurs as disseminations in amygdules and adjacent lavas (Figs. 5A and 5B), and has a dendritic shape in the lavas in backscattered electron (BSE) images (Fig. 6A). Native copper also occurs in quartz veinlets within the vesicular lavas (Figs. 5C and 5D), and a few grains can be as large as 1 × 3 mm in size (Fig. 5E). Native copper is associated with zeolite, bitumen, quartz, calcite, and chlorite as partial fillings of amygdules in the tops of lava flows, and is partially or completely surrounded by quartz or calcite grains (Fig. 5F). Native copper has either irregular shapes (Fig. 5G) or elongated fillings along fractures in the amygdules (Fig. 5H). Native copper grains in amygdules do not contain inclusions, as shown in the BSE images (Figs. 6B–6D). A close spatial relationship exists between native copper and bitumen in the Zhaotong deposit (Fig. 4D). Native copper typically occurs as thin selvages partially or completely surrounding and commonly cutting bitumen (Figs. 5H and 6C).

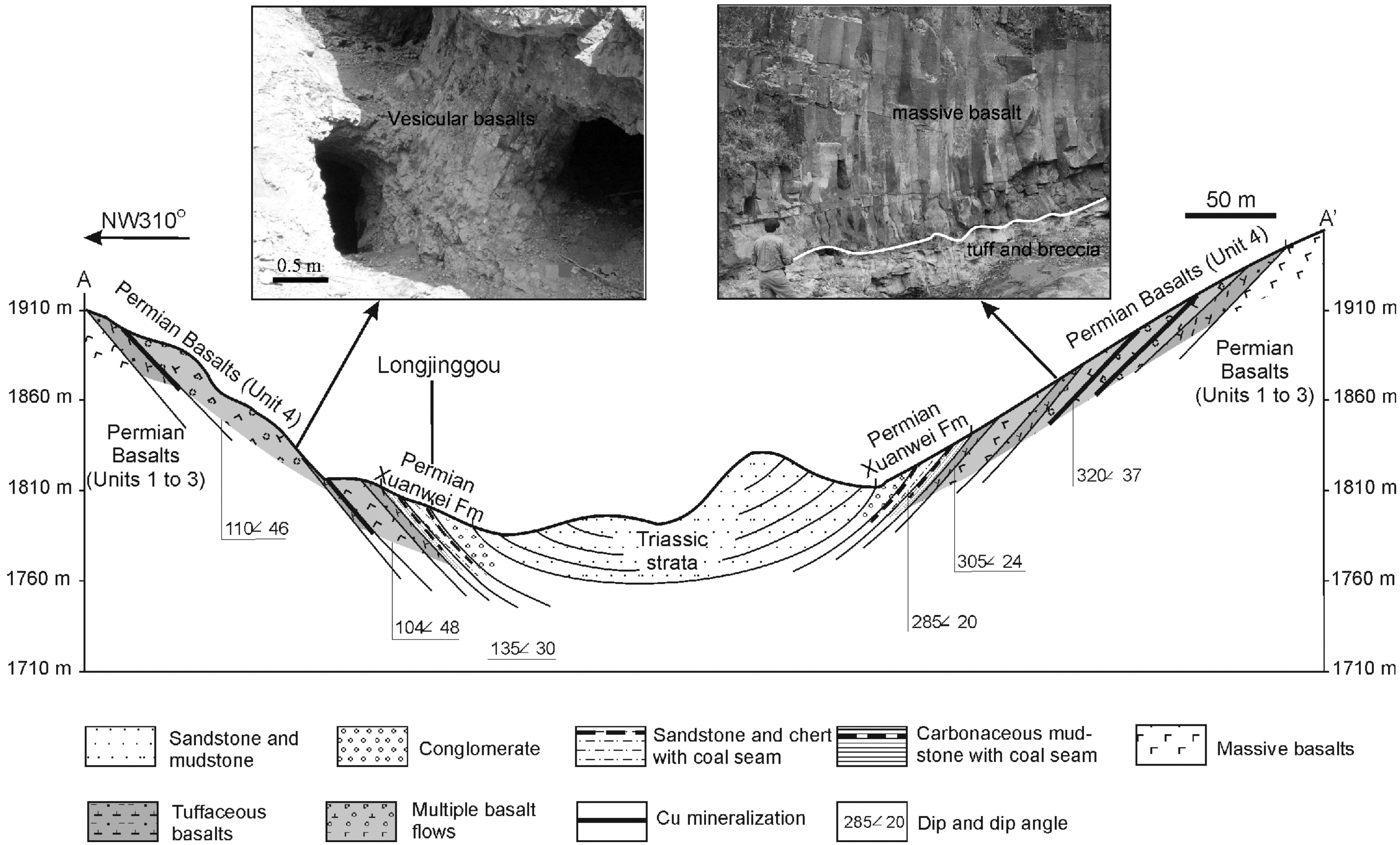

FIG. 2. Cross section showing the Xiaozhai syncline that hosts Cu mineralization.

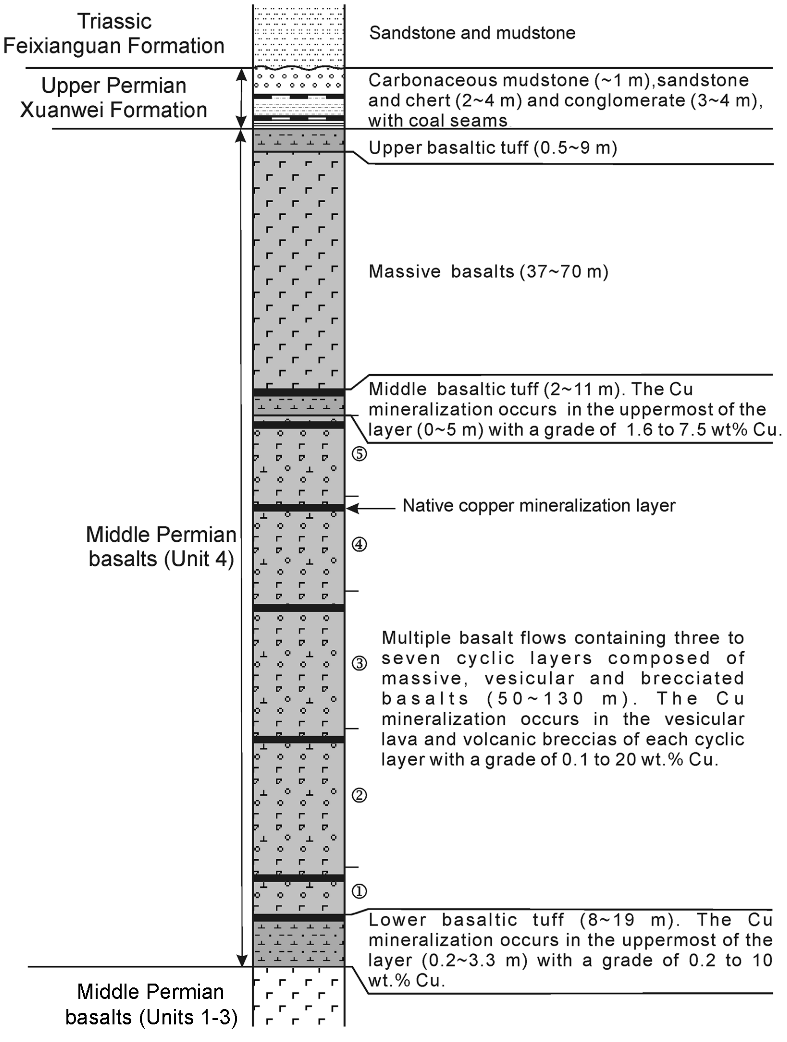

FIG. 3. Stratigraphic column showing native copper mineralization in the strata.

Sample Preparation and Analytical Methods

Because the native copper is highly variable in terms of mineral abundances, and the host basalts contain abundant amygdules with variable amounts of zeolite, bitumen, calcite, quartz, and chlorite, bulk analyses of the basalts do not have much significance. We carried out trace element and PGE analyses of pure native copper separates from the ores. We also analyzed the PGE of the massive basalts in this region for comparison. Trace element and PGE analyses were performed using a VG Plasma–Quad Excell Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at the University of Hong Kong. For trace-element analyses, native copper separates were dissolved using HNO_3. The ICP multi-element standard solution from Accu Standard Inc (USA) was used for external calibration. Indium was used as internal standard to correct for matrix effects and instrumental drift. Reproducibility is generally better than 5%.

For PGE analyses, 500 mg of native copper separates together with isotope spikes were digested in a sealed Carius tube in a steel container for about 10 hours at 220°C and then evaporated to dryness in a beaker. The residue was dissolved in 0.5 ml aqua regia and diluted in 10 ml water before separating PGEs from Cu in a cation exchange column (Dowex,

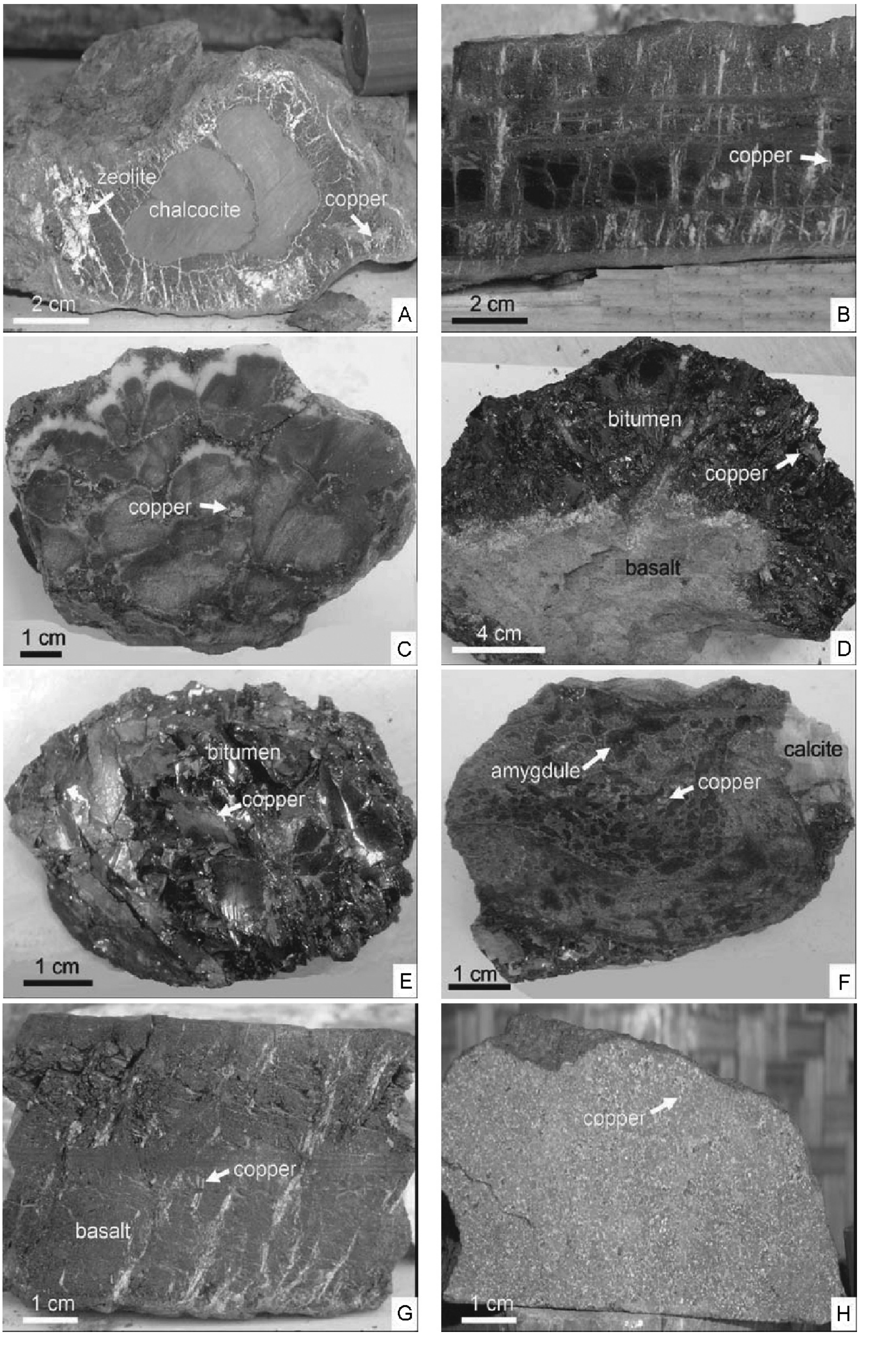

FIG. 4. Hand specimens of native copper. A. Network-like native copper and chalcocite in carbonacous mudstone. B. Native copper in silicified wood. C. Native copper in the cracks of the volcanic breccia, hematite as thin red borders around detrital grains. D and E. Native copper sheets associated with bitumen. F, G and H. Disseminated native copper in vesicular basaltic lavas.

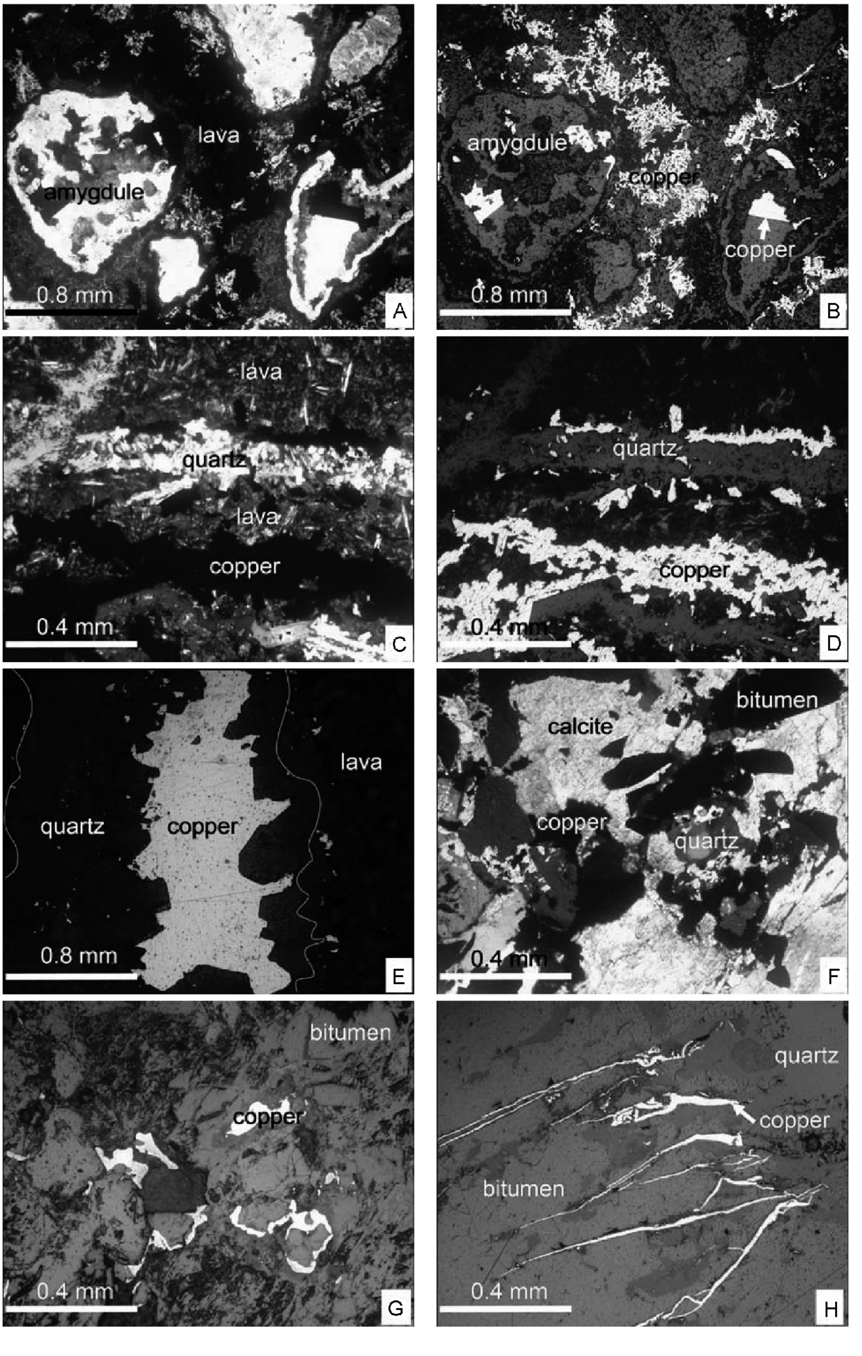

FIG. 5. Photomicrographs of native copper–bearing basalts. A and B. Vesicular lavas showing native copper filling amygdules and as disseminations in the adjacent lavas. (A. Plane-polarized, transmitted light. B. Reflected light). C and D. Disseminated native copper in quartz veinlets (C. Cross polars, transmitted light. D. Reflected light). E. Large native copper grain in quartz veinlets, reflected light. F and G. Native copper as fracture-fillings in amygdules (F. Cross polars, transmitted light. G. Reflected light). H. Elongated native copper filling open cracks in bitumen, reflected light.

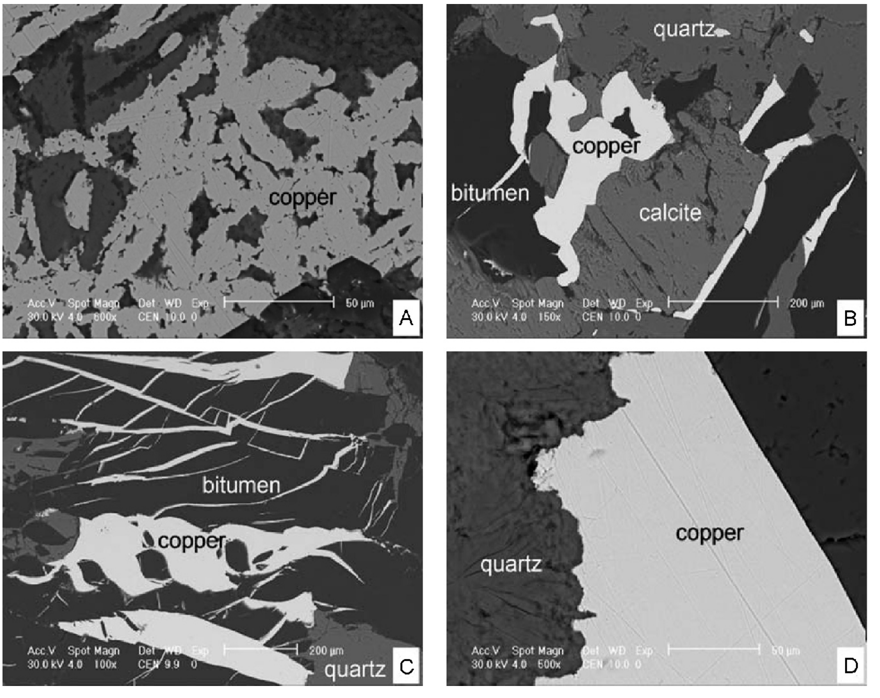

FIG. 6. BSE images of native copper. A. Dendritic native copper. B, C, and D. Granular and elongated native copper associated with bitumen in amygdules and quartz veinlets.

50wx 8, 200 to 400 mesh). The solution containing the PGEs (recovery >95%) was used for ICP-MS measurements.

PGEs in basalts were measured by isotopic dilution ICP-MS using a modified Carius tube method. Twelve grams of the samples were digested with 30 ml aqua regia in a 75 ml Carius tube, which was placed in a custom-made high-pressure autoclave. The solution was preconcentrated for PGE by Te-coprecipitation, as described in previous work (Qi et al., 2004). The total procedural blank was lower than 0.003 ppb for Ru, Rh, and Ir, 0.020 ppb for Pd, and 0.011 ppb for Pt.

Analytical Results

Trace-element and PGE contents of the native copper separates are listed in Table 1. The native copper contains 130 to 420 ppm Ag, 112 to 1117 ppm As, 0.61 to 97 ppm Ni, 0.06 to 191 ppm Cr, and 0.28 to 20.4 ppm Zn. Native copper is depleted in Ir (<0.37 ppb) and relatively enriched in Pd (2.86 to 32 ppb) and Pt (1.33 to 10 ppb), with a positive slope in PGE plots normalized to the primitive mantle (Fig. 7). The Pt/Pd ratios range from 0.1 to 1.8, and Pd/Ir ratios from 48 to 363. However, the massive basalt in this region appears to have less variation in PGE contents than the native copper. The massive basalts have Pt ranging from 7.9 to 9.5 ppb, and Pd ranging from 8.5 to 14.3 ppb. The Pt/Pd ratios of the massive basalts vary from 0.6 to 0.9, and Pd/Ir ratios from 69 to 117.

Discussion

Hydrothermal origin of the Zhaotong native copper deposit

Native copper in the Zhaotong native copper deposit mainly occurs as disseminations in amygdule and fracture-fillings within the tops of subaerial basalt flows (Figs. 4, 5, and 6). Native copper is spatially associated with zeolite, bitumen, quartz, calcite, and chlorite in the amygdules of lavas, an assemblage of low-temperature (100–150°C) hydrothermal minerals. Abundant silicified wood (Fig. 4B) is additional evidence for low temperatures; to the extent that bacterial sulfate reduction was

TABLE 1. Trace-Element and PGE Analyses of Pure Native Copper Separates and Massive Basalts from the Zhaotong Native Copper Deposit, Yunnan, Southwest China[1]

Sample no.:	GZ-83-1	GZ-83-2	GZ-84-2	SJQ-1	SJQ-2	SJQ-3	SJ-1	SJ-2	SJ-3	SJ-4	LJ-1	LJ-3	LJ-5	LJ-6	LJ-8-1	LJ-8-2	LJ-9	WGB-1	
Types	Native copper separates												Massive basalts					Gabbro	
Location:	Sujiaqing										Longjinggou		Zhaotong					Meas.	Recomm.
Trace elements, ppm																			
Ag	177	187	420	217	167	276	143	130	147	156	151	146							
As	580	594	327	613	693	650	336	137	392	165	1013	1117							
Cr	0.07	3.98	116	0.06	191	102	0.66	0.66	0.46	3.9	0.06	0.89							
Zn	0.28	13.6	11.6	4.8	13.6	20.4		0.41	1.7	1.5	0.31	10.0							
Ni	4.72	8.21	64	2.1	97	55	1.41	1.25	0.80	0.61	6.14	5.10							
PGEs, ppb																			
Ir	0.03	0.14	0.10	0.14	0.23	0.37	0.10	0.07	0.05	0.08	0.05	0.08	0.12	0.10	0.11	0.16	0.12	0.16	0.33
Ru	0.48	0.50	0.35	0.89	0.89	1.13	0.19	0.23	0.18	0.27	0.43	1.27	0.04	0.04	0.04	0.04	0.05	0.13	0.3
Rh	0.31	0.32	0.07	0.10	0.15	0.28	0.07	0.08	0.08	0.05	0.06	0.15	0.55	0.55	0.85	0.63	0.75	0.20	0.32
Pt	10.0	4.52	1.33	3.65	1.60	4.55	4.18	1.60	1.78	1.51	2.06	2.27	8.19	7.91	9.48	9.06	9.38	6.34	6.1
Pd	9.63	27.8	7.86	11.5	11.3	18.5	32.4	8.79	14.5	6.53	2.86	11.1	14.3	8.45	12.5	10.8	10.6	13.0	13.9

[1]Ag, As, Cr, Zn, and Ni contents of the massive basalts are not listed because they are lower than the detection limits.

active, the temperature is limited to under ~100°C (Rose, 1989).

There was extensive hydrothermal activity after eruption of the Emeishan basalts at 260 Ma (Zhou et al., 2002a). More than 400 Pb-Zn-(Ag) deposits, formed at about 230 Ma, have been found in the Emeishan large igneous province (Huang et al., 2003). These deposits are ~30 m.y. younger than the Emeishan flood basalts. Hydrothermal activity at ~230 Ma may have also been responsible for the formation of the Zhaotong native copper deposit. Fluids that formed the Pb-Zn-(Ag) deposits are thought to be related to the waning stage of Emeishan mafic magmatism (Huang et al., 2003). Triassic magmatism is well-documented in South China (YBGMR, 1990) and is another possible heat source. The precise timing of the native copper mineralization needs to be determined.

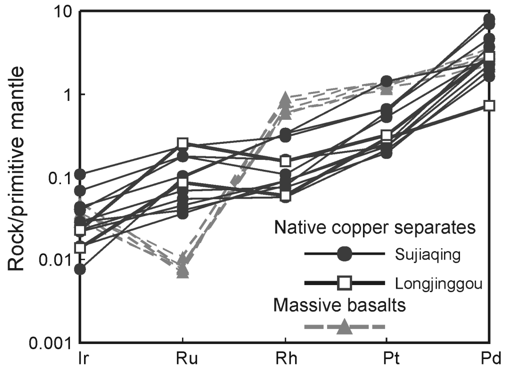

FIG. 7. Primitive mantle–normalized PGE plots of native copper separates and massive basalts from the Zhaotong area. Normalization values for Ir, Ru, Rh, Pt, and Pd are from Barnes and Naldrett (1987), and for Ni from Taylor and McLennan (1985).

Metal and bitumen sources

Besides widespread basaltic lavas in the Zhaotong area, abundant Permian diabase dikes are present in the mining area (Yang and Guan, 1994). Some intrusions in the region contain magmatic Cu-Ni-(PGE) sulfide deposits (Zhou et al., 2002b). The mafic-ultramafic rocks may have acted as the major source of metals, including Cu, Zn (Pb), V and possibly Cr and Ni.

Contacts between native copper and bitumen are sharp (see Figs. 5H and 6C). Bitumen has a wider

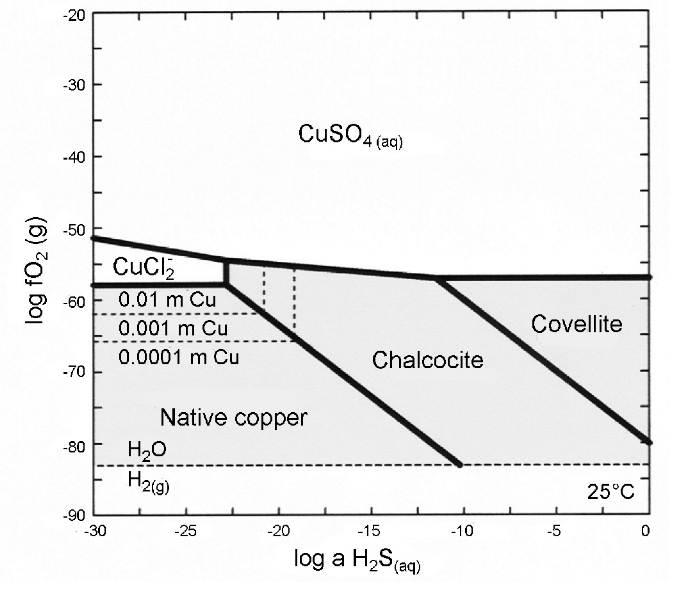

FIG. 8 Log fO_2–H_2S activity-activity diagram showing the predominant fields of copper minerals and aqueous species. The diagram is drawn at 25°C, but higher temperatures would do not change the qualitative interpretation. The pH is 5 and total chlorine activity is set to 1. The thermodynamic properties for aqueous Cu chloride complexes are from Liu et al. (2001); other aqueous species and minerals are from the Lawrence Livermore National Laboratory (LLNL) database (Wolery, 1992).

distribution than native copper, but only rarely is native copper found without bitumen. High-grade mineralization (e.g., 10–15 wt% Cu) is usually closely associated with bitumen in the rocks. Inasmuch as the Xuanwei Formation lies above the deposit, there is no obvious reason it should be the source of bitumen. Abundant silicified wood in the basaltic tuffs in the upper part of the flood basalts indicates that abundant plants had been buried with the eruption of the Emeishan flood basalts. These plants are suggested as a possible source of the bitumen.

Transportation and deposition of native copper

The most likely ore fluid for Cu transport is Cl-rich brines of intermediate redox state, in which Cu is carried as chloride complexes, e.g., $CuCl_2^-$ or $CuCl_{(aq)}$ (Liu et al., 2001). Hydrothermal fluid generated from mafic magmatism in the region could not transport significant Cu (with reduced S) below about 250°C (cf. Crerar and Barnes, 1976). Calculations based on log fO_2 and log $aH_2S_{(aq)}$ values indicate that native copper can form under reducing, S-poor conditions in an acid solution (pH = 5) with the total chloride activity set to 1 (Fig. 8). The following reactions were probably involved in the formation of the Zhaotong native copper deposit:

$$CuCl_2^- + C_{org} + 2H_2O = Cu_{(s)} + 2Cl^- + CO_2 + 4H^+,$$

$$\text{or } CuCl_2^- + CH_4 + 2H_2O = Cu_{(s)} + 2Cl^- + CO_2 + 8H^+.$$

Hence, the native copper mineralization is interpreted as related to organic-inorganic interaction.

Mobility of other chalcophile metals

The relatively high Ag and As but low Ni, Cr, and Zn in the Zhaotong native copper deposit is caused by different behavior of these elements during hydrothermal alteration of mafic-ultramafic rocks. The high Ag and As contents of the native copper suggest that both elements behaved similarly to Cu (Dryer, 1954; Stoiber and Davidson, 1959). Ni remained largely immobilized in the mafic-ultramafic rocks (White, 1968).

It is generally accepted that Pt and Pd are more mobile than the other PGE, and that Pd is more mobile than Pt in the near-surface environment (e.g., Cousins and Vermaak, 1976). In the Zhaotong deposit, Pd is enriched compared to Pt resulting in more variable Pt/Pd ratios (0.1 to 1.8 with an average of 0.3) of native copper than that of the massive basalts (0.6 to 0.9 with an average of 0.8) in the region.

Conclusions

The Zhaotong native copper deposit in Southwest China occurs in the upper Middle Permian Emeishan flood basalts. Native copper occurrences are associated with vesicular and brecciated tops of basaltic lava flows and basaltic tuffs. Native copper mineralization was a result of low-temperature hydrothermal activity in a reduced-S poor environment with strong organic-inorganic interactions.

Acknowledgments

This work was supported by an Outstanding Young Researcher Award from the National Natural Science Fund of China (Project No. 40129001 to MFZ), Natural Science Fund of Yunnan, China (Project No. 2003D0016Z to SGH), and a CRCG grant of the University of Hong Kong. We appreciate the help of Dr. W. H. Li of CSIRO in Australia for the calculation of the O_2 and H_2S activities of Cu minerals and Dr. D. P. Yan of China University of Geosciences for preparing the map. We are grateful to Drs. A. H. Hofstra, P. Emsbo, and D. Leach of the U.S. Geological Survey for their interest in this study and for providing insightful comments that helped to improve this paper.

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