H-O-S-Cu-Pb Isotopic Constraints on the Origin of the Nage Cu-Pb Deposit, Southeast Guizhou Province, SW China

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Abstract: The Nage Cu-Pb deposit, a new found ore deposit in the southeast Guizhou province, southwest China, is located on the southwestern margin of the Jiangnan Orogenic Belt. Ore bodies are hosted in slate and phyllite of Neoproterozoic Jialu and Wuye Formations, and are structurally controlled by EW-trending fault. It contains Cu and Pb metals about 0.12 million tonnes with grades of 0.2 wt% to 3.4 wt% Cu and 1.1 wt% to 9.27 wt% Pb. Massive and disseminated Cu-Pb ores from the Nage deposit occur as either veinlets or disseminations in silicified rocks. The ore minerals include chalcopyrite, galena and pyrite, and gangue minerals are quartz, sericite and chlorite. The H-O isotopic compositions of quartz, S-Cu-Pb isotopic compositions of sulfide minerals, Pb isotopic compositions of whole rocks and ores have been analyzed to trace the sources of ore-forming fluids and metals for the Nage Cu-Pb deposit. The $\delta^{65}Cu_{NBS}$ values of chalcopyrite range from -0.09% to +0.33‰, similar to basic igneous rocks and chalcopyrite from magmatic deposits. $\delta^{65}Cu_{NBS}$ values of chalcopyrite from the early, middle and final mineralization stages show an increasing trend due to ^{63}Cu prior migrated in gas phase when fluids exsolution from magma. $\delta^{34}S_{CDT}$ values of sulfide minerals range from $-2.7‰$ to $+2.8‰$, similar to mantle-derived sulfur (0±3‰). The positive correlation between $\delta^{65}Cu_{NBS}$ and $\delta^{34}S_{CDT}$ values of chalcopyrite indicates that a common source of copper metal and sulfur from magma. $\delta D_{H2O-SMOW}$ and $\delta^{18}O_{H2O-SMOW}$ values of water in fluid inclusions of quartz range from $-60.7‰$ to $-44.4‰$ and $+7.9‰$ to $+9.0‰$ ($T=260°C$), respectively and fall in the field for magmatic and metamorphic waters, implicating that mixed sources for H_2O in hydrothermal fluids. Ores and sulfide minerals have a small range of Pb isotopic compositions ($^{208}Pb/^{204}Pb=38.152$ to 38.384, $^{207}Pb/^{204}Pb=15.656$ to 17.708 and $^{206}Pb/^{204}Pb=17.991$ to 18.049) that are close to orogenic belt and upper crust Pb evolution curve, and similar to Neoproterozoic host rocks ($^{208}Pb/^{204}Pb=38.201$ to 38.6373, $^{207}Pb/^{204}Pb=15.648$ to 15.673 and $^{206}Pb/^{204}Pb=17.820$ to 18.258), but higher than diabase ($^{208}Pb/^{204}Pb=37.830$ to 38.012, $^{207}Pb/^{204}Pb=15.620$ to 15.635 and $^{206}Pb/^{204}Pb=17.808$ to 17.902). These results imply that the Pb metal originated mainly from host rocks. The H-O-S-Cu-Pb isotopes tegather with geology, indicating that the ore genesis of the Nage Cu-Pb deposit is post-magmatic hydrothermal type.

Key words: H-O-S-Cu-Pb isotopes, sources of ore-forming fluids and metals, ore genesis, Nage Cu-Pb deposit, SW China

1 Introduction

Many Au-Ag-Cu-Pb-Zn and W-Sn deposits have been found in the southeastern Yangtze Block, South China, where the NEE-SWW striking Jiangnan Orogen Belt extends for ca.1500km (e.g. Wang and Zhou, 2012). The Nage Cu-Pb deposit, a new found ore in southeast Guizhou province, is located on the southwestern margin of the Jiangnan Orogen Belt (Fig.1). It contains Cu and Pb metals about 0.12 million tonnes with grades of 0.2 wt% to 3.4 wt% Cu and 1.1 wt% to 9.27 wt% Pb (Yang et al, 2011a).

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In the Nage ore field, Neoproterozoic igneous rocks are distributed, including the Jialu basic volcanic rocks, Jiabang-Nage diabase, Motianling granite and the Jiabang buried granite porphyry. A close spatial association with igneous rocks led some researchers considered the Nage to be a magmatic hydrothermal deposit (e.g. Yang et al., 2010, 2011a, 2011b; Chen et al., 2011), whereas others suggest that it may be epithermal hydrothermal type (e.g. Liu et al., 2010). Due to lack of multiple isotopic constrains on the sources of ore-forming metals, the ore genesis of the Nage Cu-Pb deposit is still unclear.

Recent application of Multiple Collectors Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) has made it possible to analyze isotopes of transition metals (such as Cu, Zn and Fe) from hydrothermal deposit (e.g. Maréchal et al., 1999; Zhu et al., 2000; Albarède, 2004; Kelly et al., 2009; Wang et al., 2011). Some studies have demonstrated that Cu isotope is potentially important to examine possible sources of copper metal and to investigate the mechanism of copper transportation and deposition during mineralization process (e.g. Zhu et al., 2000; Jiang et al., 2002; Mason et al., 2005; Qian et al., 2006; Herzog et al., 2009; Li et al., 2009a, 2009b; Wang and Zhu, 2010; Ikehata and Hirata, 2012; Mathur et al., 2012), whereas the extents, causes and consequences of Cu isotope fractionation in Cu-bearing minerals precipitation process are still under exploration (e.g. Wang and Zhu, 2010). In addition, H-O-S-Pb isotopes are powerful tool for studying the origin of hydrothermal deposits, particularly for determining sources of ore-forming fluids and metals (e.g. Ohmoto et al., 1990; Chang et al., 2000; Han et al., 2004; Li et al., 2007; Huang et al., 2010; Wang et al., 2010; Zhou et al., 2010, 2011b, 2013a, 2013b, 2013c; Xing et al., 2012; Yang et al., 2012; Zeng et al., 2012).

This paper presents detailed geology observation and H-O-S-Cu-Pb isotopic compositions, in order to better understand origin of the Nage Cu-Pb deposit and discuss the extents, causes and consequences of Cu isotopic fractionation during chalcopyrite precipitation process.

2 Geological Setting

2.1 Regional geology

The Nage Cu-Pb deposit is located on the southwestern margin of the Jiangnan Orogen Belt, a transitional zone between the Yangtze and Cathaysia Blocks (Fig. 1; Zeng et al., 2003; Chen et al., 2007). The Yangtze Block is composed of ~2.9 Ga to ~3.3 Ga crystalline basement complexes, Meso- to Neoproterozoic folded basement and a Paleozoic to Mesozoic cover sequence (e.g. Wang and Zhou, 2012; Wang et al., 2012a). The exposed strata in the
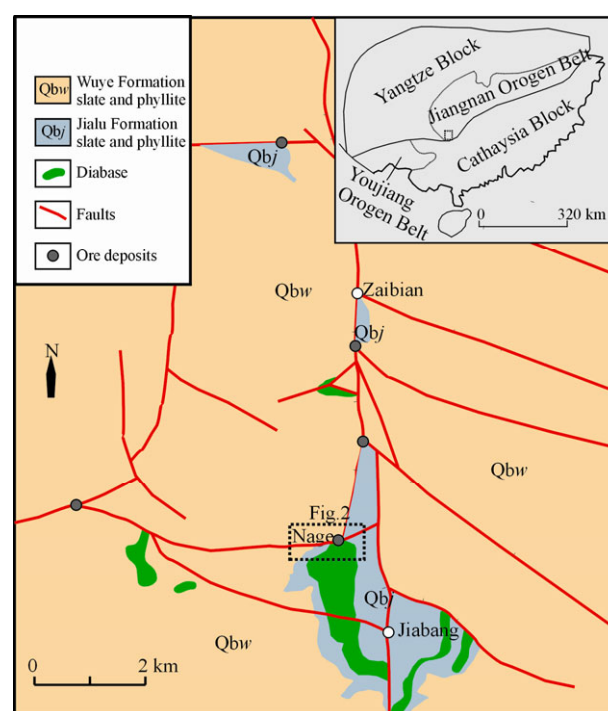

Fig. 1. Sketch regional geological map of the Nage Cu-Pb deposit (modified from Yang et al., 2011a).

southwestern Jiangnan Orogen Belt are Mesoproterozoic Sibao and Neoproterozoic Xiajiang Groups (Fanzhao, Wuye, Jialu, Hecun and Yaodeng Formations). The Neoproterozoic Xiajiang Group is composed of metamorphic sedimentary sericite slate, phyllite and sandy slate (Yang et al., 2010, 2011a). The host rocks of Cu-Pb-Zn poly-metal deposits in this region are silicified slate and phyllite of Jialu and Wuye Formations. SN, NW and NE-trending faults and folds distributed widely (Fig.1) and controlled these deposits (Liu et al., 2010; Yang et al., 2011a, 2011b; Zhou et al., 2011a). The Neoproterozoic igneous rocks are abundant, such as the Jialu basic volcanic rocks (815.8±4.4Ma, Zeng et al., 2005), Zaibian (848±14Ma, Wang et al., 2012b) and Jiabang-Nage (about 830Ma, unpublished data) diabase dykes, Motianling granite (825.0±2.4Ma, Zeng et al., 2005) and Jiabang buried granite porphyry (about 852Ma, unpublished data). Partially, the Jiabang-Nge diabase and Jiabang buried granite porphyry are close associated with the Nage Cu-Pb deposit.

2.2 Geology of the Nage Cu-Pb deposit

The Nage Cu-Pb deposit was structurally controlled by EW-trending fault and the Jiabang anticline. It is hosted in silicified phyllite and slate of the Neoproterozoic Jialu and Wuye Formations (Figs. 1 and 2). Two ore bodies have been found and are strictly controlled by the F_2 fault (Fig. 2), which is 4m to 6m in width. Massive and
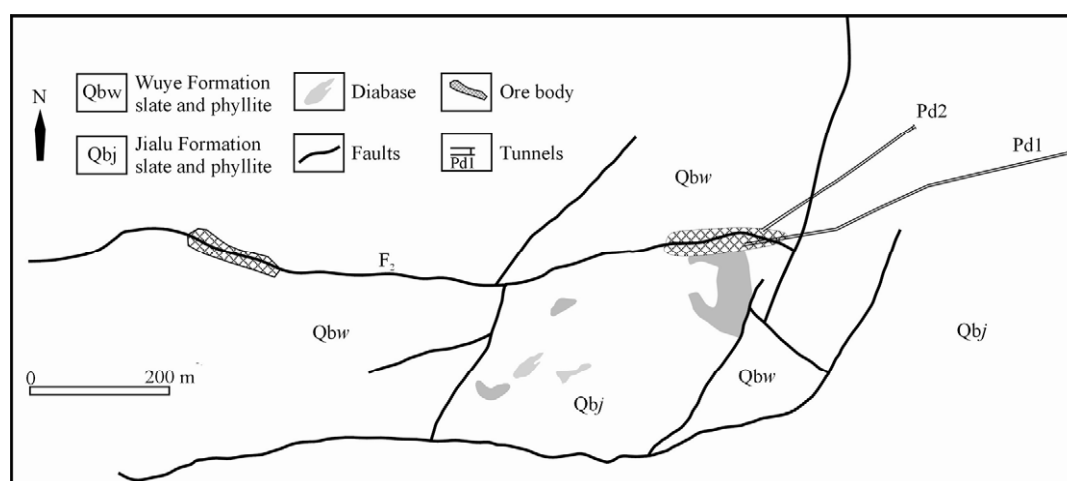
Fig. 2. Sketch geological map of the Nage Cu-Pb deposit (modified from Yang et al., 2010).

disseminations ores occur as lens and veinlets. Cu and Pb metals of the Nage Cu-Pb deposit are 0.12 million tonnes with grades of 0.2 wt% to 3.4 wt% Cu and 1.1 wt% to 9.27 wt% Pb. Ore minerals are chalcopyrite, galena, pyrite and little sphalerite, whereas gangue minerals are quartz, sericite, chlorite, dolomite and tourmaline. Ores have anhedral-subhedral-euhedral granular and banded textures, and brecciated, veined, disseminated, mesh-veined and massive structures. Three principal mineralization stages are identified on the basis of the textural and structural relationships among minerals assemblages (Liu et al., 2010; Yang et al., 2010, 2011a). Chalcopyrite of the early stage is copper color, fine-medium grained (1mm to 5mm) aggregates, with massive structure. Chalcopyrite formed in this stage was contained by late quartz and/or coexisting with the early stage pyrite (Figs. 3a, 3c, 3e). Chalcopyrite of the middle stage is bright copper color, coarse-grained (4mm to 9mm), with nodular structure and is contained by late quartz and/or coexisting with galena (Figs.3a, 3d). The late stage chalcopyrite occurs as vein and dissemination, with small size (0.1mm to 2mm), coexisting with galena and/or the metasomatism altered early stage pyrite (Figs.3b, 3f). Wall rocks alterations were developed, including silication, marbleization, pyritization, sericitization and chloritization.

3 Samples and Analytical Methods

Samples were collected from the tunnels and drill holes of the Nage Cu-Pb deposit. Ores were crushed into 40-60 meshes, and pyrite, chalcopyrite, galena and quartz separates are handpicked under a binocular microscope.

3.1 Copper isotopes

Chalcopyrite was dissolved with 6ml/L HCl and Cu was separated using a modified anion exchange chromatography procedure with AG MP-1 anion exchange resin (100-200 meshes, Tang et al., 2006). All H_2O was purified using Milli-Q system, with electric resistance of 18.2MΩ. HCl and HNO_3 were purified by sub-boiling distillation and the purification of all reagents was accomplished in a super-purification laboratory. Cu isotopes analyses were carried out using a Nu Plasam HR MC-ICP-MS in the Ministry of Land and Resources, Key Laboratory of Isotope Geology, Institute of Geology, Chinese Academy of Geological Sciences. Mass discrimination was corrected using a combined sample-standard bracketing (Cai et al., 2005) and inter-element correction procedure. All results are reported to the NIST (NBS) 976 (Maréchal et al., 1999).

3.2 Sulfur isotopes

The sulfur isotopes analyses were undertaken at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, by using Continuous Flow Mass Spectrometer. GBW 04415 and GBW 04414 Ag_2S were used as the external standards and CDT as the reference standard, with the analytical accuracy of ±0.1‰ (2σ).

3.3 Hydrogen and oxygen isotopes

Hydrogen and oxygen isotopic compositions were analyzed in the Beijing Institute of Uranium Geology by using MAT-253. SMOW as the reference standard and the analytical accuracy is ±0.2‰ (2σ) for $\delta D_{H2O\text{-}SMOW}$ value and ±2‰ (2σ) for $\delta^{18}O_{quartz\text{-}SMOW}$ values.

3.4 Lead isotopes

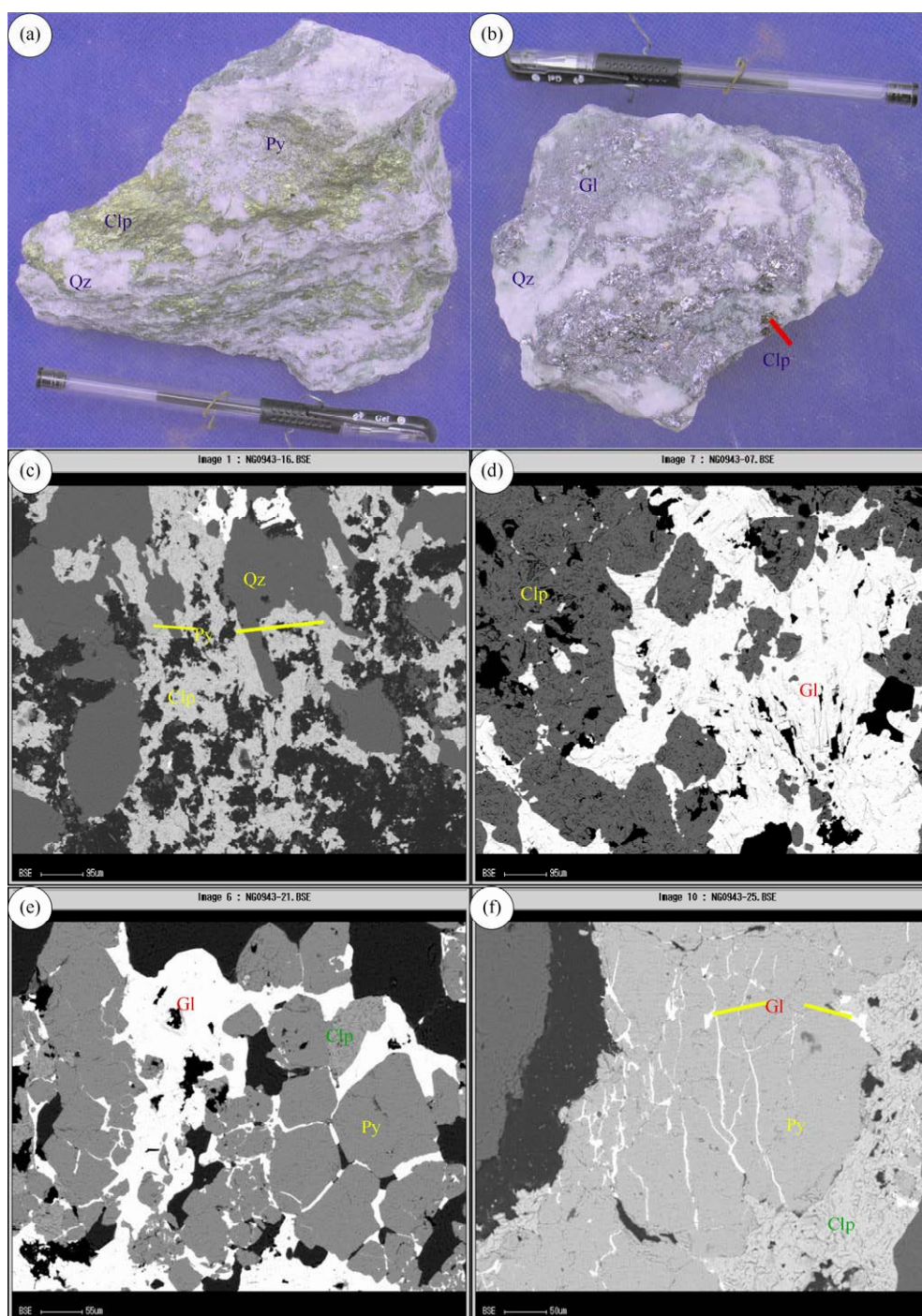Pb isotopes analyses were carried out using the GV Isoprobe–T thermal ionization mass spectrometer at the

Fig. 3. Relationship of coexisting minerals and structures and textures of ores.

(a), The chalcopyrite (Clp), pyrite (Py) and the first stage quartz (Qz) assemblage is contained by the middle stage quartz; (b), The early stage chalcopyrite coexisting with quartz is contained by the late stage quartz; (c), Colloid chalcopyrite coexisting with pyrite; (d), The early chalcopyrite is contained by the late stage galena and chalcopyrite; (e), The early stage chalcopyrite coexisting with pyrite is cemented by the late stage galena; (f), Vein galena fill into the early stage pyrite, and the late stage chalcopyrite metasomatism the early stage pyrite.

Beijing Institute of Uranium Geology. The analytical procedure involved dissolution of samples using HF and HClO$_4$ in crucibles, followed by basic anion exchange resin to purify Pb. Analytical results for NBS 981 are ^{206}Pb/^{204}Pb=16.940±0.011(2σ), ^{207}Pb/^{204}Pb=15.497±0.009 (2σ), ^{208}Pb/^{204}Pb= 36.715±0.026(2σ), in agreement with

the referenced value (Belshaw et al., 1998).

4 Results

4.1 Cu isotopic compositions

Cu isotopic compositions of chalcopyrite separates are

listed in Table. 1. Chalcopyrite from the Nage Cu-Pb deposit has $\delta^{65}Cu_{NBS}$ values ranging from −0.09‰ to +0.33‰, with a mean value of +0.14‰. Sample NG-22 and its parallel sample NG-22P* has similar $\delta^{65}Cu_{NBS}$ values within errors. Chalcopyrite precipitated in the early, middle and final mineralization stages of the Nage deposit has $\delta^{65}Cu_{NBS}$ values ranging from −0.09‰ to +0.13‰, +0.17‰ to +0.18‰ and +0.33‰, respectively. In general, the $\delta^{65}Cu_{NBS}$ values of chalcopyrite in the Nage deposit increase from the early to late mineralization stages.

4.2 S isotopic compositions

Sulfur isotopic compositions of sulfide minerals are listed in Table. 2 and are shown in Fig. 4. ^{34}S is enriched in pyrite and chalcopyrite, while ^{32}S is enriched in galena. $\delta^{34}S_{CDT}$ values of chalcopyrite, pyrite and galena range from +0.6‰ to +2.7‰, +2.8‰ and −2.7‰ to +0.7‰, respectively. The trend of $\delta^{34}_{pyrite}>\delta^{34}_{chalcopyrite}>\delta^{34}_{galena}$, suggesting that sulfur isotopic fractionation has reached balance during sulfide precipitated.

4.3 H-O isotopic compositions

Hydrogen and oxygen isotopic compositions of quartz are listed in Table. 3. $\delta D_{H2O-SMOW}$ values of water in fluid inclusions of quartz range from −44.4‰ to −60.7‰, and $\delta^{18}O$ quartz-SMOW values of quartz range from +14.9‰ to +16.0‰.

4.4 Pb isotopic compositions

Lead isotopic compositions of diabase, host rocks, ores and sulfide minerals are listed in Table. 4. $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios for diabase rocks ranging from 37.830 to 38.012, 15.620 to 15.635 and 17.808 to 17.902, respectively; for host rocks ranging from 38.201 to 38.637, 15.648 to 15.673 and 17.820 to 18.258, respectively; for ores ranging from 38.152 to 38.345, 15.656 to 17.708 and 17.991 to 18.049, respectively and for sulfide minerals ranging from 38.166 to 38.384, 5.669 to 15.687 and 17.993 to 18.122. Ores and sulfide minerals have a small range of Pb isotopic compositions, similar to host rocks, unlike whole diabase rocks.
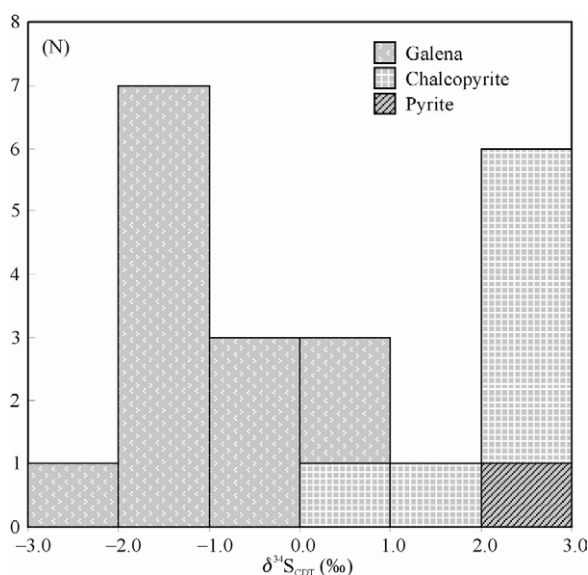

Fig. 4. Histogram of sulfur isotopic compositions of the Nage Cu-Pb deposit.

Table 1 Cu isotopic compositions of chalcopyrite from the Nage Cu-Pb deposit

No.	Obj.	$\delta^{65}Cu_{NBS\ 976}$	Error (2σ)	Source
NG-17	The early stage Clp	0.13	0.02	
NG-21-2	The final stage Clp	0.33	0.03	
NG-22	The middle stage Clp	0.17	0.01	
NG-22P*	The middle stage Clp	0.18	0.01	This paper
NG-23	The middle stage Clp	0.18	0.03	
NG-40	The early stage Clp	−0.09	0.04	
NG-43	The early stage Clp	0.08	0.04	

Note: Clp-chalcopyrite, P*- parallel sample.

Table 2 S isotopic compositions of sulfide minerals from the Nage Cu-Pb deposit

No.	Obj.	$\delta^{34}S_{CDT}$	No.	Obj.	$\delta^{34}S_{CDT}$
NG-21-1	The final stage Py	2.8	NG-20	Gl	−1.0
NG-17	The early stage Clp	2.0	NG-21-3	Gl	0.1
NG-22	The middle stage Clp	2.7	NG-31	Gl	−1.9
NG-21-2	The final stage Clp	2.5	NG-34	Gl	−1.6
NG-23	The middle stage Clp	2.4	NG-35	Gl	−1.6
NG-33	The early stage Clp	0.6	NG-36	Gl	−0.8
NG-40	The early stage Clp	1.9	NG-37	Gl	0.7
NG-43	The early stage Clp	2.5	NG-38	Gl	−1.8
NG-12	Gl	−1.9	NG-39	Gl	−1.6
NG-14	Gl	−0.9	NG-41	Gl	−1.2
NG-16	Gl	−2.7	Source: This paper and Yang et al., 2010		

Note: Clp-chalcopyrite, Py-pyrite, Gl-galena.

Table 3 $\delta D_{H2O-SMOW}$ and $\delta^{18}O_{quartz-SMOW}$ values of quartz from the Nage Cu-Pb deposits

No.	Obj.	$\delta D_{H2O-SMOW}$ /‰	$\delta^{18}O_{quartz-SMOW}$ /‰	$\delta^{18}O_{H2O-SMOW}$ /‰
NG-14	Quartz	−44.4	16.0	9.0
NG-16	Quartz	−49.8	15.8	8.8
NG-33	Quartz	−60.7	14.9	7.9
NG-40	Quartz	−52.7	15.2	8.2
NG-41	Quartz	−47.7	15.7	8.7

Note: $\delta^{18}O_{H2O-SMOW}$ values were calculated with $1000ln\alpha_{quartz-water}=4.48\times10^6/T^2 -4.77\times10^3/T+1.71$ ($T=260$; Zheng and Chen, 2000).

Table 4 Pb isotopic compositions of diabase, host rocks, ores and sulfide minerals from the Nage Cu-Pb deposit

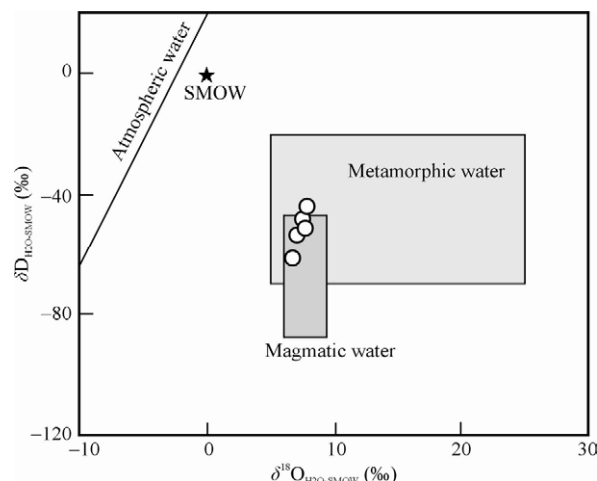| No.	Obj.	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
NG-19	Diabase	17.818	15.620	37.885
NG-45	Diabase	17.822	15.620	37.974
NG-46	Diabase	17.823	15.621	37.830
NG-47	Diabase	17.808	15.635	37.949
NG-48	Diabase	17.902	15.631	38.012
NG-02	Phyllite	17.820	15.648	38.286
NG-03	Slate	17.945	15.673	38.201
NG-08	Phyllite	18.123	15.664	38.462
NG-15	Slate	18.258	15.668	38.637
NG-18	Slate	18.042	15.670	38.241
NG-20	Gl + Clp + Qz ores	17.996	15.660	38.152
NG-21	Clp + Py + Qz ores	18.021	15.688	38.236
NG-22	Gl + Py + Clp + Qz ores	18.039	15.708	38.311
NG-23	Clp + Py + Gl + Qz ores	18.049	15.684	38.345
NG-31	Gl + Py + Clp + Qz ores	18.015	15.664	38.156
NG-33	Clp + Py + Gl + Qz ores	18.026	15.656	38.168
NG-41	Gl + Clp + Qz ores	18.021	15.670	38.203
NG-43	Clp + Py + Gl + Qz ores	17.991	15.674	38.169
NG-17	The early stage Clp	18.032	15.671	38.267
NG-20	Galena	17.993	15.669	38.174
NG-22	The middle stage Clp	18.122	15.687	38.384
NG-21-3	Galena	18.006	15.673	38.192
NG-21-1	The final stage Clp	18.020	15.671	38.219
NG-21-2	Pyrite	18.010	15.672	38.203
NG-31	Galena	18.012	15.672	38.206
NG-41	Galena	18.016	15.674	38.209
NG-43	The early stage Clp	17.997	15.670	38.166

Note: Clp-chalcopyrite, Py-pyrite, Gl-galena.

5 Discussions

5.1 Possible sources of sulfur

Primary ores from the Nage Cu-Pb deposit have simple sulfide mineralogy, including chalcopyrite, galena, pyrite and little sphalerite, but lack sulfate minerals. Therefore, sulfide's $\delta^{34}S$ values are thought to approximate the hydrothermal fluids' $\delta^{34}S$ value (e.g. Ohmoto et al., 1990; Zhou et al., 2010, 2013a, 2013b, 2013c). $\delta^{34}S_{CDT}$ values of sulfide minerals range from $-2.7‰$ to $+2.8‰$ (Table.2), similar to mantle-derived sulfur ($0\pm3‰$, Chaussidon et al., 1989). The trend of $\delta^{34}S_{pyrite}>\delta^{34}S_{chalcopyrite}>\delta^{34}S_{galena}$ suggests that the sulfur isotopic balance fractionation equation between sulfide minerals pairs could be used to calculate theirs precipitation temperature (Czamanske and Rye, 1974). The calculated mineralization temperatures range from 250°C to 450°C (mean 260°C), slightly higher than homogenization temperatures (120°C to 300°C, Yang et al., 2010). These temperatures of the Nage Cu-Pb deposit are relatively lower than those of magmatic deposits (e.g. Li et al., 2009a, 2009b; Yang et al., 2012), indicating that sulfur in ore-forming fluids maybe derived from post-magmatic hydrothermal fluids.

5.2 Sources of H$_2$O

The calculated $\delta^{18}O_{H2O-SMOW}$ values range from $+7.9‰$ to $+9.0‰$ ($1000ln\alpha_{Qz-W}=4.48\times10^6/T^2- 4.77\times10^3/T+1.71$, $T=260°C$; Zheng and Chen, 2000). In the diagram of $\delta D_{H2O-SMOW}$ vs. $\delta^{18}O_{H2O-SMOW}$ (Fig. 5), all samples fall in the

Fig. 5. Diagram of $\delta D_{H2O-SMOW}$ vs. $\delta^{18}O_{H2O-SMOW}$ for the Nage Cu-Pb deposit.

field of magmatic and metamorphic waters. As the host rocks of the Nage deposit are Neoproterozoic slate and phyllite, so mixed sources of H$_2$O in the hydrothermal fluids are reasonable.

5.3 Constraint on possible sources of ore-forming metals by Pb isotopes

Although some studies suggested that the metals of the Nage Cu-Pb deposit were provided by the Neoproterozoic igneous rocks (e.g. Liu et al., 2010), yet others studies considered that the host rocks were important sources of metals (e.g. Yang et al., 2010; Chen et al., 2011). Ores and sulfide minerals from the Nage Cu-Pb deposit have similar and homogeneous Pb isotopes (Table.4). In the plot of $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$, all samples fall close to the orogenic belt and upper crust Pb evolution curves of Zartman and Doe (1981), within the field of host rocks and near to the field of diabase (Fig. 6). The Pb isotopic data indicate that lead metal of the Nage Cu-Pb deposit is most likely consistent with metals mainly derived from host Neoproterozoic metamorphic sedimentary rocks.

5.4 Possible causes for Cu isotopic fractionation and origin of copper metals
5.4.1 Possible causes for Cu isotopic fractionation

Several processes are considered to be important for Cu isotopic fractionation, such as precipitation temperature, redox, fluids exsolution, fluids mixing, biological effect and so on (e.g. Maréchal et al., 1999; Jiang et al., 2002; Zhu et al., 2002; Larson et al., 2003; Markl et al., 2006; Qian et al., 2006; Asael et al., 2007; Lu et al., 2008; Fernandez and Borrok, 2009; Haest et al., 2009). The early stage chalcopyrite enriched in ^{65}Cu was found in modern seabed hydrothermal mineralizing system (Zhu et al., 2000; Rouxel et al., 2004) and the Dexing porphyry copper

deposits (Qian et al., 2006). Zhu et al. (2000) and Rouxel et al. (2004) considered that ^{65}Cu was prior to leach from source rocks, leading the early stage chalcopyrite enriched in ^{65}Cu, and subsequently the late stage chalcopyrite precipitated in ^{65}Cu-depleted hydrothermal fluids has low δ^{65}Cu value. However, others suggested that precipitation temperature is a main cause for such Cu isotope variation, because ^{65}Cu-enriched chalcopyrite precipitated in the early stage at high temperature, along with mineralization temperature reducing, chalcopyrite precipitated later has low δ^{65}Cu value (Jiang et al., 2002; Qian et al., 2006; Lu et al., 2008).

In our study, we find that from the early to late mineralization stages, the enrichment degree of ^{65}Cu in precipitated chalcopyrite is increasing. The same Cu isotopic variations were found in the Qulong porphyry copper deposit (Li et al., 2009b). Li et al. (2009b) suggested that the redox and biological effect are not the main causes for such Cu isotopic variation based on systematic fluids inclusion and ore deposit geochemistry data. Fluids exsolution and/or mixing were considered to be crucial for Cu isotopic fractionation during chalcopyrite precipitation process. The fluids exsolution model was based on hypothesis prior migration of ^{63}Cu in gas phase from source rocks and the fluids mixing model was based on hypothesis of ^{65}Cu-enriched oxidized atmospheric water added to the hydrothermal fluids latter (Li et al., 2009b). Previous studies have found that ^{32}S is migrated in gas phase at high temperature (e.g. Zheng and Chen, 2000). The positive correlation of δ^{65}Cu$_{NBS}$ and δ^{34}S$_{CDT}$ values for chalcopyrite (Fig. 7) indicates that ^{63}Cu also migrates in gas phase from its source rocks at relatively high temperature. As the δ^{65}Cu$_{NBS}$ values of host rocks and metamorphic water are not available, we considered that fluids exsolution is the important cause for Cu isotope fractionation, but we couldn't reject the possibility of fluids mixing.

5.4.2 Possible origin of Cu metal

The δ^{65}Cu$_{NBS}$ values of chalcopyrite separates from the Nage Cu-Pb deposit were similar to chalcopyrite from typical magmatic deposit (Fig. 8; Maréchal et al., 1999; Zhu et al., 2000; Larson et al., 2003; Wang and Zhu, 2010), unlike chalcopyrite from skarn deposit (Maher and Larson, 2007) and sedimentary deposit (Asael et al., 2007). It is also similar to that of mantle-derived basic igneous rocks (−0.5‰ to +0.5‰; Maréchal et al., 1999; Maréchal and Albarède, 2002; Zhu et al., 2000, 2002). The positive correlation of δ^{65}Cu$_{NBS}$ and δ^{34}S$_{CDT}$ values for chalcopyrite from the Nage deposit (Fig.7) also indicates that Cu metal was derived from mantle-derived magma. Therefore, the Jiabang-Nage diabase may supply copper metal for the Nage Cu-Pb deposit.
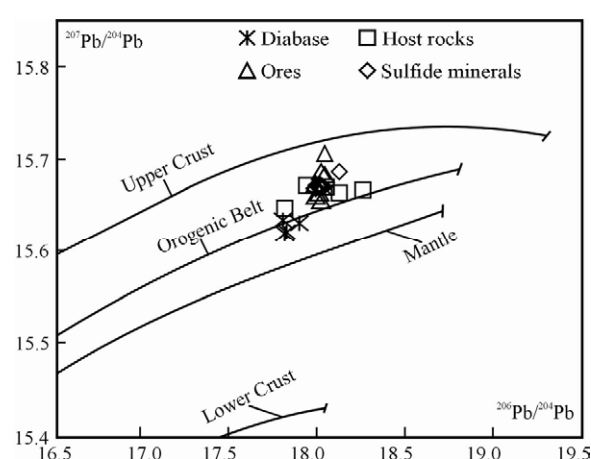

Fig. 6. Plot of ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb for the Nage Cu-Pb deposit.
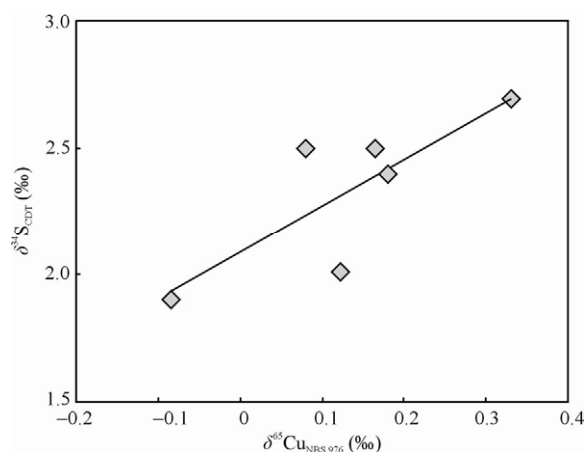

Fig. 7. Diagram of δ^{34}S$_{CDT}$ vs. δ^{65}S$_{NBS}$ values of chalcopyrite from the Nage Cu-Pb deposit.
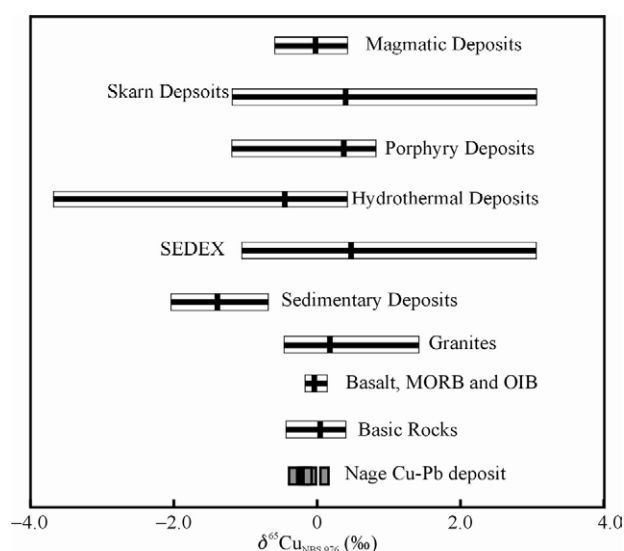

Fig. 8. Compared Cu isotopic compositions of chalcopyrite from the Nage Cu-Pb deposit with chalcopyrite from others ore genesis types and igneous rocks.
Data from Maréchal et al., 1999, 2002; Zhu et al., 2000, 2002; Larson et al., 2003; Asael et al., 2007; Maher and Larson, 2007; Wang and Zhu, 2010; Mathur et al., 2012.

5.5 Ore genesis

The Neoproterozoic igneous rocks associated with breakup of supercontinent Rodinia (~825 Ma; e.g. Zeng et al., 2003, 2005; Wang et al., 2010a, 2010b, 2012a, 2012b). Basic volcanic rocks to acidic intrusive rocks are widely distributed in the Nage ore field and especially the Jiabang -Nage diabase dyke and Jiabang buried granite porphyry are close spatially associated with the Nage deposit. H-O-S-Cu-Pb isotopic data indicate that ore-forming fluids and metals were mainly derived from magma and were partly supplied by the host Neoproterozoic metamorphic rocks. As the mineralization temperature is relatively medium (120°C to 300°C), the ore genesis of the Nage Cu-Pb maybe belongs to post-magmatic hydrothermal type.

6 Conclusions

(1) The Nage Cu-Pb deposit is hosted in silicified phyllite and slate of the Neoproterozoic Jialu and Wuye Formations and is structurally controlled by EW-trending fault and the Jiabang anticline.

(2) H_2O in hydrothermal fluids has a mixture origin of magmatic and metamorphic waters, sulfur and copper metal were sourced from mantle-derived magma, and Lead metal was originated from the host Neoproterozoic metamorphic rocks.

(3) From the early to late mineralization stages, ^{65}Cu-enriched in precipitated chalcopyrite is largely due to prior migration of ^{63}Cu in gas phase during fluids exsolution from magma.

(4) The ore genesis of the Nage Cu-Pb deposit maybe belongs to post-magmatic hydrothermal type.

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