

# The occurrence of metallic copper and redistribution of copper in the shocked Suizhou L6 chondrite

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**Abstract** Copper possesses very strong chalcophile properties, but under the conditions found in meteorites, its behavior is like that of siderophile elements. The Suizhou meteorite is a highly shocked L6 chondrite. Troilite and taenite are considered the main primary carrier of copper in this meteorite, and the post-shock thermal episode is considered the main reason that elemental Cu migrates from its original host phase and forms metallic grains. The Suizhou meteorite contains a few very thin shock melt veins. The occurrence and behavior of metallic copper in this meteorite were studied by optical microscopic examination, electron microprobe analyses, and high-resolution X-ray elemental intensity mapping. Our results show that metallic copper is abundant in the Suizhou chondritic rock. Metallic copper grains adjacent to small troilite grains inside FeNi metal are the most common occurrence, and those at the FeNi metal–troilite interface are the second most common case. The metallic copper grains occurring at the interface of FeNi metal/troilite and silicate are rather rare. Metallic copper grains are not observed within the Suizhou shock veins, Instead, Cu in elemental form is transferred through shock metamorphism into FeNi metal + troilite intergrowths. Four different occurrence types of Cu in the FeNi metal + troilite intergrowths have been identified: the concentrations of Cu in the FeNi + FeS intergrowths for four occurrence types are rather close, we estimate it might be lower than 1 wt%.

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## 1 Introduction

Copper possesses a distinct chalcophile nature. However, when subjected to the conditions formed in meteorites, copper demonstrates behavior similar to that of siderophile elements (Liu et al 1984). Metallic copper is commonly found as one of the opaque accessory minerals in ordinary chondrites (Ramdohr 1973; Rubin 1994a, 1997). According to Liu et al. (1984), troilite (FeS) is identified as the primary carrier of copper in meteorites. The concentrations of copper in meteorites exhibit the following trends: higher concentrations in metallic minerals, followed by troilite, and lower concentrations in silicates. Tomkins (2009) and Luszczek and Krzesinska (2020) also reported that troilite may be the primary carrier of copper in meteorites, but taenite is another important phase.

Tomkins (2009) and Luszczek and Krzesinska (2020) suggested that post-shock thermal episode is a key to mobilizing elemental Cu to move from its original host phase and to form metallic grains in ordinary chondrites. The Suizhou meteorite is a heavily shock-metamorphosed chondrite, in which almost all plagioclase grains have been transformed to its glassy phase (maskelynite) at a pressure range of 25–30 GPa and a temperature of about 1000 °C (Xie and Chen 2016). Hence, we assume that this *P-T* regime provides a good condition suitable for the migration of Cu, formation of metallic copper, and redistribution of Cu in the shock veins of this meteorite.

Rubin (1994a) documented nine different occurrences of metallic copper in ordinary chondrites. The two most

common cases are: (1) at kamacite-troilite interface, and (2) adjacent to small troilite grains inside Ni-rich metal. In almost all cases the metallic copper grains exhibit irregular shapes and have grain sizes 1–6  $\mu\text{m}$ . However, there have been rare occurrences of unusually large copper grains that have been described (Olsen 1973). Limited electron microprobe data indicate that the metallic copper contains ~1.5 wt%–2.0 wt% Ni in solid solution (Olsen 1973; Rubin 1994a). Fortunately, small grains of metallic copper were observed in the Suizhou L6 chondrite by optical and scanning electron microscopic studies (Chen 1990). Shen and Zhuang (1990) also reported the presence of a few metallic copper grains in this meteorite.

In our previous studies on the Suizhou L6 chondrite, only a few grains of metallic copper were found in the chondritic rock, and no copper minerals were observed in its shock melt veins. However, we utilized laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to analyze the concentrations of chalcophile elements, including Cu, Zn, Pb, As, Sb, Au, Hg, and Bi, in the silicate minerals outside the veins and within the vein matrix in the Suizhou chondrite (Xie and Chen 2016). It was found that in comparison with the silicate minerals in the Suizhou chondritic rock, copper enriched in FeNi metal- and troilite-rich vein matrix (144 vs 25.3 ppm in olivine, 96 ppm in pyroxene) (Xie and Chen 2016). This is consistent with the above-described trend of copper in ordinary chondrites (FeNi metal > troilite > silicates). Due to the very small size (a few microns and less) of minerals in the vein matrix and the limited number of analyses conducted on mineral phases outside and inside melt veins, the precise distribution and redistribution features of copper in different phases before and after shock events are still not fully understood. Further research and a more comprehensive analysis are needed to gain a clearer understanding of how copper is distributed and redistributed in chondrite samples during and after shock. More recently, our detailed microscopic study on Suizhou chondrite observed more than one hundred metallic copper grains in various occurrences. Furthermore, our laboratory is equipped with an advanced electron microprobe analyzer, which has provided us with the opportunity to make observations and high-resolution X-ray elemental intensity mapping of Cu and its coexisting elements in the micron- and nano-sized mineral phases within the shock veins of the Suizhou chondrite. In this paper, we report our newly obtained results on the occurrences of metallic copper and the redistribution of Cu within the shock veins of the Suizhou chondrite.

## 2 Samples and analytical methods

The Suizhou L6 chondrite fell on April 15, 1986, at Dayanpo, Suizhou City, Hubei Province, China. This meteorite

consists of olivine, low-Ca pyroxene, diopside, plagioclase, FeNi-metal, troilite, merrillite, chlorapatite, chromite, ilmenite, pyrophanite, metallic copper, and shenzhuangite (Xie et al. 2001a, b; Xie and Chen 2016; Bindi and Xie 2017). The Suizhou meteorite was classified as strongly shock-metamorphosed (S6) L-group chondrite due to the presence of transformation of plagioclase to maskelynite (Xie et al. 2001a). This meteorite contains a few very thin shock-produced melt veins, and up to 18 high-pressure phases were identified inside or adjacent to melt veins. These high-pressure phases are ringwoodite, majorite, lingunite, tuite, xieite, chenmingite, wandaodeite, magnesiowüstite, majorite-pyrope<sub>ss</sub>, hemleyite, akimotoite, asimowite, poirierite, hiroseite, elgoesyite, ahrensite, bridgemenite and TiO<sub>2</sub>-II (Bindi et al. 2021; Chen et al. 2003, 2008; Xie and Chen 2016; Xie et al. 2002, 2003, 2019, 2023).

A total of 11 polished thin sections was prepared from fragments of the Suizhou meteorite. All observations and physical and chemical analyses are performed *in situ* on these sections. The mineral assemblages in polished thin sections of the samples were investigated by optical microscopy using a Leica DM 2500p microscope. A Shimadzu 1720 electron microprobe (EPMA) in the School of Geosciences and Info-Physics, Central South University, was used to study the mineral occurrence in back-scattered electron (BSE) mode and to quantitatively determine the chemical composition using the wavelength dispersive technique at 15 kV accelerating voltage and beam current of 10 nA. Natural and synthetic phases of well-known compositions were used as standards, such as Cu metal for Cu, Fe metal for Fe, Zn metal for Zn, Co metal for Co, and Ni metal for Ni, and the data were corrected using a ZAF program.

High-resolution X-ray elemental intensity mapping for Cu, Fe, Ni, S, and Si was applied on carbon-coated thin sections. The X-ray mapping was carried out using a JEOL JXA-8230 electron microprobe at the Key Laboratory of Mineralogy and Metallogeny in the Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences (CAS). The operation conditions of an accelerated voltage of 20 kV, a probe current of 100 nA, and a beam size of 0.5  $\mu\text{m}$  or 1  $\mu\text{m}$  were adopted for mapping depending on the scan area size. Fe and S were analyzed using a PETJ crystal. Si and Ni were analyzed using a TAP crystal. Cu was analyzed with a LIFH crystal to strengthen X-ray intensity. The step size was set to 0.5–1  $\mu\text{m}$  and the dwell time was set to 100 ms for each point.

## 3 Results

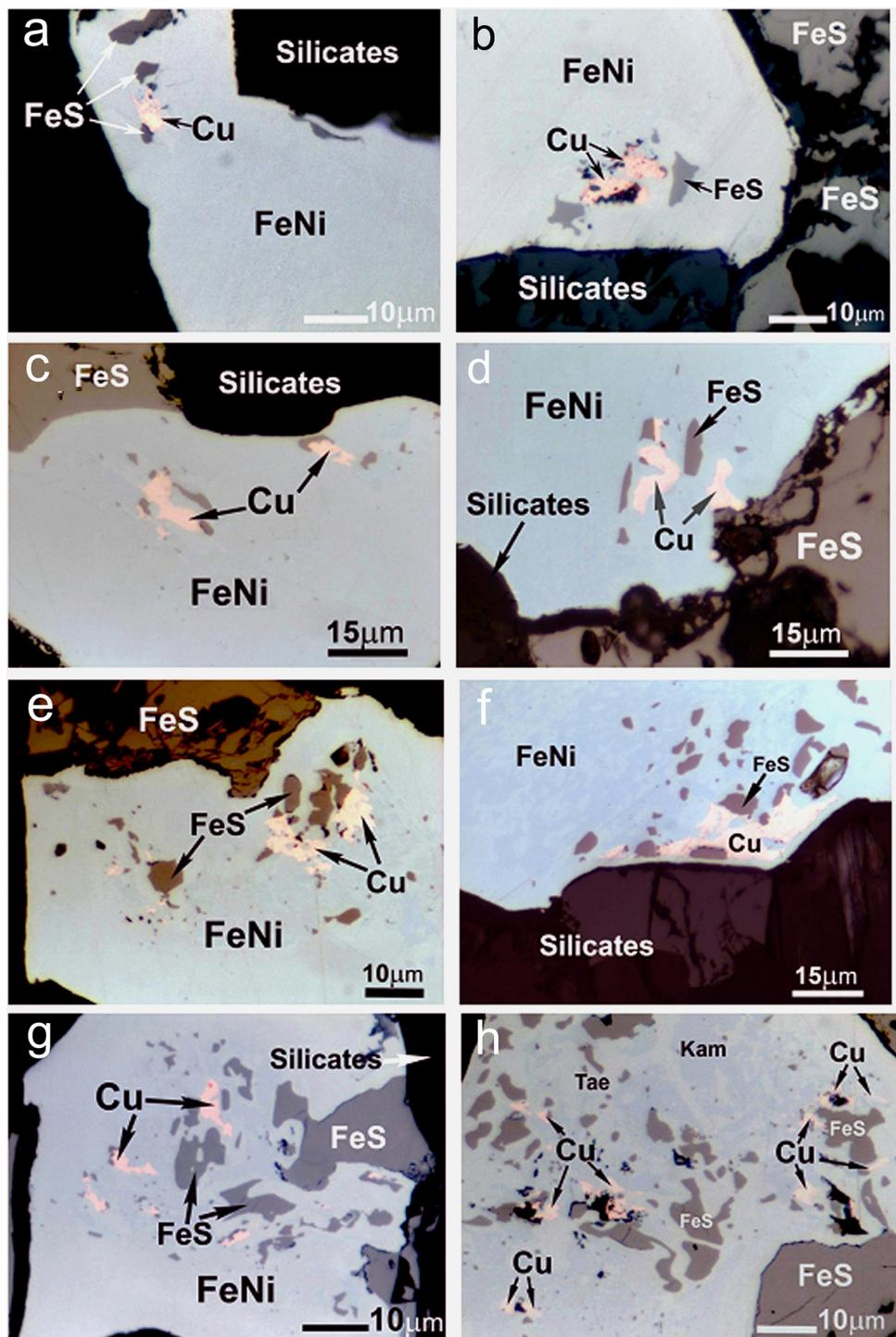
### 3.1 The occurrence of metallic copper in the Suizhou chondrite

A total of 11 polished sections was analyzed in our study, and each of them contains metallic copper. Under reflected

light, metallic copper exhibits a distinct violet-red color and possesses isotropic optical properties. It typically appears in granular or irregular shapes. Metallic copper occurs in the Suizhou meteorite either as a small mineral inclusion in FeNi metal (kamacite and taenite), or as individual grains in the interfaces of kamacite, taenite, and troilite, and, in rare cases, in the interfaces of kamacite, taenite, and silicate minerals. Figure 1a–h show some metallic copper grains

with a grain size of  $5 \times 8$  to  $8 \times 15 \mu\text{m}$  are embedded in FeNi metal grains, but in close contact with irregular troilite that occurs as inclusions within the metal grains. Figure 2a–f display some individual metallic copper grains occurring at the interfaces of FeNi metal and troilite, and Fig. 2g and h demonstrate that metallic copper grains are enclosed in troilite. It was also discovered that certain individual grains of metallic copper are present at the troilite–silicate interface (Fig. 3a,

**Fig. 1** Reflect light microphotographs of the occurrences of metallic copper (Cu) in FeNi metal. Note the irregular copper grains (a–h) are all adjacent to small irregular troilite (FeS) grains inside FeNi metal

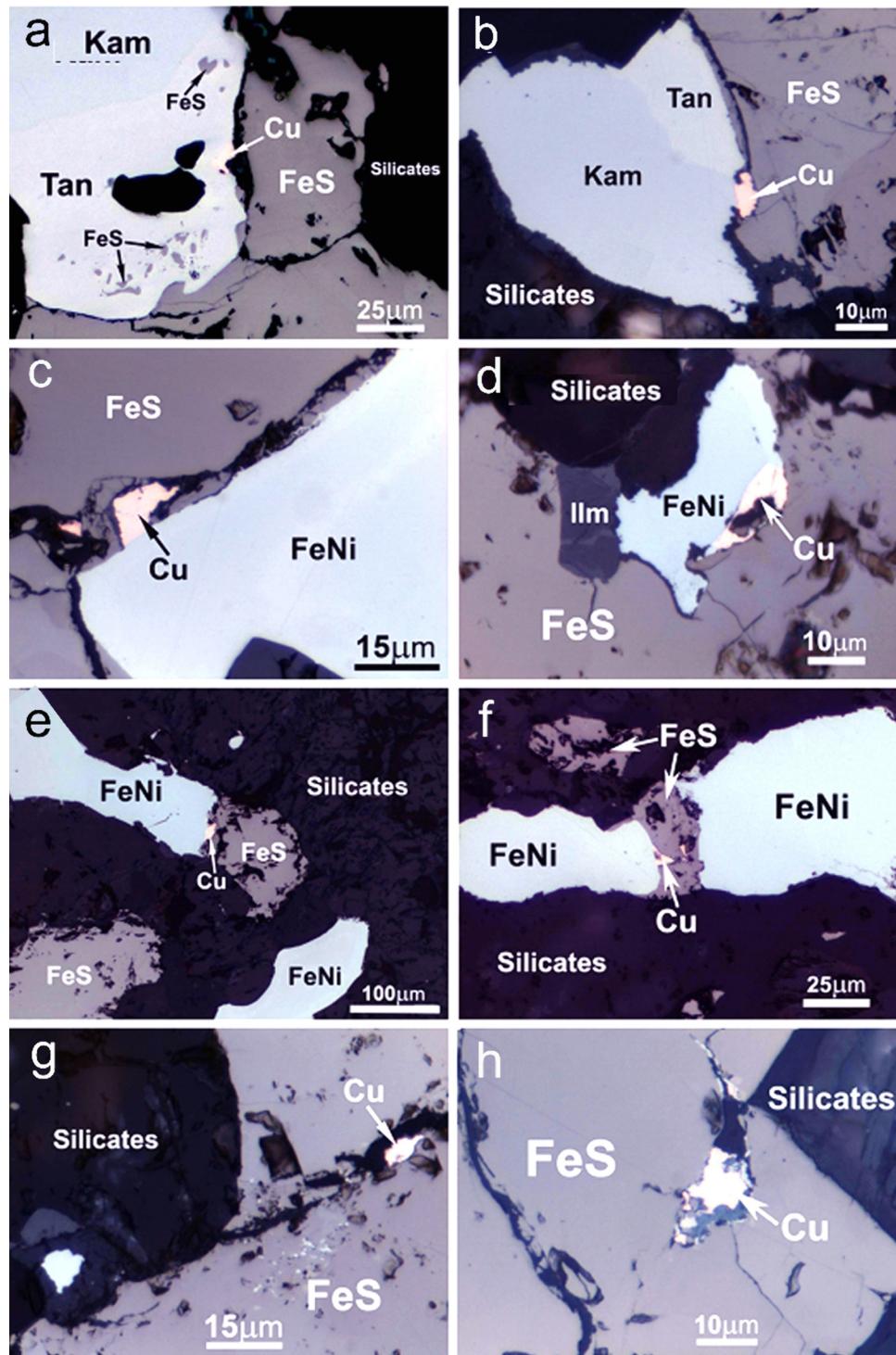


b), as well as at FeNi metal–silicate interface (Fig. 3c), and even at FeNi metal–troilite–silicate interface (Fig. 3d). It is important to note that during the shock metamorphism of the Suizhou meteorite, certain elongated metallic copper grains within the FeNi metal exhibit evidence of migration towards the interfaces between the metal and troilite (Fig. 3e–h). This suggests that the shock-induced dynamic

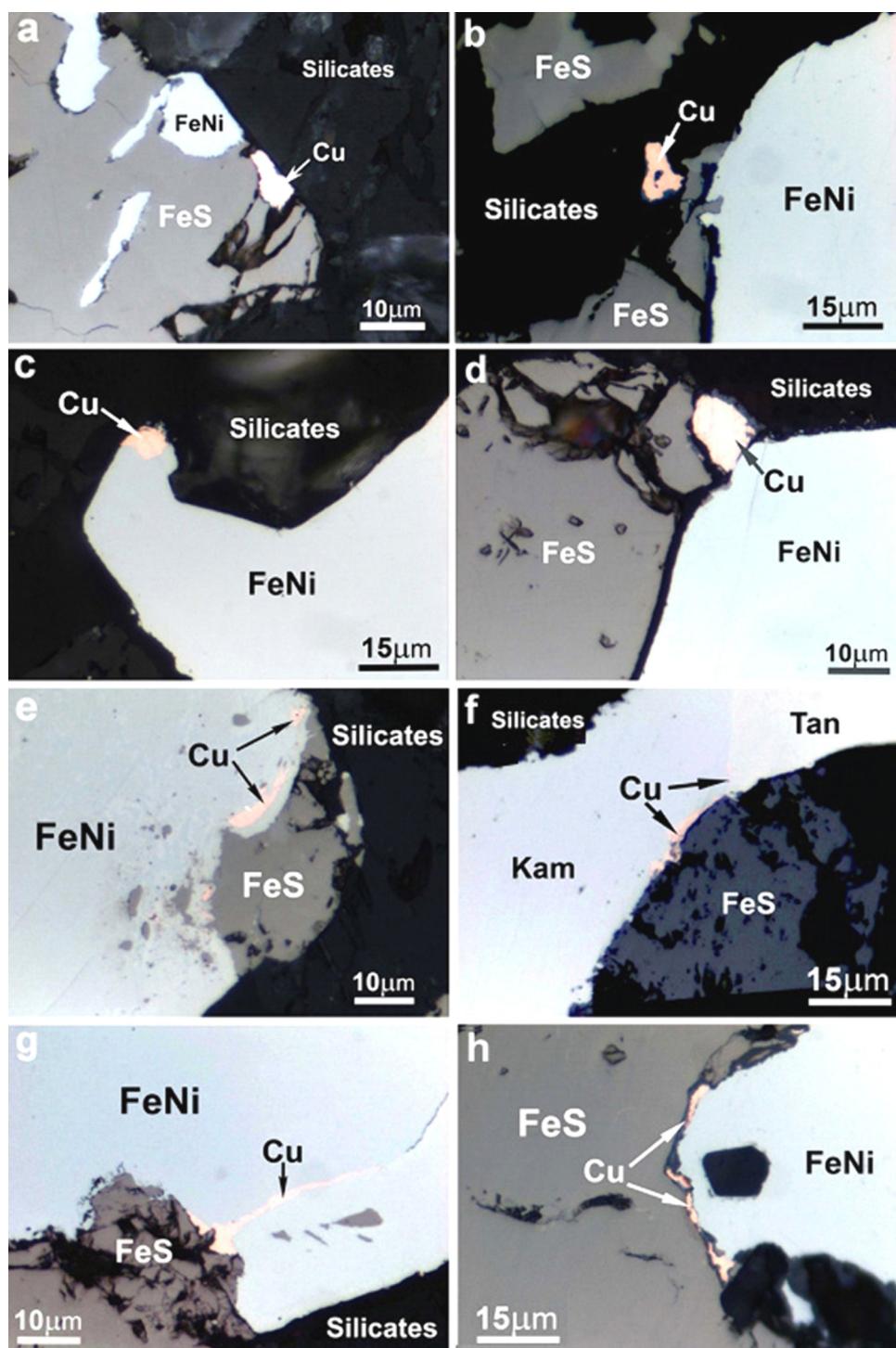
and thermal processes could lead to the redistribution and movement of metallic copper within the meteorite. The migration of metallic copper grains may have been influenced by the shock-induced deformation and transformation of the surrounding materials.

We conducted a statistical analysis of 61 metallic copper grains in the Suizhou chondritic rock. The results are listed

**Fig. 2** Reflect light microphotographs of occurrences of native copper (Cu) in troilite (FeS). Note the small metallic copper grains are at the FeNi metal–troilite interface (a–f), or enclosed in troilite (g–h). h. Kam = kamacite, tan = taenite, Ilm = ilmenite



**Fig. 3** Reflect light microphotographs showing the occurrence of metallic copper (Cu) at troilite (FeS)-silicate interface (a, b), at FeNi metal–silicate interface (c), FeNi metal–troilite–silicate interface (d), and showing the migration of copper from FeNi metal to the FeNi metal–troilite interface (e–h). Kam = kamacite, Tan = taenite



in Table 1. The table reveals that the most common occurrence among the six identified occurrences is the metallic copper grains adjacent to small and irregular troilite grains within FeNi metal. The second is metallic copper grains at the interface between FeNi metal and troilite. Metallic copper grains occurring at the interface of FeNi metal/troilite and silicate represent only a small percentage. The statistical results regarding the occurrences of metallic copper in the

Suzhou L6 chondrite are consistent with the results reported by Rubin (1994a, b) for ordinary chondrites.

### 3.2 Chemical composition of metallic copper in the Suzhou chondrite

Metallic copper in meteorites commonly contains Fe and Ni (Liu et al 1984). Our electron microprobe analysis for

**Table 1** The occurrence of metallic copper in the Suzhou chondritic rock

Occurrence	Grain number	Percentage
1 Adjacent to small troilite grains inside FeNi metal grains	40	65
2 Metal–troilite interface	13	21
3 Enclosed in troilite	3	5
4 Troilite–silicate interface	3	5
5 Metal–silicate interface	1	2
6 Metal–troilite–silicate interface	1	2

the metallic copper in the Suizhou meteorite gives the following average results in wt%: Cu 92.59, Fe 5.23, Ni 2.53, Co 0.02, Zn < 0.01, total 100.37 (Table 2). Shen and Zhuang (1990) also conducted electron microprobe analysis for a metallic copper grain in the Suizhou meteorite and got the following results in wt%: Cu 91.63, Fe 5.14, Ni 2.29, Ga 0.02, Ge 0.37, and S 0.18. The results of both ours and theirs analyses for the Suizhou metallic copper are similar. The calculated chemical formula of our metallic copper is  $\text{Cu}_{0.91}\text{Fe}_{0.06}\text{Ni}_{0.05}$ . The average Cu, Fe and Ni compositions of Suizhou metallic copper can also be compared with those in chondrites studied by Luszczek and Krzesinska in 2020 (95.56 wt%–97.30 wt% Cu, 3.29 wt%–5.12 wt% Fe, 1.54 wt%–2.46 wt% Ni), and in Eldee 001 (L6) chondrite (~ 5 wt%–6 wt% Fe, 3.0 wt% Ni) (Tomkins 2009). The average Ni content (2.53 wt%) in Suizhou metallic copper is a little higher than that of metallic copper in Blansko and Jelica meteorites (~ 1.5 wt%–2.0 wt%). It has been suggested that the element Ni might exist in solid solution with copper and iron (Olsen 1973; Rubin 1994b).

**Table 2** Composition of metallic copper in the Suizhou L6 chondrite (wt %)

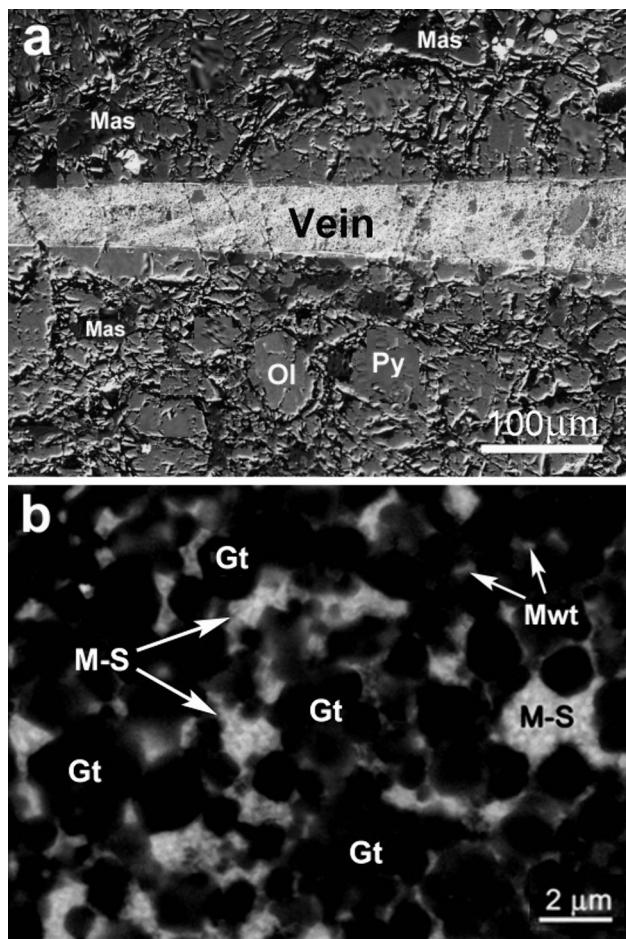
	Grain 1	Grain 2	Grain 3	Grain 4	Grain 5	Average
Mass %						
Cu	95.32	92.18	91.94	91.68	91.84	92.59
Fe	3.53	6.09	5.90	5.20	5.45	5.23
Ni	1.92	2.68	2.24	3.12	2.71	2.53
Co	0.01	0.03	0.03	0.03	0.02	0.02
Zn	n.d.	n.d.	0.01	n.d.	n.d.	< 0.01
Total	100.78	100.99	100.11	100.03	100.02	100.37
Atoms per formula based on total=1						
Cu	0.94	0.90	0.91	0.91	0.91	0.91
Fe	0.04	0.07	0.007	0.06	0.06	0.06
Ni	0.02	0.03	0.02	0.03	0.03	0.03
Co	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Zn	n. d.	n. d.	< 0.01	n. d.	n. d.	< 0.01
Total	1	1	1	1	1	1

Noe: n.d.=not detected

### 3.3 Redistribution of copper in the Suizhou shock melt veins

The Suizhou chondrite contains a few very thin shock melt veins, ranging from 100 to 200  $\mu\text{m}$  in width. These veins consist of a fine-grained vein matrix along with coarse-grained ringwoodite, majorite, maskelynite, and some other high-pressure phases (Xie et al. 2023). The vein matrix is primarily comprised of garnet, magnesiowüstite, and intergrowths of FeNi metal and troilite (Fig. 4) (Xie and Chen 2016). The whole overview of a shock melt vein in the Suizhou meteorite is shown in Fig. 4a, and the enlarged image of the fine-grained vein matrix is shown in Fig. 4b. From Fig. 4b it is clear that the metal + troilite intergrowths consist of troilite matrix and small round-shaped metal grains dispersedly embedded in the troilite matrix, and no metallic copper grains were observed within the intergrowths. From this, we can see that metallic copper occurs abundantly in Suizhou chondritic rock but never occurs in shock melt veins (Figs. 6, 7, 8, 9).

The concentrations of copper in the Suizhou silicate minerals both outside the veins and within the veins matrix were analyzed by LA-ICP-MS (Xie and Chen 2016). The results indicated that the vein matrix exhibited a significant enrichment of Cu with a concentration of 144 ppm. This concentration is considerably high compared to the Cu concentrations found in olivine (25.3 ppm) and pyroxene (96 ppm) located outside the veins. However, due to the very small grain size (less than 1  $\mu\text{m}$ ), it was not possible to analyze the Cu concentrations for the widely distributed FeNi metal and FeS intergrowths in the Suizhou vein matrix at that time. Very recently, we have been able to conduct the high-resolution X-ray elemental intensity mapping of Cu, Fe, Ni, S, and Si for different metallic and silicate phases



**Fig. 4** Back-scattered electron images showing the mineral assemblages in a Suizhou shock melt vein. a. The whole overview of the vein; b. enlarged image showing the fine-grained garnet (Gt), metal + troilite intergrowths (M+T), and magnesiowüstite (Mwt) in this vein. Note no metallic copper grains can be observed within these metal + troilite intergrowths (Xie and Chen 2016)

by a JEOL JXA-8230 electron microprobe in our institute. Hence, we could roughly evaluate the redistribution of Cu in the Suizhou shock melt veins.

To investigate the redistribution of copper in the shock veins of the Suizhou chondrite, we initially examined the presence of fine-grained FeNi metal and troilite within these veins. Our observations revealed four distinct types of occurrences for FeNi metal and troilite: (1) Type 1 occurrence: the fine-grained FeNi + FeS particles are spreading over the entire veins (Fig. 5a). (2) Type 2 occurrence: larger individual grains of FeNi metal and troilite are sparsely distributed within veins (Fig. 5b). (3) Type 3 occurrence: fine irregular-shaped veinlets composed of FeNi metal and troilite are present within the veins (Fig. 5c), and (4) Type 4: long and straight bands of FeNi metal and troilite at the margin of veins (Fig. 5d). By characterizing these different occurrences, we aim to gain insights into the redistribution

patterns of Cu within the shock veins of the Suizhou chondrite. We conducted high-resolution X-ray elemental intensity mapping of Cu, Fe, Ni, S, and Si for each of the four types mentioned above. The results are shown in Figs. 6, 7, 8 and 9. Upon analyzing these figures, it is evident that within the shock veins of the Suizhou chondrite, elemental Cu is primarily concentrated in the fine-grained intergrowths of FeNi metal and troilite. Additionally, it appears that the Si-rich silicate does not contain significant amounts of copper. These findings suggest a preferential association of Cu with the FeNi metal and troilite phases within the shock veins.

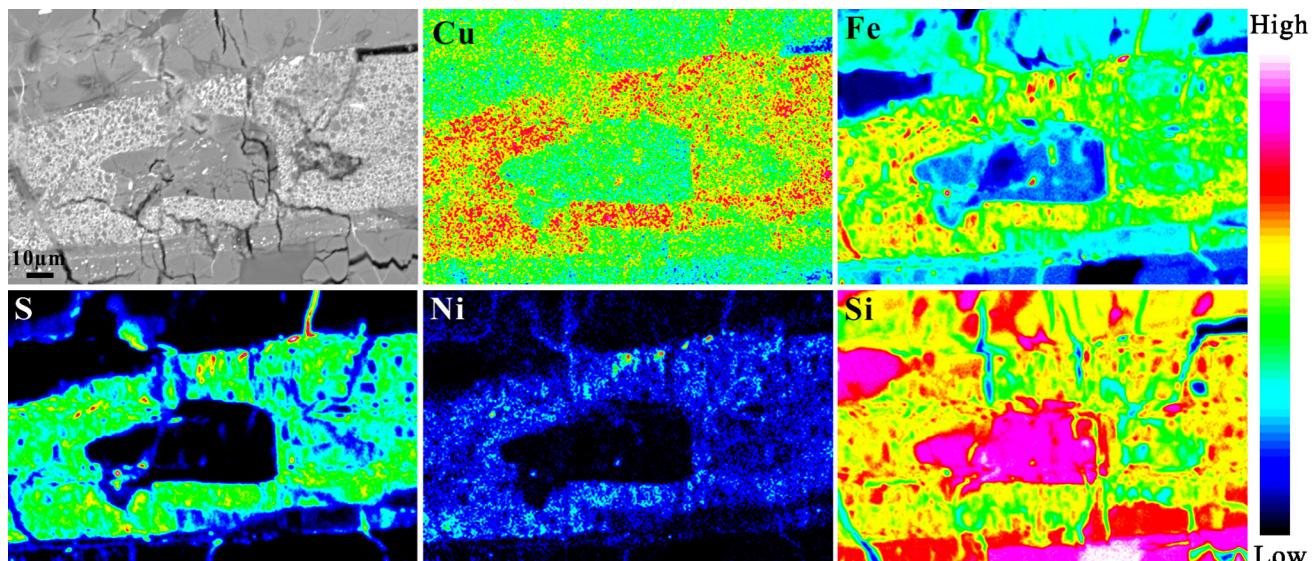
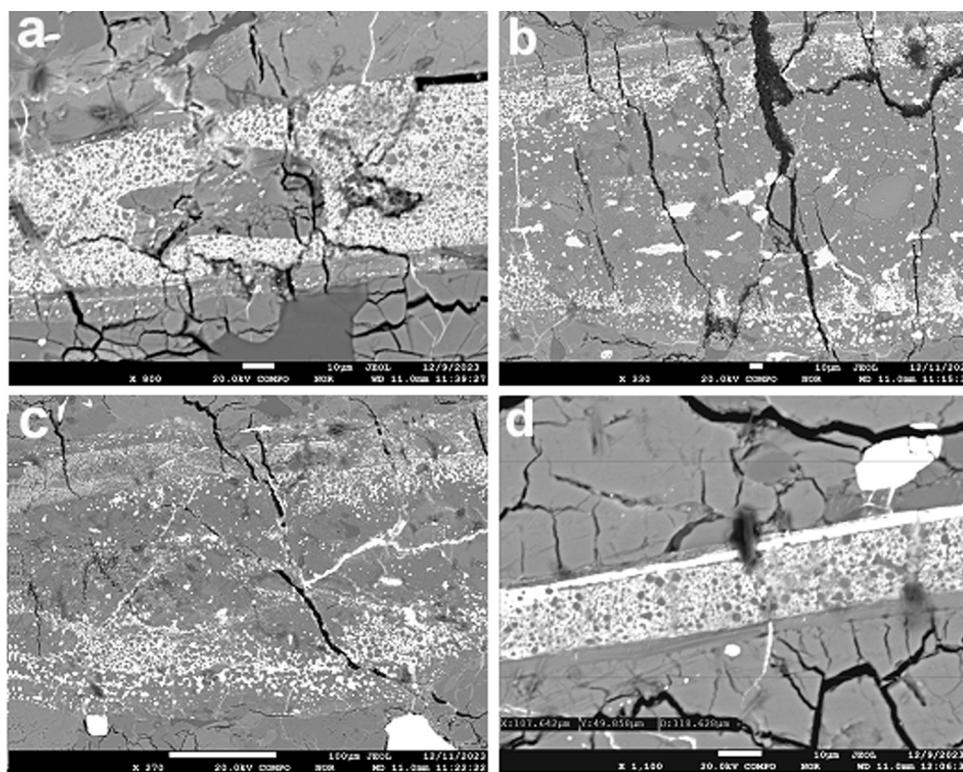
Based on the concentration histograms attached to elemental intensity maps of Cu, we could approximately estimate the concentrations of Cu for these four occurrence types. The results show that their Cu concentrations are similar and they all are lower than 1 wt%.

#### 4 Discussion

Metallic copper is one of the opaque accessory minerals in ordinary chondrites. For discussion of the redistribution of Cu in a meteorite, it is important to know the primary carrier of copper within it. According to the investigations of Tomkins (2009) and Luszczek and Krzesinska (2020), copper is primarily a constituent of Fe, Ni-alloy and also occurs in a native form, and sulfides do not host a significant amount of Cu. Among Fe, Ni-alloys, major Cu carrier phases are high-Ni taenite and tetrataenite. Shen and Zhuang (1990) reported that the Suizhou L6 chondrite contains 3.87 vol% of kamacite + taenite and 5.93 vol% of troilite. They also analyzed the average contents of Cu in metallic minerals of this chondrite by EPMA: kamacite-0.13wt% (from 12 analyses), taenite-0.30 wt% (from 15 analyses) and troilite-0.23 wt% (from 9 analyses). This result is not so consistent with that obtained by Tomkins (2009) and Luszczek and Krzesinska (2020) for seven H-group chondrites (kamacite-up to 0.02 wt% Cu, taenite-up to 0.19 wt% Cu and troilite-only up to 0.01 wt% Cu).

It was suggested that post-shock thermal episode is a key to mobilizing elemental Cu to move from its original host phase and to form metallic grains in ordinary chondrites (Tomkins 2009; Luszczek and Krzesinska 2020). According to statistical analysis on 106 ordinary chondrites conducted by Rubin (1994a), metallic copper occurs in at least 66% of ordinary chondrites as heterogeneously distributed, small (typically < 20 μm) rounded to irregular grains. The Suizhou meteorite is an L-group ordinary chondrite. Our finding of more than one hundred metallic copper grains in polished thin sections of this ordinary chondrite implies that the Suizhou meteorite could be listed as one of the richest ordinary chondrites in metallic copper.

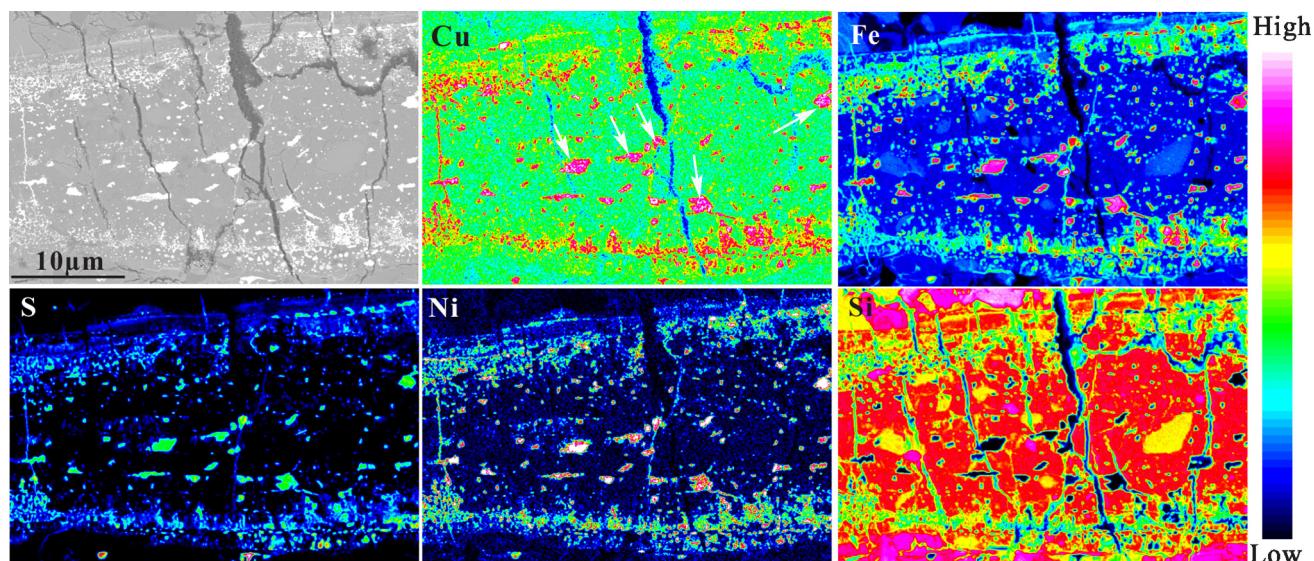
**Fig. 5** BSE images showing the four types of FeNi + FeS occurrence. **a** Wide distribution of FeNi + FeS particles over the entire vein. **b** Sparsely distribution of larger individual grains within the vein. **c** Fine irregular-shaped veinlets present in a vein. **d** A long and straight band occurring in a vein upper margin



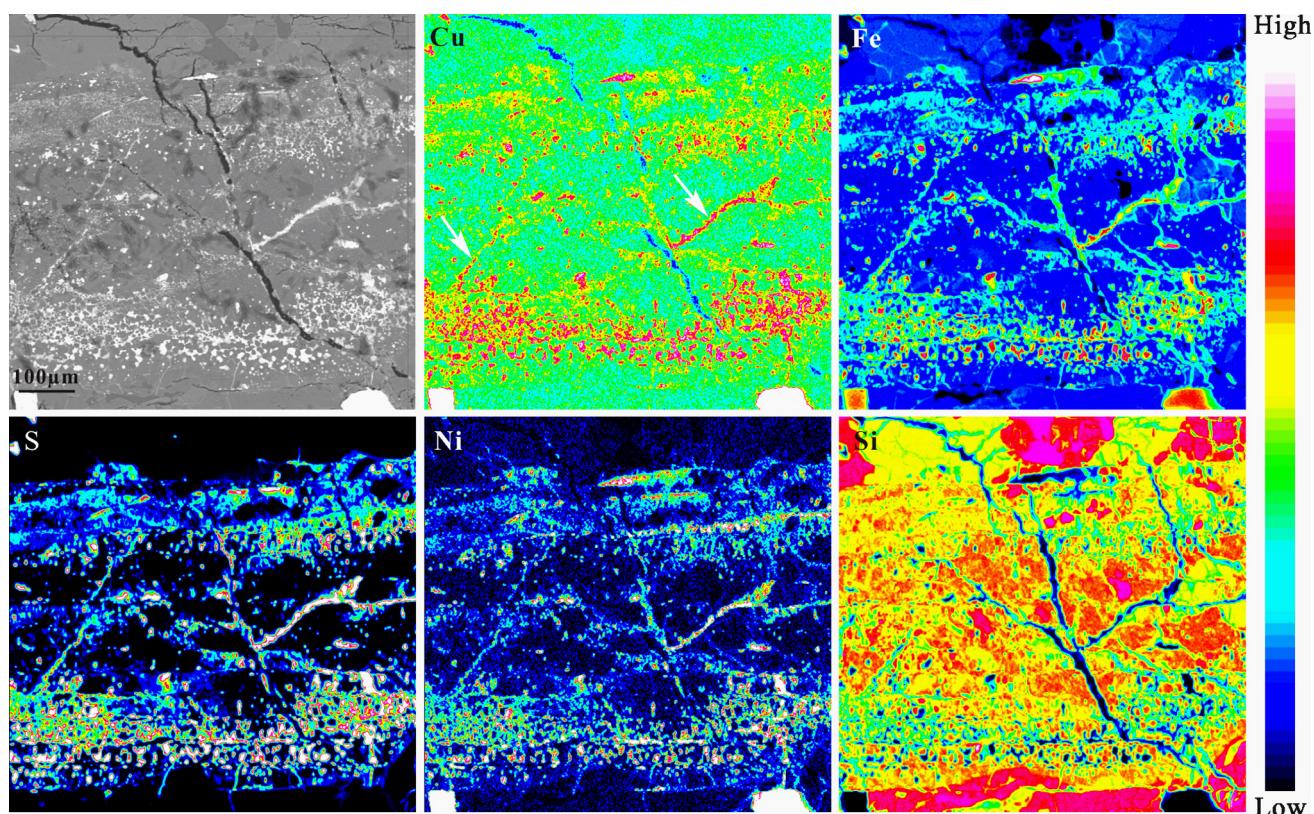
**Fig. 6** High-resolution X-ray elemental intensity maps of Cu, Fe, Ni, S, and Si for FeNi + FeS of type 1 occurrence. Note the element Cu is enriched in fine-grained FeNi + FeS intergrowths and is spreading over the entire vein, and the Si-rich silicates almost do not contain copper

Rubin (1994a) reported that in more than 75% of the metallic-Cu-bearing ordinary chondrites, the metallic copper occurs at FeNi metal–troilite grain boundaries, or occurs within troilite, within FeNi metal, or at the boundaries of these phases with silicates or chromite. He found that the most common occurrence is that the metallic copper grains are adjacent to small troilite grains inside FeNi metal, and the

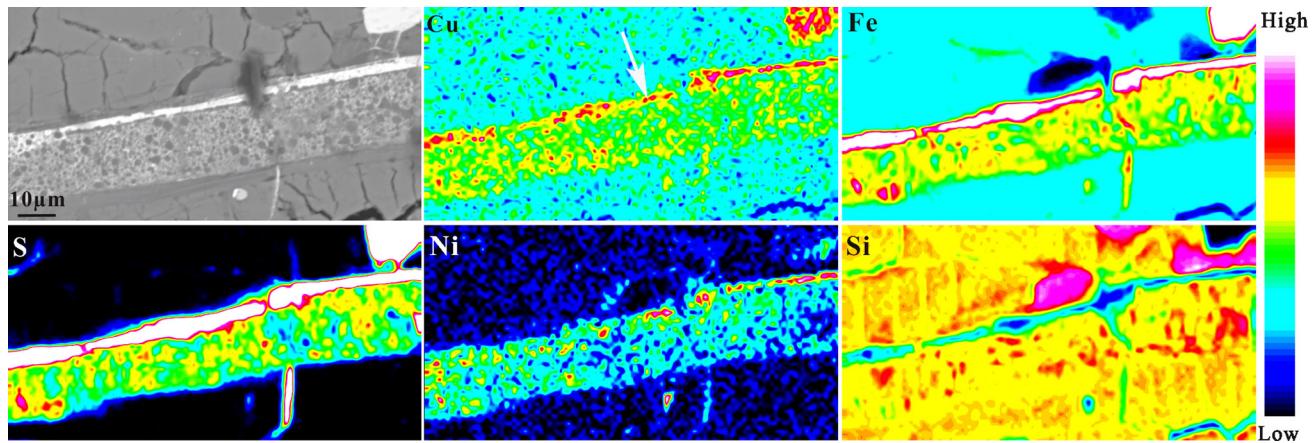
second most common occurrence is at the FeNi metal–troilite interface. Our statistical analysis of 61 metallic copper grains in the Suizhou meteorite indicates that 65% of metallic copper grains are adjacent to small irregular troilite grains within the FeNi metal. The occupation proportion of metallic copper grains occurring at the metal–troilite interface is 24%, and that occurring within troilite or at the boundaries



**Fig. 7** High-resolution X-ray elemental intensity maps of Cu, Fe, Ni, S, and Si for FeNi+FeS of type 2 occurrence. Note the element Cu is enriched in the individual FeNi+FeS grains sparsely distributed in a shock vein (white arrows), and the Si-rich silicates almost do not contain copper



**Fig. 8** High-resolution X-ray elemental intensity maps of Cu, Fe, Ni, S, and Si for FeNi+FeS of type 3 occurrence. Note the element Cu is enriched in the irregular-shaped FeNi+FeS veinlets in a vein (white arrows), and the Si-rich silicates almost do not contain copper



**Fig. 9** High-resolution X-ray elemental intensity maps of Cu, Fe, Ni, S, and Si for FeNi+FeS of type 4 occurrence. Note the element Cu is enriched in a long and straight FeNi+FeS band occurring at the vein upper margin (white arrow), and the Si-rich silicates almost do not contain copper

of metal or troilite with silicates is only 9% (Table 1). The results of our statistics are quite similar to those performed by Rubin on ordinary chondrites.

It was found that the ordinary chondrites containing a relatively large number of occurrences of metallic copper per square millimeter tend to have experienced moderately high degrees of shock (Rubin 1994a). Shock processes can cause local melting of chondritic rock and the forming of melt veins and melt pockets, in which melting, transportation, and recrystallization of FeNi metal and troilite appear. Hence, we could observe abundant fine-grained eutectic intergrowths of FeNi metal and troilite in the melt regions of many ordinary chondrites (Xie and Chen 2016, 2020). During shock events, copper should also get redistributed in these chondrites. Tomkins (2009) and Luszczek and Krzesinska (2020) suggested different models of such a formation mechanism in H-group chondrites (melting of FeNi, diffusion of Cu in prolonged cooling time, and its exsolution from taenite). We assume that the lack of metallic copper in Suizhou shock veins can be explained in light of existing models assuming that cooling in veins was too fast for the diffusion of Cu from taenite, while in the surrounding rock, thermal equilibration took longer, and diffusion could have been possible.

## 5 Conclusion

- Copper possesses very strong chalcophile properties, but in the conditions of meteorites, the property of Cu is also close to that of siderophile elements. FeNi-alloys, especially taenite, are considered as the main primary carrier of copper in Suizhou meteorite, and post-shock thermal episode is considered the main reason for the

migration of elemental Cu from its original host phase and the formation of metallic grains.

- The Suizhou meteorite is a shock vein containing L-group chondrite. More than one hundred irregular grains of metallic copper were observed in the chondritic rock of this meteorite. The average composition of metallic copper is (in wt%): Cu 92.59, Fe 5.23, Ni 2.53, Co 0.02, total 100.37.
- Metallic copper grains adjacent to small troilite grains within FeNi metal are the most common occurrence, and those at the FeNi metal–troilite interface are the second most common case. The metallic copper grains occurring at the interface of FeNi metal /troilite and silicate are rather rare.
- Metallic copper grains are not observed within the Suizhou shock veins, Instead, copper is transferred into the intergrowth of FeNi metal and troilite during the shock event. The silicates in shock veins almost do not contain copper.
- Four occurrence types of Cu in the intergrowths of FeNi metal and troilite are discovered in Suizhou shock veins: (1) Cu is enriched in fine-grained FeNi+FeS intergrowths and is spreading over the entire shock veins. (2) Cu is enriched in the individual FeNi+FeS grains sparsely distributed in shock veins. (3) Cu is enriched in the irregular shaped FeNi+FeS veinlets. (4) Cu is enriched in a long and straight FeNi+FeS band occurring at the vein margin.
- The concentrations of Cu in the FeNi+FeS intergrowths for four occurrence types are similar. It can be approximately estimated to be lower than 1 wt%.

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**Author contributions** Xiande Xie: research project design and implementation, sample selection and processing, observation under an optical microscope, image production, and writing the initial draft of the paper; Xiangping Gu: reflective microscopy observation of minerals and observation of mineral back scatter images and composition analysis on electron probes, participating the discussion of the initial draft of the paper; Yiping Yang: responsible for the high resolution X-ray elemental intensity mapping of Cu and copper friendly elements, and participating the discussion of the initial draft of the paper.

## Declarations

**Conflict of interest** The authors declare that they do not have any known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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