Chemical Geology 347 (2013) 9–19

Contents lists available at SciVerse ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Re – Os and S isotopic constraints on the origins of two mineralization events at the Tangdan sedimentary rock-hosted stratiform Cu deposit, SW China

Xiao-Wen Huang [a,b], Xin-Fu Zhao [c,d,*], Liang Qi [a], Mei-Fu Zhou [d]

[a] State Key Lab of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] Faculty of Earth Resources, China University of Geosciences (Wuhan), Wuhan 430074, China
[d] Department of Earth Sciences, The University of Hong Kong, Hong Kong SAR, China

ARTICLE INFO

Article history:
Received 18 September 2012
Received in revised form 25 March 2013
Accepted 29 March 2013
Available online 8 April 2013

Editor: L. Reisberg

Keywords:
Re – Os isotopes
Sulfur isotopes
Sedimentary rock-hosted stratiform deposit
Kangdian region
South China

ABSTRACT

The Tangdan stratiform Cu deposit in the Kangdian region of South China is hosted in sedimentary rocks of the late Paleoproterozoic to early Mesoproterozoic Dongchuan Group. Orebodies mainly occur in dolostone and black shale above a thick sequence of hematitic sandstone and siltstone. Mineralization consists mainly of bedding-parallel stratiform ores, with minor amounts of discordant vein-type ores. Both stratiform and vein-type ores are composed of bornite and chalcopyrite with minor chalcocite and digenite, associated with gangue minerals including ankerite, dolomite, calcite, and quartz.

Cu-sulfides from vein-type ores contain ~122–293 ppb Re, much higher than those of stratiform ores (~0.6–14 ppb Re). They have highly radiogenic Os with Re – Os model ages ranging from 1413 to 1457 Ma and a weighted mean Re – Os model age of 1432 ± 19 Ma (2σ, MSWD = 0.30), which is within uncertainty in agreement with isochron ages of 1401 ± 30 Ma (2σ, MSWD = 0.67) and 1397 ± 71 Ma (2σ, MSWD = 0.22) using ^{187}Re/^{188}Os versus ^{187}Os/^{188}Os and ^{187}Re versus ^{187}Os regression, respectively. In contrast, sulfides from stratiform ores did not yield meaningful model ages due to the extremely low concentrations of Re and radiogenic Os. However, early studies have shown that the stratiform ores were likely formed at ~1700 Ma during the diagenesis of the host strata.

Sulfides from the vein-type ores have δ^{34}S values ranging from −15‰ to −8‰, significantly lower than those of stratiform ores (−3‰ to +10‰), suggesting that organic matter may have been involved in the formation of the vein-type ores. Contrasting Re – Os and S isotopes suggest that the two types of ores at the Tangdan deposit were likely formed from different ore-forming fluids. We propose that stratiform ores were precipitated from basinal fluids during the early evolution of the rift basin, whereas the vein-type ores were formed due to a much younger thermal event during which hydrothermal fluids interacted with overlying black shale to account for the high Re and negative δ^{34}S values. This study demonstrates that Re – Os isotopes of sulfides can be used to study the origin of hydrothermal system.

1. Introduction

Sediment-hosted stratiform copper (SSC) deposits occur generally at the contact between subaerial red-bed sequences and overlying marine or lacustrine shales, siltstones, sandstones, or carbonate rocks within sedimentary basins (e.g. Kirkham, 1989; Brown, 1997; Hitzman et al., 2010). SSC deposits are commonly considered to form during the entire evolutionary history of a rift basin. Several studies have documented that ore formation may postdate ore-hosting strata by up to hundreds of millions of years (e.g. Brown, 2005; Hitzman et al., 2005; Selley et al., 2005; Symons et al., 2011). However, precise dating of SSC deposits is difficult due to the lack of suitable phases that can be unequivocally linked to mineralization and that are suitable for traditional isotopic dating (e.g. U – Pb and Ar – Ar methods). Re – Os isotopic dating of sulfides, such as pyrite, bornite, chalcopyrite and chalcocite, may provide precise age determination for SSC deposits (e.g. Morelli et al., 2004; Tristá-Aguilera et al., 2006; Schneider et al., 2007; Selby et al., 2009). In addition to age dating, Re – Os isotopes of sulfide minerals may also provide useful information about the sources of ore components because different reservoirs may have various Re – Os isotopic compositions (Stein et al., 2000).

The Kangdian region of South China hosts numerous sediment-hosted, stratiform copper deposits in late Paleoproterozoic strata, commonly known as the “Dongchuan-type” in the Chinese literature (Gong

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* Corresponding author at: Faculty of Earth Resources, China University of Geosciences (Wuhan), Wuhan 430074, China.
E-mail address: xinfuzhao@gmail.com (X.-F. Zhao).

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http://dx.doi.org/10.1016/j.chemgeo.2013.03.020

and Wang, 1981; Hua, 1990; Sun et al., 1991; Chen and Ran, 1992; Gong et al., 1996; Zhao et al., 2012, 2013). These deposits have total ore reserves > 391 Mt at 1 wt.% Cu, making this region the third or fourth largest SSC province in the world (Zhao et al., 2012). The SSC deposits in the Kangdian region consist of both stratiform ores and discordant vein-type ores. The mineralization ages of the two types of ores, however, are poorly constrained and the sources of metals and ore-forming fluids have been matters of prolonged debate (review by Gong et al., 1996).

In this study, we report Re – Os isotopic compositions of chalcopyrite and bornite from both stratiform and vein-type ores of the Tangdan deposit, the largest SSC deposit in the Kangdian region. The new analyses yielded a reliable isotopic age for vein-type ores, indicating that they are much younger than the stratiform ores. In combination with the sulfur isotope data, the Re – Os isotope systematics also shed light on the sources of the ore-forming fluids, which have significant implications for ore genesis.

2. Geological background

The Kangdian region is situated in the western Yangtze Block. The Yangtze Block is separated from the North China Craton by the Triassic Qinling–Dabie–Sulu orogenic belt to the north and bounded by the Songpan–Ganze Terrane of the Tibetan Plateau to the west (Fig. 1a). To the southeast, the Yangtze Block is separated from the Cathaysia Block by a Neoproterozoic suture zone most likely formed at ~830 Ma (e.g. Zhou et al., 2009; Zhao et al., 2011).

Paleo- to Mesoproterozoic strata, including the Dahongshan, Kunyang and Dongchuan Groups, are widespread in the Kangdian region (Fig. 1b), and are considered to have formed in an intra-continental rift (Wu et al., 1990; Greentree and Li, 2008; Zhao et al., 2010). These strata are distributed along the Luzhijiang Fault and are bounded by a series of subordinate faults striking north to northeast (Fig. 1b).

Rocks of the Dongchuan Group are distributed discontinuously in a narrow belt more than 300 km long and less than 35 km wide (Fig. 1b). They consist of conglomerate, sandstone, dolostone, carbonaceous slate and minor tuffaceous volcanic rocks, which were weakly deformed and subjected to lower greenschist facies metamorphism during the Neoproterozoic (Wu et al., 1990). The Dongchuan Group is composed, from base upward, of the Yinmin, Luoxue, E'touchang and Luzhijiang Formations, all of which contain variable copper mineralization (Figs. 2 and 3) (Sun et al., 1991; Gong et al., 1996; Zhao et al., 2012).

The Yinmin Formation, the basal unit of the Dongchuan Group, is composed mainly of purplish-red, hematite-bearing sandstone and mudstone, with rhythmic sequences. Pseudomorphs of halite and anhydrite crystals have been identified in this zone, indicating an evaporite protolith (Hua, 1993; Xiong et al., unpublished report). Tuffaceous rocks from the Yinmin Formation have a LA-ICPMS zircon U – Pb age of 1742 ± 13 Ma (Zhao et al., 2010). The Luoxue Formation conformably overlies the Yinmin Formation and consists of thick-layered, gray-white dolostone and argillaceous to arenaceous dolostone. Dolostone of the lower Luoxue Formation contains abundant stromatolites (Gong and Wang, 1981; Wu et al., 1990) and has a Pb – Pb isochron age of 1716 ± 56 Ma (Chang et al., 1997). The E'touchang Formation is composed of carbonaceous slate with minor dolostone, siltstone, and tuffaceous rocks. The age of this formation is not well constrained, but an interbedded tuff unit of the Heishan Formation from the Dongchuan area, which is thought to be equivalent to the E'touchang Formation, has a zircon SHRIMP U – Pb age of 1503 ± 17 Ma (Sun et al., 2009).

There are only sparse Paleoproterozoic and Mesoproterozoic igneous rocks in the Kangdian region. In contrast, widespread Neoproterozoic igneous plutons have ages ranging from ca. 860 Ma to ca. 740 Ma (e.g. Zhou et al., 2002b; Zhao et al., 2008). They are composed of tonalite–trondhjemite–granodiorite (TTG) gneisses, granites, diorites and gabbros (Zhou et al., 2002a,b).

3. Sedimentary rock-hosted, stratiform copper deposits in the Kangdian region

Numerous SSC deposits are hosted in the rocks of the Dongchuan Group (Fig. 1b), and they include both stratiform and vein-type ores. Stratiform ores consist predominantly of bedding-parallel, disseminated, and/or veinlet Cu-sulfides, and are roughly concordant with the stratification, whereas vein-type ores are composed of massive or vein Cu-sulfides, quartz, and carbonate minerals along faults, fractures, and joints (Ran, 1989). Stratiform ores account for > 90% of the total copper reserves and have an average copper grade of ~1 wt.% (Xue et al., 1997). Vein-type ores only account for 3% to 10% of the total Cu reserves, but they commonly have higher grades of 5–10 wt.% Cu (Xue et al., 1997).

4. Geology of the Tangdan Cu deposit

Ore-hosting strata of the Tangdan deposit include the Yinmin, Luoxue, and E'touchang Formations of the Dongchuan Group (Figs. 2 and 3). In the mining district, the Yinmin and Luoxue Formations are cut by a fault to the southeast and covered by carbonaceous slates of the E'touchang Formation to the northwest (Fig. 2). The Dongchuan Group is unconformably overlain by Late Neoproterozoic carbonates (Fig. 2). The E'touchang and Luoxue Formations are intruded by a gabbroic body that has a pyroxene K – Ar age of ~1059 Ma (Gong et al., 1996) and a LA-ICPMS zircon U – Pb age of 1047 ± 3 Ma (Zhao, 2010).

The geology, mineralogy, and paragenesis of the deposit have been described by Zhao et al. (2012), and are only briefly summarized here. Stratiform ores are predominantly hosted in stromatolitic dolostone of the basal unit of the Luoxue Formation, but minor ores are also hosted in dolostone of the uppermost unit of the Yinmin Formation (Figs. 2 and 3). Vein-type ores mainly occur in the hanging-wall of the stratiform orebodies and less commonly in the footwall or in tectonic breccia zones. Copper-bearing quartz veins are also locally hosted in carbonaceous slates/black shales of the E'touchang Formation (Wang, 1984). Stratiform ores only occur in dolostones, whereas vein-type ores occur in both the dolostones and carbonaceous slates (Fig. 3).

Stratiform ores are composed of copper sulfide bands in the dolostones where they typically exhibit laminar, banded, horsetail and oolitic structures (Fig. 4a–d). Fine-grained sulfides are disseminated along bedding planes in the dolostone (Fig. 4a, b), forming more or less continuous to discontinuous laminar/banded structures. Densely disseminated copper sulfides in stromatolite form horsetail-like structures (Fig. 4c). Locally, copper sulfides coat ooids in the dolostone (Fig. 4d). Vein-type ores mostly consist of quartz, ankerite, and Cu-sulfides in tensional fractures (Fig. 4e-h) and stockwork zones (Fig. 4e, f), but locally develop massive structures (Fig. 4g, h).

Vein-type ores structurally crosscut stratiform ores, but they have similar mineral assemblages dominated by chalcopyrite and bornite, which may locally be replaced by chalcocite and digenite. In both types of ore, pyrite occurs as euhedral to subhedral crystals enclosed in chalcopyrite or country rock, and is locally replaced by late chalcopyrite and chalcocite (Fig. 5a, b). Chalcopyrite is intimately intergrown with bornite or partially replaced by bornite that is, in turn, replaced by digenite (Fig. 5d, e). Exsolution textures of chalcocite within chalcopyrite (Fig. 5f) and bornite suggest a hypogene origin for the chalcocite (Fig. 5g). However, most chalcocite is thought to be supergene in origin, commonly replacing chalcopyrite and bornite (Fig. 5h-i).

5. Analytical protocols

Five samples of stratiform ores and six of vein-type ores were collected from a tunnel at the 1770 m level in the Tangdan mine. Pure bornite and chalcopyrite separates (1 to 2 g) were handpicked under a binocular microscope after crushing and magnetic separation. Sulfide separates collected from the stratiform ores are generally smaller than

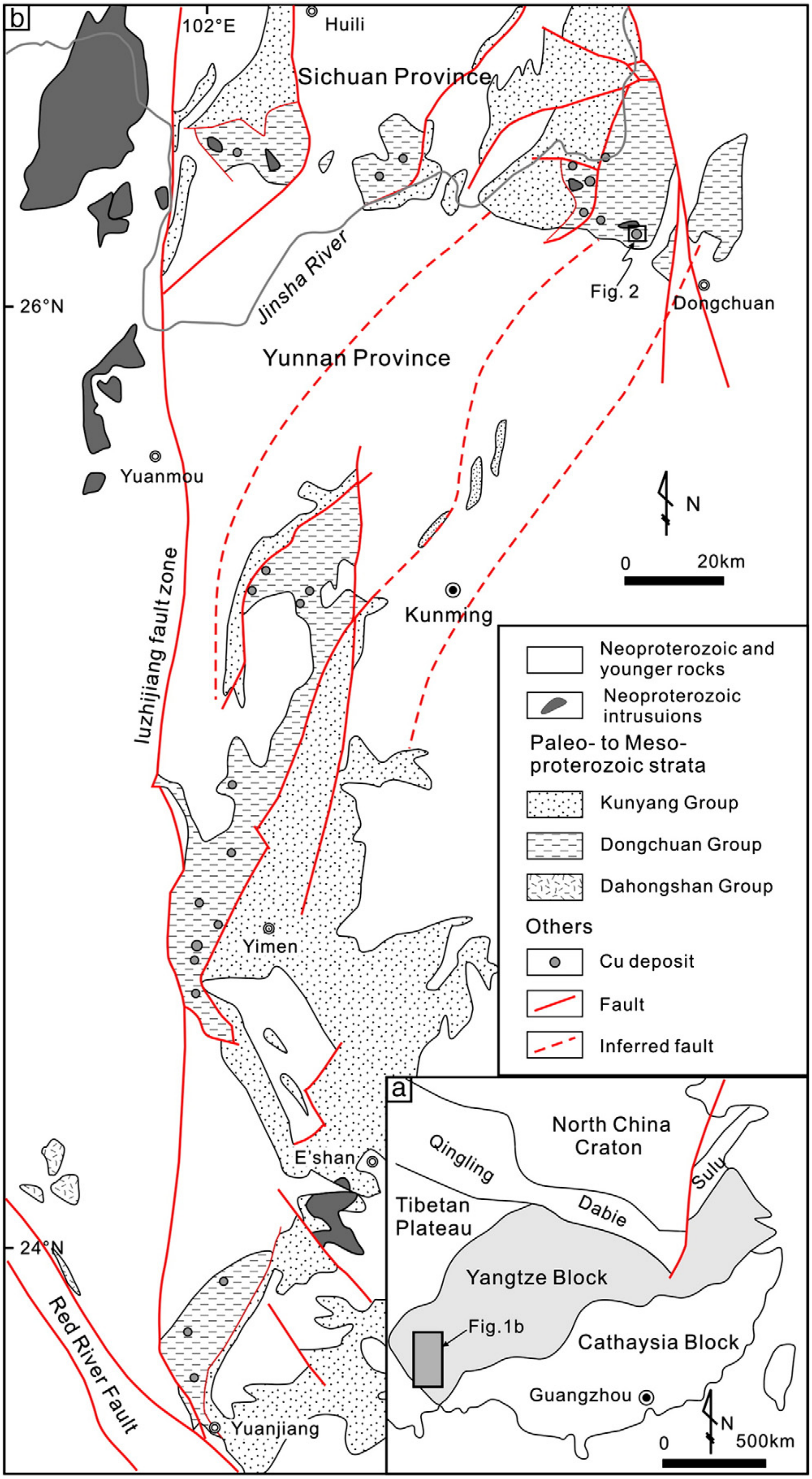

Fig. 1. (a) Simplified tectonic map showing the location of the Kangdian region in the Yangtze Block; (b) a sketch map showing the distribution of Precambrian strata and the SSC deposits in the Kangdian region, SW China (modified from Zhao et al., 2012).

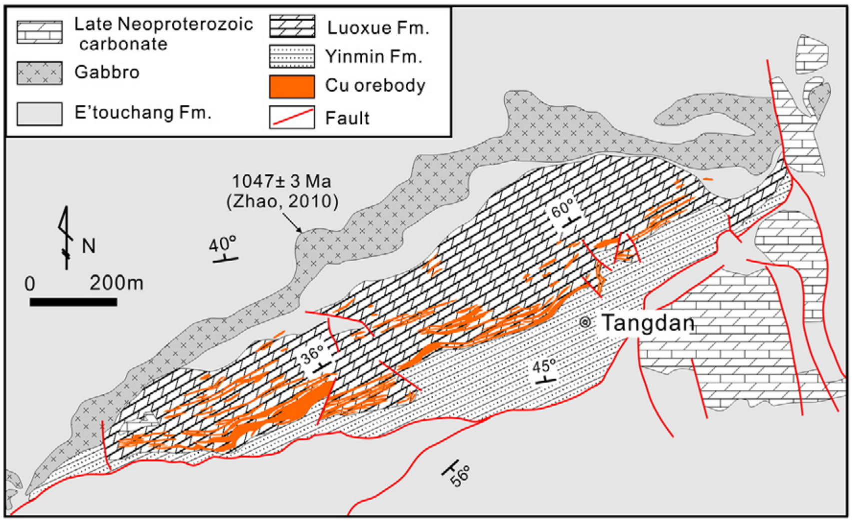

Fig. 2. Geological map of the Tangdan deposit (modified from Zhao et al., 2012).

100 mesh, whereas those from the vein-type ores are commonly smaller than 60 mesh.

5.1. Re–Os isotopes

Re–Os isotope analyses were performed at the State Key Lab of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. Samples of approximately 0.2 to 1 g of bornite or chalcopyrite were accurately weighed and loaded into a 120 ml Carius tube with known amounts of ^{185}Re and ^{190}Os spikes (Shirey and Walker, 1995). Samples were digested and equilibrated using 10–20 ml of concentrated HNO_3 and 2 ml of HCl at 200 °C for about 12 h. Osmium was separated as OsO_4 from the matrix using the *in-situ* distillation equipment described in Qi et al. (2010). The volume of trapped solution is about 0.6 ml for Os-poor samples and 1.5 ml for Os-rich samples using a trapping tube with a 4 mm inner diameter (Qi et al., 2010). Rhenium was separated from the remaining solution after Os distillation using the anion exchange resin (Biorad AG 1 × 8, 200–400 mesh) technique described by Qi et al. (2007).

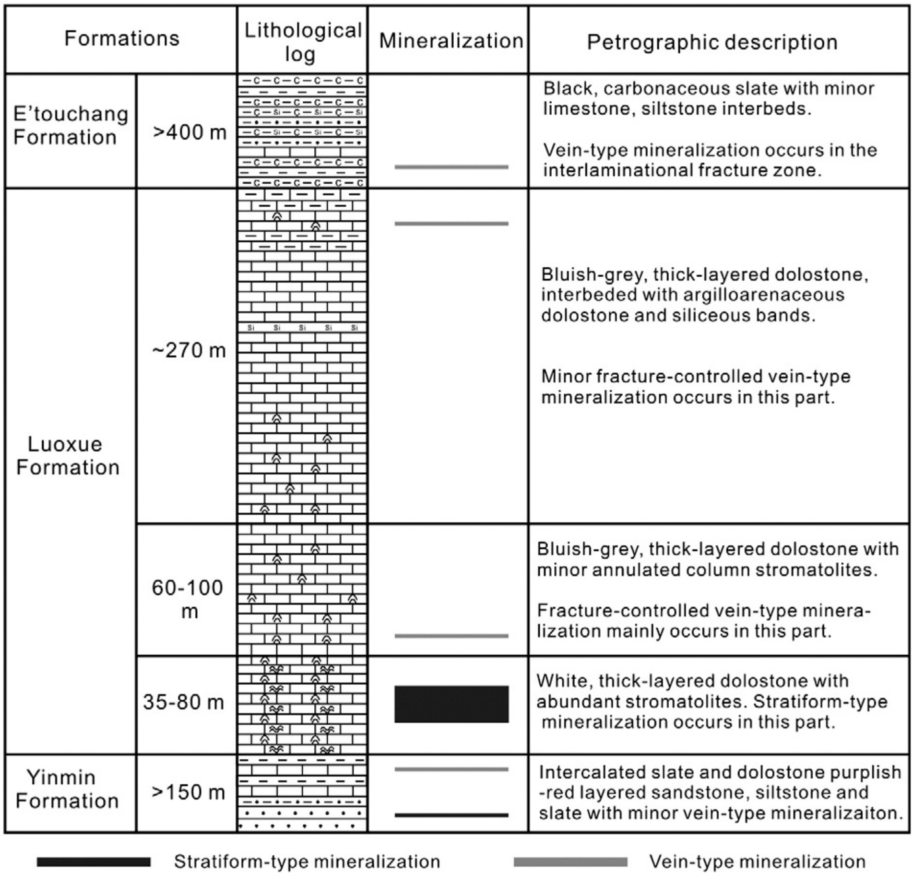
Formations		Lithological log	Mineralization	Petrographic description
E'touchang Formation	>400 m			Black, carbonaceous slate with minor limestone, siltstone interbeds. Vein-type mineralization occurs in the interlaminational fracture zone.
Luoxue Formation	~270 m			Bluish-grey, thick-layered dolostone, interbeded with argilloarenaceous dolostone and siliceous bands. Minor fracture-controlled vein-type mineralization occurs in this part.
	60-100 m			Bluish-grey, thick-layered dolostone with minor annulated column stromatolites. Fracture-controlled vein-type mineralization mainly occurs in this part.
	35-80 m			White, thick-layered dolostone with abundant stromatolites. Stratiform-type mineralization occurs in this part.
Yinmin Formation	>150 m			Intercalated slate and dolostone purplish-red layered sandstone, siltstone and slate with minor vein-type mineralizaiton.

Fig. 3. Stratigraphic column of the Dongchuan Group at the Tangdan deposit (modified from Gong et al., 1996) and mineralization extents of stratiform and vein-type ores.

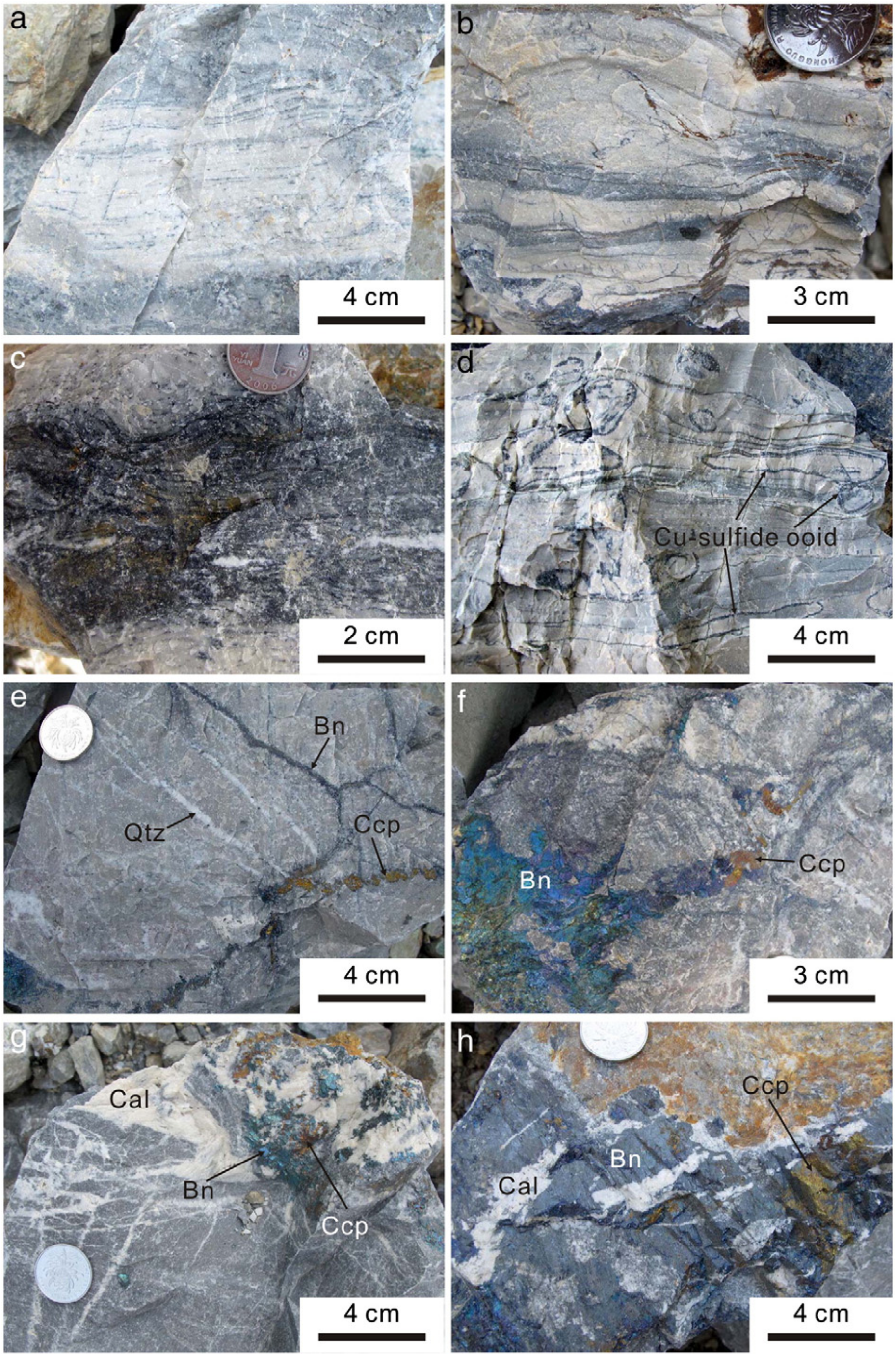

Fig. 4. Field photos of typical ore textures. (a, b) Laminar and banded structures of stratiform ores — the black bands are sulfide-rich; (c) banded structure of stratiform ores — note the plastic deformation of sulfide-rich veinlets; (d) oolitic structure of stratiform ores. Copper sulfides are cemented by argillaceous fragments, dolomite and authigenic quartz; (e, f) veinlet or stockwork structures of vein-type ores — note the fractures infilled with sulfides that crosscut stratification; (g, h) high-grade, vein-type ores consisting of massive chalcopyrite, bornite, and carbonate minerals. Abbreviation: Bn, Bornite; Ccp, Chalcopyrite; Qtz, Quartz; Cal, Calcite.

Re contents of sulfides from stratiform ores and Re–Os isotopes of sulfides from vein-type ores were determined with a PE ELAN DRC-e ICP-MS, whereas Os isotopes of sulfides from stratiform ores were determined using a Bruker Auraro M90 ICP-MS due to the extremely low Os contents. The sensitivity of the Bruker Auraro M90 was adjusted to >1,000,000 cps for 1 ng ml^{-1} of ^{115}In and 400,000 cps for 1 ng ml^{-1} of ^{232}Th using the high sensitivity mode in order to achieve the desired detection limits. The sensitivity of the PE ELAN DRC-e was adjusted to about 30,000 cps for 1 ng ml^{-1} of ^{103}Rh. Most analyses yielded a RSD (relative standard deviation) of <5% for ^{187}Os/^{190}Os ratios (5 blocks, each consisting of 40 scans).

Duplicate analyses of mineral separates from two samples of stratiform ore yielded consistent results, especially for Re contents. To monitor long-term mass spectrometry reproducibility, in-house standard solutions of Re and Os were analyzed repeatedly. The Re standard (~1 ppb) yielded an average ^{187}Re/^{185}Re ratio of 1.697 ± 0.031 (1σ, $n = 10$), whereas the Os standard (~50 pg/g) yielded an average ^{187}Os/^{188}Os ratio of 0.117 ± 0.003 (1σ, $n = 10$). Total procedural blanks were

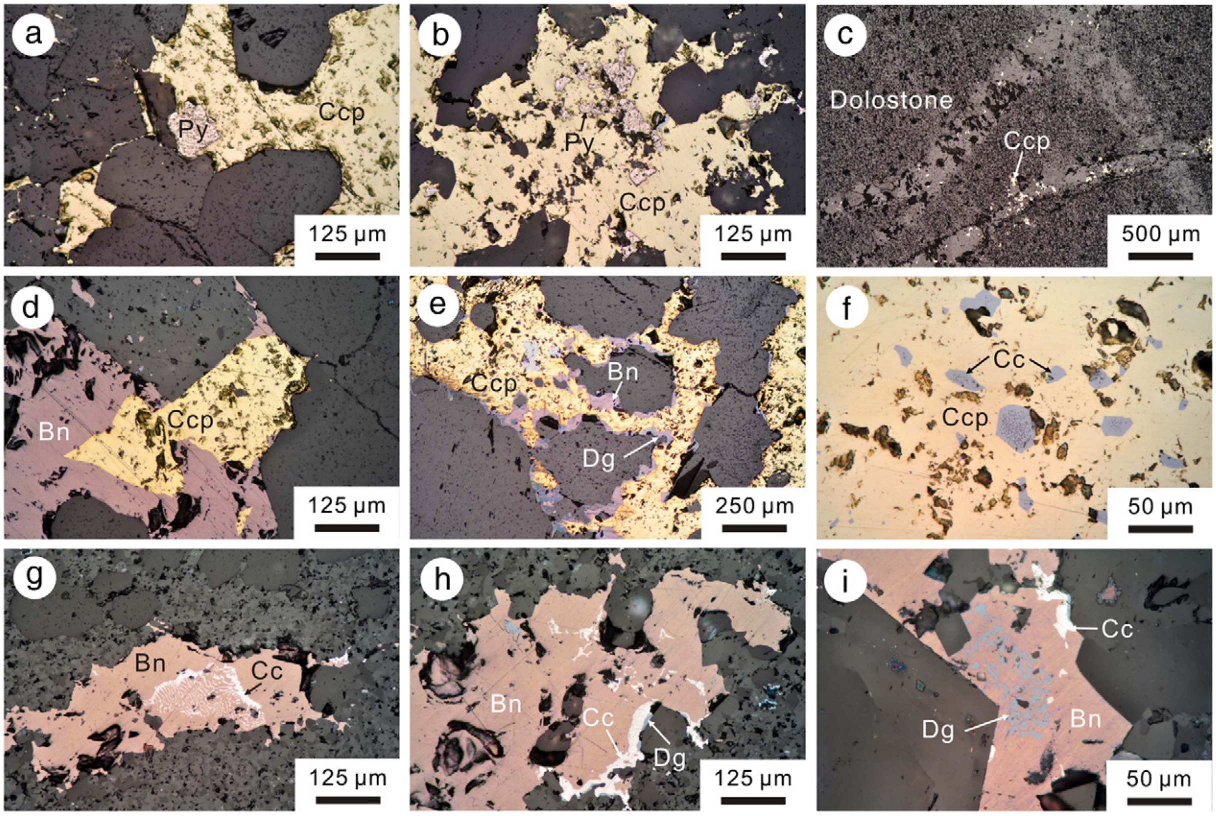

Fig. 5. Photomicrographs of ore minerals (under reflected light). (a, b) Euhedral to subhedral pyrites are replaced by chalcopyrite; (c) disseminated chalcopyrite within quartz-carbonate veins in the host dolostone; (d) chalcopyrite closely associated with bornite suggesting coeval phases; (e) chalcopyrite was partially replaced by bornite at the margin, which was in turn replaced by digenite; (f, g) disseminated chalcocite within chalcopyrite and bornite indicating hypogene origin of chalcocite; (h, i) bornite is marginally replaced by chalcocite, which in turn, is replaced by digenite, suggesting that this chalcocite is probably of supergene origin. Abbreviation: Py, Pyrite; Ccp, Chalcopyrite; Bn, Bornite; Cc, Chalcocite; Dg, Digenite.

mostly the same for the two types of ICP-MS, with Re and Os blanks being 6.4 ± 1.1 pg and 2.0 ± 0.4 pg, respectively, and an average ^{187}Os/^{188}Os value of 0.70 ± 0.11 (1σ, $n = 5$). Iridium was added to the Re- and Os-bearing solutions for mass discrimination correction as proposed by Schoenberg et al. (2000) for Re. We also applied this technique to Os, as common Os contents were too low to allow us to perform accurate internal fractionation corrections using the measured ^{192}Os/^{188}Os ratios of the samples. To ensure the efficiency of the correction method, ^{187}Os/^{188}Os ratios of Chinese national Re–Os reference materials, JCBY (Cu–Ni sulfides) and RCOR (cobalt-rich ferromanganese crusts), were determined during the course of this study. The analytical results of JCBY and RCOR are 0.329 ± 0.005 and 0.889 ± 0.015 (1σ, n = 5), respectively, in good agreement with the certified values of 0.3363 ± 0.0029 and 0.8782 ± 0.0102 (1σ) (Qu et al., 2010, 2011). Absolute uncertainties of Re–Os data are reported at the 2-sigma level. All uncertainties are determined by error propagation of uncertainties in Re and Os mass spectrometer measurements, blank abundances and spike calibrations.

5.2. Sulfur isotopes

Sulfur isotopes were analyzed by EA-IRMS (Elemental Analysis-Isotope Ratio Mass Spectrometry), using a EuroVector EA3000 element analyzer and a GV IsoPrime spectrometer at the Institute of Geochemistry, Chinese Academy of Sciences. Appropriate amounts of powdered sulfide separates were weighed and packed in tinfoil. Sulfur in sulfide minerals was converted to SO_2 for isotopic analysis by burning in the reactor under a constant temperature of about 1000 °C using a stream of purified oxygen. The sulfur dioxide was then carried by helium into the mass spectrometer. The sulfur isotopic compositions are expressed using the delta per mil notation (δ^{34}S) with respect to Vienna Canyon Diablo Troilite (V-CDT). Repeated analyses of national Ag_2S standards GBW04414 and GBW04415 yielded δ^{34}S values of −0.07 ± 0.09‰ (1σ, n = 27) and 22.33 ± 0.09‰ (1σ, n = 3), respectively, in good agreement with the certified values of −0.07 ± 0.13‰ and 22.15 ± 0.14‰ (1σ) (Zheng and Chen, 2000).

6. Analytical results

6.1. Re–Os isotopes

6.1.1. Stratiform ores

Copper sulfides from the stratiform ores have ~0.6 to 14 ppb Re and ~3.4 to 256 ppt total Os. They have ~1.9 to 48.7 ppt common Os and ~0.6 to 200 ppt ^{187}Os (Table 1), with ^{187}Re/^{188}Os ratios of < ~3000 and low ^{187}Os/^{188}Os ratios. The extremely low ^{188}Os contents, comparable in some cases to the blank contribution, have resulted in imprecise ^{187}Os/^{188}Os ratios which are not presented in Table 1. All of the samples contain considerable amounts of common Os, relative to the fairly low radiogenic ^{187}Os contents, and thus cannot be used to calculate model ages.

6.1.2. Vein-type ores

Three bornite and three chalcopyrite separates from the vein-type ores have ~122 to 293 ppb Re and ~1.9 to 4.5 ppb total Os, significantly higher than those of sulfides from the stratiform ores (Table 1; Fig. 6). However, their common Os contents range from ~8.6 to 39.9 ppt, similar to those of stratiform-type ores. Radiogenic ^{187}Os (^{187}Os^{r}) thus accounts for >98% of the total ^{187}Os budget (Table 1). The extremely

Table 1

Re – Os isotope data of bornite and chalcopyrite from the Tangdan deposit, southwest Yunnan Province, China.

Sample no.	Mass (g)	Mineral	Total Re (ppb)[a]	2σ	Total Os (ppt)[a]	2σ	Common Os (ppt)[a,b]	2σ	^{187}Re (ppb)[a]	2σ	^{187}Os (ppt)[a,c]	2σ
Stratiform ores												
TDH-2	0.8014	Bornite	1.65	0.13	5.3	0.5	4.5	0.4	1.04	0.08	0.86	0.05
TDH-7A[h]	0.5075	Bornite	14.29	0.73	256.5	14.8	48.7	2.6	8.95	0.45	207.85	12.61
TDH-7B[h]	0.5093	Bornite	14.41	0.81	230.3	19.9	38.8	2.2	9.02	0.50	191.46	18.09
TDH-8	0.1515	Bornite	5.27	0.54	65.5	6.4	30.7	3.4	3.30	0.34	34.80	3.26
TDH-9	0.3610	Bornite	1.10	0.12	2.7	0.5	1.9	0.4	0.69	0.08	0.80	0.14
TDH-10A[h]	0.9972	Chalcopyrite	0.61	0.05	3.8	0.3	3.2	0.2	0.38	0.03	0.57	0.11
TDH-10B[h]	0.9969	Chalcopyrite	0.60	0.05	3.4	0.2	2.8	0.2	0.38	0.03	0.57	0.09
Vein-type ores					Total Os (ppb)						^{187}Os^{r} (ppb)[i]	
TDH-22	0.5152	Bornite	287.0	3.9	4.365	0.104	13.8	3.9	180.4	2.4	4.330	0.112
TDH-24	0.5074	Bornite	183.5	1.9	2.797	0.029	8.6	6.0	115.3	1.2	2.775	0.043
TDH-31	0.5125	Bornite	174.0	4.1	2.657	0.058	22.8	2.9	109.3	2.5	2.598	0.098
TDH-37	0.5058	Chalcopyrite	292.5	8.9	4.464	0.025	39.9	5.4	183.8	5.6	4.361	0.138
TDH-49	0.5193	Chalcopyrite	122.3	3.8	1.911	0.021	13.2	4.3	76.9	2.4	1.877	0.052
TDH-51	0.5120	Chalcopyrite	165.8	5.0	2.631	0.082	31.1	4.1	104.2	3.2	2.551	0.133

Sample no.	^{187}Re/^{188}Os[a]	2σ	^{187}Os/^{188}Os[a,d]	2σ	Rho[e]	%^{187}Os^{r}[f]	Model age (Ma)[g]	2σ
Stratiform ores								
TDH-2	1768	222						
TDH-7A[h]	1411	105						
TDH-7B[h]	1786	143						
TDH-8	825	125						
TDH-9	2859	672						
TDH-10A[h]	909	91						
TDH-10B[h]	1027	104						
Vein-type ores								
TDH-22	99,760	27,981	2365	664	1.00	99.5	1429	42
TDH-24	102,776	71,888	2442	1708	1.00	99.5	1433	27
TDH-31	36,669	4814	868	114	0.97	98.6	1415	63
TDH-37	35,205	4862	833	113	0.97	98.6	1413	62
TDH-49	44,538	14,531	1080	351	0.99	98.9	1454	61
TDH-51	25,638	3447	628	83	0.95	98.1	1457	88

[a] Results are blank corrected. Blanks for Re and Os were 6.4 ± 1.1 pg and 2.0 ± 0.4 pg , respectively, with an average ^{187}Os/^{188}Os value of 0.70 ± 0.11 (1σ, $n = 5$).

[b] Common Os concentrations and their uncertainties were calculated using ^{187}Os/^{188}Os value of 12 ± 26 from the regression of ^{187}Re/^{188}Os and ^{187}Os/^{188}Os data.

[c] Total ^{187}Os concentrations for stratiform ores.

[d] It was impossible to calculate these ratios for the stratiform ores due to the large blank contribution.

[e] Uncertainty correlation factor (ρ) is applied to assess the degree of correlation between ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios (Ludwig, 1980).

[f] Percentage of all measured ^{187}Os determined from the radiogenic decay of ^{187}Re.

[g] Model ages are calculated using $^{187}\mathrm{Os}^{r}/^{187}\mathrm{Re} = e^{\lambda t} - 1$, where λ (^{187}Re decay constant) $= 1.666 \times 10^{-11}$ a^{-1} with a relative uncertainty of ±0.31% (Smoliar et al., 1996).

[h] Sample numbers ended with "A" and "B" represent replicate analyses of mineral separates from the same sample.

[i] Radiogenic ^{187}Os for vein-type ores are calculated using initial ^{187}Os/^{188}Os value and its uncertainty from the regression of ^{187}Re/^{188}Os and ^{187}Os/^{188}Os data.

high ^{187}Re/^{188}Os values (~25,000 to ~102,000) and highly radiogenic ^{187}Os/^{188}Os ratios (~600 to 2400) of these samples identify them as "LLHR" (low-level, highly radiogenic) sulfides as defined by Stein et al. (2000).

Because the low ^{188}Os contents cannot be determined precisely because of the blank correction, traditional ^{187}Re/^{188}Os and ^{187}Os/^{188}Os plots for "LLHR" sulfides would introduce large uncertainties. An uncertainty correlation factor (rho) was devised by Cumming (1969) for assessing the correlation of uncertainties of Pb in the U – Pb system. Using the same method (Ludwig, 1980), rho was also used to assess the degree of correlation between ^{187}Re/^{188}Os and ^{187}Os/^{188}Os ratios. Sulfides from the vein-type ores have rho values of 0.95 to 1 (Table 1), and hence plots of ^{187}Re versus ^{187}Os are used instead of ^{187}Re/^{188}Os versus ^{187}Os/^{188}Os to avoid correlated uncertainties. Plots of ^{187}Re/^{188}Os versus ^{187}Os/^{188}Os of these samples are also presented for comparison (Figs. 7a and b).

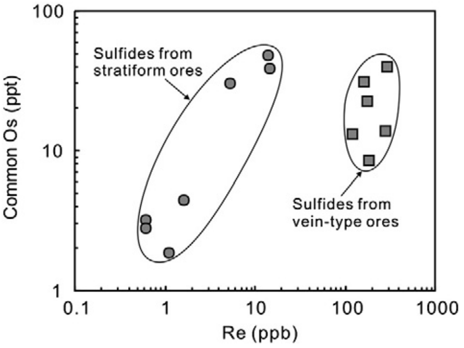

Fig. 6. Re versus common Os plot showing distinct Re – Os isotopic compositions of sulfides from stratiform and vein-type ores.

^{187}Re/^{188}Os versus ^{187}Os/^{188}Os regression plots of sulfides from the vein-type ores yield a model 1 isochron age of 1401 ± 30 Ma, with an initial ^{187}Os/^{188}Os value of 12 ± 26 (2σ, MSWD = 0.67; Fig. 7a). A model 1 age determined by *Isoplot Ver. 3.23* assumes that the scatter of the linear regression is derived only from assigned uncertainties (Ludwig, 2003). A direct regression of ^{187}Re against ^{187}Os^{r} for these sulfides yields a model 1 isochron age of 1397 ± 71 Ma (2σ, MSWD = 0.22; initial ^{187}Os^{r} = 0.06 ± 0.14; Fig. 7b), which is within the uncertainty consistent with the isochron age of the ^{187}Re/^{188}Os versus ^{187}Os/^{188}Os regression. The very low common Os/radiogenic Os ratios allow us to calculate model ages of each sample. Their model ages range from 1413 to 1457 Ma (Table 1), with a weighted mean average of 1432 ± 19 Ma (2σ) (Fig. 7c; MSWD = 0.30, probability = 0.91), which is within uncertainty indistinguishable from both ^{187}Re/^{188}Os versus ^{187}Os/^{188}Os and ^{187}Re versus ^{187}Os^{r} regression isochron ages.

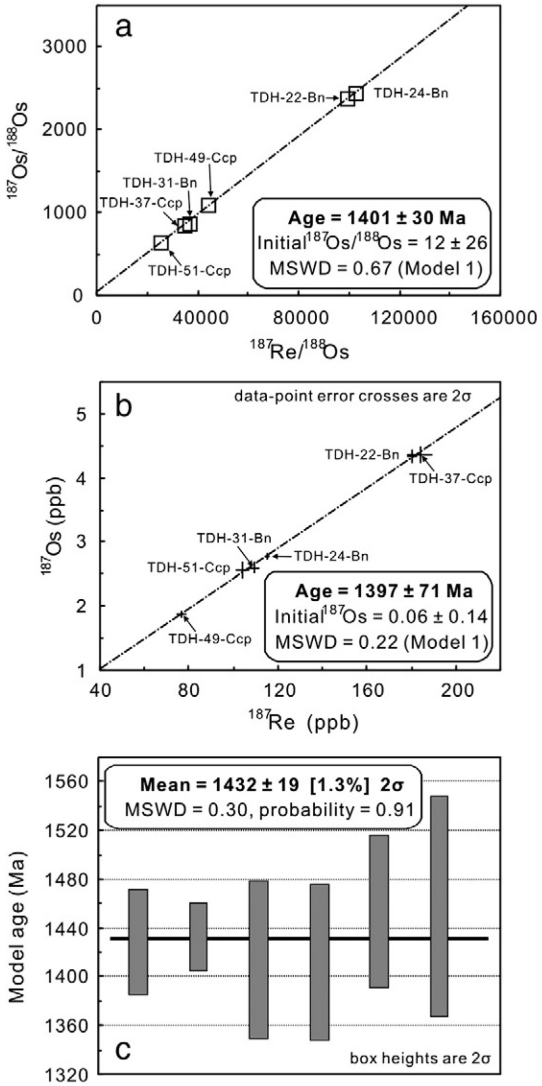

Fig. 7. (a) ^{187}Re/^{188}Os versus ^{187}Os/^{188}Os plot and (b) ^{187}Re versus ^{187}Os plots of sulfides from vein-type ores; (c) Re–Os model age diagram for the vein-type ores. The weighted average age and isochron ages were calculated with Isoplot/Ex *ver. 3.23* (Ludwig, 2003).

6.2. Sulfur isotope

Bornite and chalcopyrite from the Tangdan deposit have similar δ^{34}S values, ranging from −14.7‰ to +4.6‰ and from −13.6‰ to +9.3‰, respectively (Table 2). Except for one sample, Tang 4a, with a much higher δ^{34}S value of +26.75‰, δ^{34}S values of supergene chalcocite are similar to those of hypogene bornite and chalcopyrite, indicating that isotopic fractionation during the supergene processes was not significant. Most of the copper sulfides from the stratiform ores have δ^{34}S values from −3‰ to +10‰, much higher than those of the vein-type ores that range from −14.7‰ to +5‰ (Fig. 8).

7. Discussion

7.1. Two Cu mineralization events at the Tangdan deposit

Field relationships show that vein-type ores crosscut stratiform ores in the Tangdan deposit. Both types of ores have similar mineral assemblages such that the vein-type ores are thought to have resulted from local remobilization of the stratiform ores during deformation or later tectonothermal events (Gong et al., 1996). However, this hypothesis has not been verified due to the lack of constraints on the age of mineralization and the source of the ore-forming fluids.

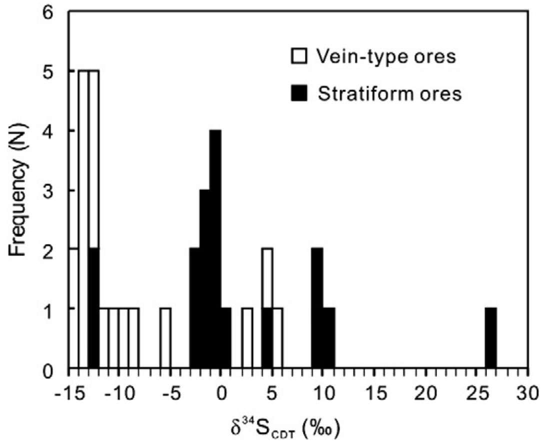

Fig. 8. Histogram of sulfur isotope compositions of sulfide minerals from stratiform and vein-type ores at the Tangdan deposit.

Copper sulfides from the stratiform ores have δ^{34}S values of −3‰ to +10‰ much higher than those of most vein-type ores, which have values ranging from −14.7‰ to +5‰ (Table 2; Fig. 8), indicating different resources of sulfur. Cu-sulfides of the stratiform ores have Re–Os isotopic signatures distinct from those of vein-type ores. The vein-type ores have much higher Re contents than the stratiform ores, but similar contents of common Os (Table 1, Fig. 6) suggesting that they were precipitated from distinct hydrothermal fluids.

Based on the textural evidence, Zhao et al. (2012) suggested that stratiform Cu mineralization in the Tangdan deposit could have started during diagenesis and continued even after the host rocks were thoroughly lithified. Although we have not obtained accurate isotopic ages for the stratiform ores, previous zircon U–Pb and sulfide Re–Os dating of other SSC deposits in the Dongchuan region yielded ages of ~1700 Ma (Zhao et al., 2013). We therefore suggest that the stratiform ores most likely formed during the early diagenetic stage.

This study obtained well-constrained Re–Os ages for vein-type ores that have reproducible model ages with a weighted mean age of 1432 ± 19 Ma and isochron ages of 1401 ± 30 Ma and 1397 ± 71 Ma. These ages provide the best estimate for the formation age of the vein-type ores, which are significantly younger than the stratiform ores. The new geochronological data, together with the field and textural relationships, indicate that there were at least two Cu mineralization events in the Tangdan deposit and, by inference, in other SSC deposits of the Kangdian region.

7.2. Sources of metals and ore-forming fluids

7.2.1. Stratiform-type ores

It is generally accepted that the red beds of the Yinmin Formation were the principal sources of metals for the stratiform ores in the Kangdian region (Ran, 1983; Hua, 1990). Ore-forming fluids responsible for Cu-sulfide precipitation were oxidized, copper-bearing, saline brines (Ran, 1989; Ruan et al., 1991). The Re contents (mostly <6 ppb) of sulfides from the stratiform ores are comparable to sulfides from sediment-hosted ore systems elsewhere (Tristá-Aguilera et al., 2006; Schneider et al., 2007), and suggest a typical sedimentary source for Re and, by inference, Cu. Therefore, the Yinmin Formation was most likely the source of Cu and Re for the stratiform ores of the Tangdan deposit. This view is consistent with the wide range of sulfur isotopic signatures in the stratiform ores (Fig. 8) that imply multiple sources. Some samples of stratiform ores have highly positive δ^{34}S, indicating derivation of sulfur from marine evaporites

Table 2
Sulfur isotope data of both stratiform and vein-type ores from the Tangdan deposit.

Sample no.	Ore type	Mineral	$\delta^{34}S_{CDT}$ (‰)	Reference
TDH-22	Vein-type	Bornite	−12.5	This study
TDH-24	Vein-type	Bornite	−14.7	This study
TDH-25	Vein-type	Bornite	−5.2	This study
TDH-26	Vein-type	Bornite	−12.7	This study
TDH-27	Vein-type	Bornite	−13.9	This study
TDH-28	Vein-type	Bornite	−9.4	This study
TDH-29	Vein-type	Bornite	−12.5	This study
TDH-30	Vein-type	Bornite	−14.1	This study
TDH-31	Vein-type	Bornite	−13.3	This study
TDH-32	Vein-type	Bornite	−8.6	This study
TDH-34	Vein-type	Chalcopyrite	−13.6	This study
TDH-37	Vein-type	Chalcopyrite	−13.3	This study
TDH-40	Vein-type	Chalcopyrite	−13.6	This study
TDH-44	Vein-type	Chalcopyrite	5.1	This study
TDH-47	Vein-type	Chalcopyrite	2.5	This study
TDH-48	Vein-type	Chalcopyrite	4.0	This study
TDH-49	Vein-type	Chalcopyrite	−11.3	This study
TDH-51	Vein-type	Chalcopyrite	−10.6	This study
YN07-411	Stratiform	Chalcopyrite	−1.1	Zhao et al. (2012)
YN07-412	Stratiform	Chalcopyrite	−0.3	Zhao et al. (2012)
YN07-414	Stratiform	Bornite	−0.7	Zhao et al. (2012)
YN07-415	Stratiform	Bornite	4.6	Zhao et al. (2012)
YN07-416	Stratiform	Bornite	−1.1	Zhao et al. (2012)
YN07-419	Stratiform	Chalcocite	9.3	Zhao et al. (2012)
Tang 4a	Stratiform	Chalcocite	26.7	Zhao et al. (2012)
Tang 4b	Stratiform	Bornite	−12.7	Zhao et al. (2012)
Tang 4c	Stratiform	Chalcocite	−12.3	Zhao et al. (2012)
Tang 5a	Stratiform	Chalcocite	−2.4	Zhao et al. (2012)
Tang 5b	Stratiform	Bornite	−2.9	Zhao et al. (2012)
Lou-2a	Stratiform	Chalcopyrite	−0.9	Zhao et al. (2012)
Lou-2b	Stratiform	Bornite	0.1	Zhao et al. (2012)
Tang 8a	Stratiform	Chalcopyrite	9.3	Zhao et al. (2012)
Tang 8b	Stratiform	Chalcocite	10.2	Zhao et al. (2012)
Tang 9a	Stratiform	Chalcocite	−0.5	Zhao et al. (2012)
Tang 9b	Stratiform	Chalcocite	−1.4	Zhao et al. (2012)

(average ~ +20‰; Strauss, 1993) in the Dongchuan Group by thermodynamic reduction (Zhao et al., 2012).

7.2.2. Vein-type ores

Sulfides of the vein-type ores have much higher Re contents than the stratiform ores. Such a Re–Os budget (high Re and almost 100% radiogenic Os) could be controlled by micro-intergrowths of molybdenite within Cu-sulfides (e.g. Selby et al., 2009). However, no molybdenite has been observed in the Tangdan deposit and sulfides investigated by this study have very low Mo content (<5 ppm, our unpub. data). In addition to molybdenite, intergrowths of Ge-enriched sulfide minerals, such as germanite and renierite, may also host Re (Selby et al., 2009). The sulfide separates used for Re–Os analyses have extremely low Ge content (0.52-1.60 ppm, average 0.93 ppm, Y. M. Meng, unpub. data), and there is no linear correlation between Re and Ge. Therefore, the high Re contents of sulfides from the vein-type ores are not due to Ge-enriched minerals.

High Re and Os contents of sulfides can be potentially derived from magmas or magmatic fluids (Stein et al., 2000). However, the Re–Os ages of sulfide samples at Tangdan are significantly older than the ~1050 Ma gabbroic intrusions (Zhao, 2010). The 1400–1500-Ma igneous activity in the Kangdian region was very weak and is unlikely to have been the source of the ore-forming fluids.

Hydrothermal fluids can be enriched in Re through interaction with organic-rich sediments (e.g. Xiong and Wood, 1999; Morelli et al., 2004; Kendall et al., 2009; Selby et al., 2009). Sulfides from the vein-type ores rich in Re are similar to pyrites from the black shale-hosted Red Dog Zn–Pb–Ag deposit, Brooks Range, Alaska (Morelli et al., 2004) and pyrite, chalcopyrite and bornite from carbonate-hosted copper deposits at Ruby Creek, Brooks Range, Alaska (Selby et al., 2009). These authors attributed the elevated Re contents in ore-forming fluids to organic matter in the sedimentary sequences, e.g. anthraxolite in dolomitized breccia at Ruby Creek has ~35 ppb Re (Selby et al., 2009). At the Tangdan deposit, the 1600-m-thick carbonaceous slates of the E'touchang Formation, which immediately overlie the major ore-hosting strata of the Luoxue Formation, have an average Re content of 10 ppb (up to ~20 ppb; our unpub. data). The E'touchang Formation has a zircon SHRIMP U–Pb age of 1503 ± 17 Ma (Sun et al., 2009), slightly older than the vein-type ore-forming event (~1430 Ma). Therefore, interaction of ore fluids with carbonaceous slates of the E'touchang Formation may have provided a source of Re in the sulfides of the vein-type ores.

Involvement of organic matter in the formation of the Tangdan deposit is also supported by stable isotopes. The mineralized and unmineralized dolostones of the Luoxue Formation have $\delta^{13}C_{V\text{-}PDB}$ values of 0.2‰–1.3‰ and 0.6‰–1.0‰, respectively, (Zhao et al., 2012), similar to those of Paleoproterozoic dolostone elsewhere (Kah et al., 1999; Bartley et al., 2001), indicating that diagenesis and fluid–rock interaction did not change the carbon isotopes of the dolostone. However, some carbonate minerals from the vein-type ores are characterized by shift toward lighter carbon isotope compositions, likely resulting from isotopic exchange between ore-forming fluids and organic-rich rocks (Zhao et al., 2012). Sulfides from the vein-type ores have $\delta^{34}S$ values ranging from −15‰ to −8‰, which also indicate derivation from a reduced source, such as the carbonaceous slates of the E'touchang Formation. Collectively, the Re–Os, C and S isotopic data imply that organic-enriched strata were likely responsible for the elevated Re contents in sulfide minerals of the vein-type ores.

7.3. Implications for ore mineralization of SSC deposits

The timing of ore mineralization of the SSC deposits in the Kangdian region has long been controversial, largely due to the lack of precise age constraints. Previous studies suggested that Cu mineralization of the SSC hydrothermal system may have taken place at anytime from early diagenesis to late basin inversion (e.g. Brown, 1997; Selley et al., 2005; Hitzman et al., 2010), and multiple stages of mineralization have been documented in SSC deposits elsewhere (Selley et al., 2005; Symons et al., 2011). Hitzman et al. (2010) proposed that the formation of giant SSC deposits may be a protracted process lasting tens to hundreds of millions of years. For example, copper mineralization in the Zambian Copperbelt occurred over an extended interval from ~815 Ma to ~500 Ma (Selley et al., 2005); and SSC deposits hosted in the Kupferschiefer black shale in Germany may have formed between ~254 Ma and ~149 Ma (Symons et al., 2011). The present Re–Os geochronological study demonstrates that the Tangdan deposit records a protracted history of ore mineralization, providing compelling evidence that vein-type mineralization in SSC deposits may have formed hundreds of millions years after deposition of the ore-hosting strata.

It is noteworthy that the Tangdan deposit was likely generated by repeated mineralization events rather than a single, continuous process. The distinct Re–Os and C–O–S isotopes of the stratiform and vein-type ores indicate their formation from different ore-forming fluids. This study highlights the importance of sulfide Re–Os isotopic data in constraining the age of mineralization of SSC deposits and in tracing sources of ore fluids and other components from which the SSC deposits were precipitated.

8. Conclusions

The Tangdan deposit in the Kangdian region, South China, consists of stratiform and vein-type ores typical of SSC deposits elsewhere. Sulfides from the stratiform ores contain low Re and low common Os, whereas those from the vein-type ores have much higher Re but similar common Os contents. Isotopic ages are not available for the stratiform ores due to their extremely low radiogenic Os, but these deposits likely formed at ~1700 Ma based on analogy with similar dated SSC deposits in the Dongchuan region. Sulfides from the vein-type ores have a weighted mean Re – Os model age of ~1430 Ma, much younger than the age of the stratiform ores.

Our study revealed two copper mineralization events in the Tangdan deposit. The majority of the copper sulfides from the stratiform ores have much higher δ^{34}S values ($-3‰$ to $+10‰$) than those of the vein-type ores ($-15‰$ to $-8‰$). Sulfur of the stratiform ores was most likely derived from thermochemical reduction of marine sulfates, whereas light sulfur of sulfides from the vein-type ores was enriched through interaction with organic matter in the ore-hosting strata.

Sulfides of the vein-type ores enriched in Re were likely precipitated from ore-forming fluids that interacted with organic-bearing rocks. This study highlights the utilization of Re – Os systematics of sulfide minerals in unraveling the history of mineralization of SSC deposits and tracing the sources of ore fluids and other components.

Acknowledgments

This study was financially supported by the Chinese 973 project (2012CB416804), the Research Grant Council of Hong Kong (HKU707210P and HKU 707511P), the “CAS Hundred Talents” Project from the Chinese Academy of Sciences (KZCX2-YW-BR-09) to Qi Liang, and the National Natural Science Foundation of China (NSFC40773070). Field work was assisted by Wang Wei from the University of Hong Kong. We thank Meng Yumiao from the Institute of Geochemistry, Chinese Academy of Sciences for obtaining the germanium data and Prof. Paul Robinson for polishing the language. We are grateful to Prof. Laurie Reisberg, Dr. David Selby and an anonymous reviewer for their constructive comments which have significantly improved the manuscript.

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