## **Supplementary Information**

# A potential natural chalcopyrite reference material for *in situ* copper, iron, and sulfur isotope measurements

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Table S1 Summary of the instrument parameters

| Farada | Faraday Cup Configurations for Fe isotopes on Neptune Plus and S isotopes on Neptune |    |                  |                  |                  |    |                  |                  |  |  |  |  |  |
|--------|--|----|------------------|------------------|------------------|----|------------------|------------------|--|--|--|--|--|
| L4     | L3   | L2 | L1               | С                | H1               | H2 | H3               | H4               |  |  |  |  |  |
|        | <sup>63</sup> Cu   |    | <sup>65</sup> Cu |                  |                  |    |                  |                  |  |  |  |  |  |
|        | <sup>53</sup> Cr   |    | <sup>54</sup> Fe | <sup>56</sup> Fe | <sup>57</sup> Fe |    | <sup>58</sup> Fe | <sup>60</sup> Ni |  |  |  |  |  |
|        |  |    | $^{32}S$         | <sup>33</sup> S  | <sup>34</sup> S  |    |                  |                  |  |  |  |  |  |

Neptune / Neptune Plus MC-ICP-MS

| RF power          | 1200 W              | Interface cones     | Sample cone: standard cone, Skimmer cone: X cone                     |
|-------------------|---------------------|---------------------|--|
| Plasma gas        | 16 L/min (Ar)       | Make up gas         | About 0.80 ~ 1.3 L/min (Ar)  |
| Auxiliary gas     | 0.9 L/min (Ar)      | Sample depth        | About -0.6 ~ -1.2 mm   |
| Resolution        | High resolution     | mode for Fe and     | S isotopes measurements (m/ $\Delta m$ ~8000-9000), while low        |
| Resolution        | resolution mode     | for Cu isotope mea  | asurement  |
| Integration       | A single analysis   | consists of a block | x of 60 cycles with an integration time of 0.262 s per cycle for     |
| Integration       | Cu, Fe and S iso    | tope ratio analysis |  |
| NWRFemto Las      | er Ablation System  | п                   |  |
| Wavelength        | 257 nm              | Pulse duration      | $70 \sim 90 \text{ fs}$  |
| Beam size         | 25, 40 and 40 µr    | n for Cu, Fe and S  | isotope ratio analysis, respectively                                 |
| Pulse repeat rate | e 4, 8 and 15 Hz fo | or Cu, Fe and S iso | tope ratio analysis, respectively                                    |
| Energy density    | Approximate 0.1     | , 0.14 and 0.14 J/c | m <sup>2</sup> for Cu, Fe and S isotope ratio analysis, respectively |
| Carrier gas       | About 700 mL/n      | nin (He) for Cu, Fe | and S isotope ratio analysis   |
|                   |                     |                     |  |

#### Cu and Fe purification procedures

#### Cu purification procedure for the second aliquot chalcopyrite sample:

Purification was carried out using PFA microcolumns packed with 2 mL of anion exchange resin (Bio-Rad AG-MP-1M, 100–200 mesh). Prior to loading the sample, the resin was thoroughly cleaned with 0.5 mol/L HNO<sub>3</sub> and ultrapure water (18.2 M $\Omega$ ·cm resistivity), then conditioned with the same 6 mol/L HCl + 0.001% H<sub>2</sub>O<sub>2</sub> mixture. Subsequently, 1 mL sample solution in 6 mol/L HCl + 0.001% H<sub>2</sub>O<sub>2</sub> was loaded onto the microcolumn.

Matrix elements were eluted using 5 mL 6 mol/L HCl + 0.001% H<sub>2</sub>O<sub>2</sub>, while the Cu fraction was selectively collected using 26 mL of the same eluent. The isolated Cu fraction was evaporated to dryness, and then diluted with 2% HNO<sub>3</sub> (m/m) for Cu isotope measurement. The yield of Cu exceeded 99%, and total procedure blank was less than 5 ng, which was negligible when compared to about 1 µg Cu loaded on the resin.

#### Fe purification procedure for the second aliquot chalcopyrite sample:

Purification was carried out using Bio-Rad AG1-X8 anion exchange resin with a mesh size of 200-400. After thorough cleaning with 8 mol/L HNO<sub>3</sub>, 1 mol/L HNO<sub>3</sub>, and ultrapure water (18.2 M $\Omega$ ·cm), followed by conditioning with 6 mol/L HCl, 1 mL of the sample solution in 6 mol/L HCl was introduced onto the resin-packed column.

Matrix elements were flushed out with 6 mol/L HCl, whereas Fe was selectively eluted using 4 mL of 0.5 mol/L HCl, succeeded by rinses of 1 mL 8 mol/L HNO<sub>3</sub> and 0.5 mL ultrapure water (18.2 M $\Omega$ ·cm). The collected Fe fraction was evaporated to dryness and finally redissolved in 2% HNO<sub>3</sub> (m/m) for Fe isotope measurement. The Fe recovery rate exceeded 99%, and the total procedural blank was approximately 20 ng, which is considered insignificant relative to the about 50 µg Fe initially loaded onto the resin.

| C. AN    |            | Element concentrations (wt%) |      |      |      |      |      |      |      |       |
|----------|------------|------------------------------|------|------|------|------|------|------|------|-------|
| Spot No. | Grain No.  | Cu                           | Fe   | S    | Co   | Ni   | Zn   | As   | Pb   | Total |
| 1        | IGGCcp G01 | 34.1                         | 29.8 | 34.5 | 0.91 | -    | 0.02 | 0.02 | 0.03 | 99.4  |
| 2        | IGGCcp G02 | 33.6                         | 29.2 | 34.5 | 0.90 | -    | 1.19 | 0.05 | 0.06 | 99.5  |
| 3        | IGGCcp G03 | 33.5                         | 29.8 | 34.5 | 0.94 | 0.05 | -    | -    | 0.08 | 98.9  |
| 4        | IGGCcp G04 | 33.7                         | 29.8 | 34.5 | 0.93 | 0.02 | -    | 0.03 | 0.05 | 99.0  |
| 5        | IGGCcp G05 | 33.9                         | 29.7 | 34.4 | 0.94 | 0.03 | -    | 0.02 | 0.05 | 99.0  |
| 6        | IGGCcp G06 | 33.7                         | 29.7 | 34.5 | 0.95 | 0.04 | 0.05 | 0.05 | 0.09 | 99.0  |
| 7        | IGGCcp G07 | 33.9                         | 29.8 | 34.4 | 0.94 | -    | 0.03 | 0.02 | 0.04 | 99.1  |
| 8        | IGGCcp G08 | 33.8                         | 29.8 | 34.3 | 0.94 | 0.03 | 0.02 | -    | -    | 98.8  |
| 9        | IGGCcp G09 | 33.8                         | 29.9 | 34.4 | 0.95 | -    | 0.03 | -    | 0.07 | 99.2  |
| 10       | IGGCcp G10 | 34.2                         | 29.9 | 34.6 | 0.93 | -    | -    | 0.02 | 0.06 | 99.7  |
|          | average    | 33.8                         | 29.7 | 34.5 | 0.93 |      |      |      | 0.05 | 99.2  |
|          | 1S         | 0.2                          | 0.2  | 0.1  | 0.02 |      |      |      | 0.03 | 0.3   |
|          |            |                              |      |      |      |      |      |      |      |       |
| 11       | IGGCcp G11 | 34.0                         | 29.8 | 34.3 | 0.93 | -    | -    | 0.04 | 0.07 | 99.1  |
| 12       |            | 34.1                         | 30.0 | 34.5 | 0.94 | -    | -    | 0.02 | 0.03 | 99.7  |
| 13       |            | 33.9                         | 29.7 | 34.7 | 0.93 | -    | 0.02 | 0.04 | 0.05 | 99.4  |
| 14       |            | 33.9                         | 30.0 | 34.5 | 0.95 | -    | 0.02 | 0.03 | -    | 99.5  |
| 15       |            | 34.1                         | 29.9 | 34.4 | 0.95 | -    | -    | -    | 0.07 | 99.4  |
| 16       |            | 34.1                         | 29.9 | 34.5 | 0.93 | -    | -    | 0.02 | 0.08 | 99.6  |
| 17       |            | 34.2                         | 30.0 | 34.6 | 0.94 | -    | -    | -    | 0.06 | 99.7  |
| 18       |            | 34.2                         | 29.7 | 34.4 | 0.92 | -    | 0.03 | 0.02 | 0.04 | 99.3  |
| 19       |            | 34.0                         | 29.9 | 34.3 | 0.94 | 0.03 | -    | 0.04 | 0.05 | 99.3  |
| 20       |            | 33.9                         | 29.8 | 34.6 | 0.94 | 0.03 | -    | -    | 0.06 | 99.3  |
| 21       |            | 34.1                         | 29.7 | 34.4 | 0.93 | -    | -    | 0.03 | 0.06 | 99.3  |
| 22       |            | 34.3                         | 29.8 | 34.5 | 0.93 | 0.02 | 0.04 | -    | 0.10 | 99.7  |
| 23       |            | 33.9                         | 29.8 | 34.6 | 0.94 | 0.04 | 0.17 | 0.02 | 0.06 | 99.6  |
| 24       |            | 34.3                         | 29.7 | 34.6 | 0.92 | 0.04 | -    | -    | 0.05 | 99.5  |
| 25       |            | 34.2                         | 29.8 | 34.6 | 0.94 | 0.03 | 0.03 | 0.04 | 0.02 | 99.6  |
| 26       |            | 34.0                         | 29.9 | 34.7 | 0.92 | 0.05 | 0.02 | -    | 0.04 | 99.7  |
| 27       |            | 34.0                         | 29.8 | 34.3 | 0.91 | 0.05 | 0.02 | -    | 0.03 | 99.2  |
| 28       |            | 34.0                         | 30.0 | 34.6 | 0.95 | 0.08 | 0.02 | -    | 0.03 | 99.6  |
| 29       |            | 34.0                         | 29.8 | 34.3 | 0.95 | 0.09 | -    | 0.03 | 0.06 | 99.3  |
| 30       |            | 34.2                         | 29.9 | 34.6 | 0.94 | 0.10 | -    | -    | 0.06 | 99.8  |
|          | average    | 34.1                         | 29.8 | 34.5 | 0.94 |      |      |      | 0.05 | 99.5  |
|          | 1S         | 0.1                          | 0.1  | 0.1  | 0.01 |      |      |      | 0.02 | 0.2   |
|          |            |                              |      |      |      |      |      |      |      |       |
| 31       | IGGCcp G12 | 33.9                         | 29.6 | 34.5 | 0.96 | 0.30 | 0.03 | 0.03 | 0.03 | 99.4  |
| 32       |            | 34.1                         | 29.7 | 34.4 | 0.94 | 0.18 | 0.03 | 0.02 | 0.04 | 99.4  |
| 33       |            | 34.2                         | 29.7 | 34.5 | 0.94 | 0.11 | -    | -    | 0.02 | 99.5  |
| 34       |            | 34.1                         | 29.7 | 34.5 | 0.94 | 0.08 | -    | -    | 0.08 | 99.4  |
| 35       |            | 34.2                         | 29.7 | 34.5 | 0.92 | 0.08 | 0.05 | -    | 0.02 | 99.4  |

Table S2 Element concentrations (wt%) of IGGCcp-1 chalcopyrite by EPMA

| Table S2 contin | lueu    |      |      |      |      |      |      |      |      |      |
|-----------------|---------|------|------|------|------|------|------|------|------|------|
| 36              |         | 34.1 | 29.9 | 34.4 | 0.95 | 0.06 | 0.12 | 0.02 | 0.05 | 99.5 |
| 37              |         | 34.2 | 30.0 | 34.5 | 0.93 | 0.03 | -    | 0.03 | 0.06 | 99.8 |
| 38              |         | 34.1 | 29.6 | 34.6 | 0.92 | 0.03 | -    | -    | 0.08 | 99.3 |
| 39              |         | 34.1 | 30.0 | 34.6 | 0.93 | 0.04 | -    | -    | 0.04 | 99.6 |
| 40              |         | 34.2 | 29.7 | 34.5 | 0.92 | 0.02 | -    | -    | 0.06 | 99.4 |
| 41              |         | 34.3 | 29.8 | 34.3 | 0.93 | -    | 0.02 | 0.03 | 0.07 | 99.4 |
| 42              |         | 34.2 | 29.8 | 34.6 | 0.94 | -    | -    | 0.04 | 0.06 | 99.6 |
| 43              |         | 33.9 | 29.8 | 34.5 | 0.92 | 0.02 | -    | -    | 0.02 | 99.2 |
| 44              |         | 34.1 | 29.8 | 34.6 | 0.94 | 0.02 | -    | 0.03 | 0.05 | 99.5 |
| 45              |         | 34.0 | 29.8 | 34.5 | 0.95 | 0.02 | 0.04 | 0.04 | -    | 99.3 |
| 46              |         | 34.1 | 29.7 | 34.8 | 0.92 | 0.03 | 0.08 | -    | 0.03 | 99.6 |
| 47              |         | 34.4 | 29.7 | 34.4 | 0.92 | -    | -    | 0.03 | 0.02 | 99.5 |
| 48              |         | 34.2 | 29.9 | 34.5 | 0.92 | -    | 0.03 | 0.02 | 0.02 | 99.6 |
| 49              |         | 34.3 | 29.7 | 34.5 | 0.95 | -    | -    | 0.02 | 0.10 | 99.7 |
|                 | average | 34.1 | 29.8 | 34.5 | 0.93 |      |      |      | 0.05 | 99.5 |
|                 | 1S      | 0.1  | 0.1  | 0.1  | 0.01 |      |      |      | 0.03 | 0.1  |

Table S2 continued

'-' indicates 'Not detected'.

| Sample No.                         | $\delta^{65}Cu_{5\ to\ 4}$ | $\delta^{65}Cu_{2\ to\ 4}$ | $\delta^{65}Cu_{3\ to\ 5}$ | $\delta^{65}Cu_{1\ to5}$ |
|------------------------------------|----------------------------|----------------------------|----------------------------|--------------------------|
| 1                                  | 0.00                       | 0.04                       | -0.16                      | 0.15                     |
| 2                                  | 0.04                       | 0.02                       | -0.13                      | 0.18                     |
| 3                                  | 0.04                       | 0.03                       | -0.20                      | 0.32                     |
| 4                                  | 0.00                       | 0.05                       | -0.16                      | 0.14                     |
| 5                                  | 0.06                       | 0.08                       | -0.16                      | 0.18                     |
| 6                                  | 0.01                       | 0.06                       | -0.18                      | 0.13                     |
| 7                                  | -0.01                      | 0.02                       | -0.27                      | 0.18                     |
| 8                                  | -0.05                      | 0.02                       | -0.25                      | 0.21                     |
| 9                                  | 0.00                       | 0.01                       | -0.10                      | 0.20                     |
| 10                                 | -0.04                      | -0.01                      | -0.19                      | 0.19                     |
| 11                                 | 0.00                       | 0.04                       | -0.17                      | 0.18                     |
| 12                                 | 0.05                       | 0.03                       | -0.18                      | 0.13                     |
| 13                                 | 0.00                       | 0.04                       | -0.11                      | 0.11                     |
| 14                                 | 0.05                       | 0.01                       | -0.13                      | 0.13                     |
| 15                                 | 0.10                       | 0.01                       | -0.12                      | 0.11                     |
| 16                                 | 0.07                       | -0.04                      | -0.07                      | 0.43                     |
| 17                                 | 0.07                       | -0.03                      | -0.09                      | 0.11                     |
| 18                                 | 0.06                       | 0.01                       | -0.16                      | 0.14                     |
| 19                                 | 0.01                       | 0.00                       | -0.16                      | 0.17                     |
| 20                                 | 0.00                       | -0.02                      | -0.13                      | 0.17                     |
| 21                                 | 0.11                       | -0.07                      | -0.20                      | 0.12                     |
| average                            | 0.03                       | 0.01                       | -0.16                      | 0.18                     |
| 2S                                 | 0.04                       | 0.03                       | 0.05                       | 0.08                     |
| <sup>a</sup> t                     | 3.00                       | 1.86                       | 15.00                      | 10.66                    |
| <sup>b</sup> t <sub>critical</sub> | 2.09                       |                            |                            |                          |

Table S3 Position effects within a TV2 cell on Cu isotope composition measurement

 $t = \frac{|x - \mu|}{S} \sqrt{n}$ . In the context,  $\overline{x}$  denoted the mean of the measured deviations in Cu isotopic composition between two specific positions; S represented the standard deviation of these measured values, while n was the total count of such values.  $\mu$  represents the population mean of deviations in Cu isotopic composition between any two measurement positions. If there are no systematic biases, including those from position-dependent effects, and if the measurements are solely affected by random errors,  $\mu$  should theoretically approach or equal 0. This condition indicates that under ideal circumstances, with a homogeneous distribution of isotopes and no systematic variation, the mean deviation between any two measured positions would not deviate from zero.

<sup>b</sup>: The critical *t*-values calculated using TINV function in Excel under two-tailed hypothesis at significance level of 0.05, with a degree of freedom of 20.

#### Introduction of IGGCcp-2 chalcopyrite sample

The IGGCcp-2 chalcopyrite specimen was meticulously extracted from a diminutive chalcopyrite ore sample obtained within the Kalatongke magmatic Ni-Cu deposit, graciously provided by Professor Ke-Zhang Qin.

To evaluate the isotopic homogeneity of Cu, Fe, and S, alongside its major elemental components, we employed the same analytical techniques used in IGGCcp-1, descripted in the main article. Specifically, Laser Ablation Multi-Collector Inductively Coupled Plasma Mass Spectrometry (LA-MC-ICP-MS) was utilized for Cu and Fe isotopes, Secondary Ion Mass Spectrometry (SIMS) for S isotopes, and Electron Probe Microanalysis (EPMA) for major elements. The homogeneity assessment revealed exceptional isotopic consistency in Cu, Fe, and S, as well as remarkable agreement in the major elemental compositions, within IGGCcp-2.

The S isotopic composition was measured through Elemental Analysis-Isotope Ratio Mass Spectrometry (EA-IRMS), while the Cu and Fe isotopic compositions were derived using the consistent Solution Nebulizing Multi-Collector Inductively Coupled Plasma Mass Spectrometry (SN-MC-ICP-MS) method applied to IGGCcp-1, as well as descripted in the main article. The comprehensive results of these isotopic measurements were presented in Tables S5, S6, and S7, respectively.

From EPMA measurements conducted on eleven chalcopyrite grains from IGGCcp-2, the mean Cu, Fe, and S contents were determined to be  $33.9 \pm 0.3$  (1S) weight percent (wt %),  $29.7 \pm 0.1$  (1S) wt %, and  $34.5 \pm 0.2$  (1S) wt %, respectively. Additionally, the IGGCcp-2 samples contained a minor yet amount of cobalt (Co), averaging  $0.93 \pm 0.02$  (1S) wt %. Lead (Pb) was detected at a low but discernible average concentration of  $0.04 \pm 0.02$  (1S) wt %, whereas nickel (Ni), zinc (Zn), and arsenic (As) levels were either below or marginally above the detection limits. These detailed compositional data have been systematically organized in Table S8 for convenient reference.

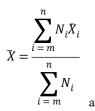
| Table S4 S isotope composition of IG | GGCcp-2 measured by EA-IRMS |
|--------------------------------------|-----------------------------|
| No.                                  | δ <sup>34</sup> S (‰)       |
| 01                                   | -0.28                       |
| 02                                   | -0.12                       |
| 03                                   | -0.29                       |
| 04                                   | -0.15                       |
| 05                                   | -0.11                       |
| 06                                   | -0.11                       |
| 07                                   | 0.17                        |
| 08                                   | 0.15                        |
| 09                                   | -0.02                       |
| Average                              | -0.08                       |
| 28                                   | 0.32                        |

Table S4 S isotope composition of IGGCcp-2 measured by EA-IRMS

| Sample No.                         | \$65Cm                    | 1S   | Ν  | with/without chemical    |
|------------------------------------|---------------------------|------|----|--------------------------|
| Sample No.                         | $\delta^{65}Cu_{NIST976}$ | 15   | IN | chromatography procedure |
| Analyzed by USTC                   |                           |      |    |                          |
| 1                                  | -0.32                     | 0.01 | 2  | with                     |
| 2                                  | -0.29                     | 0.02 | 2  | with                     |
| 3                                  | -0.30                     | 0.01 | 2  | with                     |
| <sup>a</sup> Weighted<br>average   | -0.31                     | 0.04 | 6  |                          |
| 4                                  | -0.34                     | 0.03 | 2  | with not                 |
| 5                                  | -0.35                     | 0.01 | 2  | with not                 |
| 6                                  | -0.32                     | 0.04 | 2  | with not                 |
| <sup>a</sup> Weighted<br>average   | -0.34                     | 0.04 | 6  |                          |
| <sup>b</sup> t                     | 2.45                      |      |    |                          |
| <sup>b</sup> t <sub>critical</sub> | 2.78                      |      |    |                          |
| <sup>a</sup> Weighted              | 0.00                      | 0.04 | 10 |                          |
| average                            | -0.32                     | 0.06 | 12 |                          |
| Analyzed by                        | CUG                       |      |    |                          |
| 7                                  | -0.32                     | 0.01 | 3  | with                     |
| 8                                  | -0.32                     | 0.04 | 3  | with                     |
| <sup>a</sup> Weighted              | 0.22                      | 0.02 | (  |                          |
| average                            | -0.32                     | 0.03 | 6  |                          |
| 9                                  | -0.32                     | 0.05 | 3  | with not                 |
| 10                                 | -0.33                     | 0.03 | 3  | with not                 |
| 11                                 | -0.32                     | 0.05 | 3  | with not                 |
| 12                                 | -0.32                     | 0.06 | 3  | with not                 |
| 13                                 | -0.32                     | 0.05 | 3  | with not                 |
| 14                                 | -0.32                     | 0.06 | 3  | with not                 |
| <sup>a</sup> Weighted              | 0.22                      | 0.05 | 18 |                          |
| average                            | -0.32                     | 0.05 | 10 |                          |
| <sup>b</sup> t                     | 1.83                      |      |    |                          |
| <sup>b</sup> t <sub>critical</sub> | 2.45                      |      |    |                          |
| <sup>a</sup> Weighted              | -0.32                     | 0.05 | 24 |                          |
| average                            | -0.32                     | 0.05 | 24 |                          |
| <sup>b</sup> t                     | 0.16                      |      |    |                          |
| <sup>b</sup> t <sub>critical</sub> | 2.18                      |      |    |                          |
| <sup>a</sup> Weighted              | -0.32                     | 0.05 | 36 |                          |
| average                            | 0.52                      | 0.05 | 50 |                          |

Table S5 Cu isotopic composition of IGGCcp-2 measured by MC-ICP-MS

<sup>a</sup>: a weight average of Cu isotopic composition measured and the standard deviation for z parallel



IGGCcp-2 chalcopyrite samples were calculated using the following formulas:

$$S = \sqrt{\frac{\sum_{i=m}^{n} (N_i - 1)S_i^2 + \sum_{i=m}^{n} N_i (X_i - X)^2}{\sum_{i=m}^{n} N_i - z}}$$

 $\sqrt{i=m}$ , respectively. Here,  $N_i$  and  $\overline{X}_i$  signified the times of measurement and the mean of the  $N_i$  measured values for ith parallel sample, respectively.  $S_i$  denoted the standard deviation for  $\overline{X}_i$  of  $N_i$  measured values of ith sample.

For data obtained from USTC and treated with chemical chromatography procedure, m and n were set to 1 and 3, respectively, and for those without chemical chromatography procedure, m and n took the values of 4 and 6 respectively. considering all data from USTC, m was assigned 1 and n was 6.

For data analyzed by CUG, when applying chemical chromatography procedure, m and n were set to 7 and 8 respectively; while those without chemical chromatography, m and n had the values of 9 and 14 correspondingly. For all data from CUG, regardless of treatment, m was assigned 7 and n was 14. For all 14 parallel IGGCcp-2 chalcopyrite samples analyzed by USTC and CUG, m was set as 1 and n was 14.

<sup>b</sup>: the pooled standard deviation and *t*-values were calculated using the following formulas:

Pooled S = 
$$\sqrt{\frac{\sum_{i=n}^{m} (\bar{X}_{i} - \bar{X}_{a})^{2} + \sum_{i=o}^{p} (\bar{X}_{i} - \bar{X}_{b})^{2}}{z_{a} + z_{b} - 2}}$$
 and  $t = \frac{|\bar{X}_{a} - \bar{X}_{b}|}{Pooled S} \sqrt{\frac{z_{a}z_{b}}{z_{a} + z_{b}}}$ , respectively. Here,  $\bar{X}_{i}$ 

represented the mean of measured values for the Cu isotopic composition in the ith sample.

Within the dataset analyzed at USTC,  ${}^{Z_a}$  and  ${}^{Z_b}$  indicated the quantities of parallel samples that underwent treatment with or without a chemical chromatography step, respectively. The weighted averages for these two groups were given as  ${}^{X_a}$  for those treated with chromatography and  ${}^{X_b}$  for those without. Specifically, in this case, m and n were set to 1 and 3, whereas o and p had values of 4 and 6, respectively.

For the data analyzed at CUG,  ${}^{Z_a}$  and  ${}^{Z_b}$  again represented the quantities of parallel samples subjected to either chemical chromatography or no such treatment. The respective weighted averages for these two

groups were given as  $\bar{X}_a$  and  $\bar{X}_b$ . Specifically, in this case, m and n were set to 7 and 8, whereas o and p had values of 9 and 14, respectively.

Considering all chalcopyrite sample data collectively from both USTC and CUG,  ${}^{Z_a}$  and  ${}^{Z_b}$  signified the total quantities of parallel samples analyzed across the two institutions. Their corresponding weighted averages for each group were once more designated as  ${}^{X_a}$  and  ${}^{X_b}$ . In this comprehensive case, m and n values were established as 1 and 6, while o and p equated to 7 and 14, respectively.

The critical *t*-values were calculated using Excel's T.INV.2T function, applying a significance level of 0.05 under a two-tailed hypothesis.

| Sample No.                         | $\delta^{56}Fe_{IRMM-014}$ | 2S   | $\delta^{57}Fe_{IRMM\text{-}014}$ | 2S   | N  | with/without chemical chromatography procedure |
|------------------------------------|----------------------------|------|-----------------------------------|------|----|--|
| Analyzed by USTC                   |                            |      |                                   |      |    |  |
| 1                                  | 1.15                       | 0.03 | 1.69                              | 0.05 | 3  | with   |
| 2                                  | 1.11                       | 0.02 | 1.61                              | 0.05 | 3  | with   |
| 3                                  | 1.19                       | 0.03 | 1.73                              | 0.08 | 3  | with   |
| <sup>a</sup> Weighted<br>average   | 1.15                       | 0.08 | 1.68                              | 0.15 | 9  |  |
| 4                                  | 1.13                       | 0.01 | 1.66                              | 0.05 | 3  | with not                                       |
| 5                                  | 1.12                       | 0.03 | 1.66                              | 0.08 | 6  | with not                                       |
| 6                                  | 1.22                       | 0.03 | 1.80                              | 0.14 | 6  | with not                                       |
| <sup>a</sup> Weighted<br>average   | 1.16                       | 0.11 | 1.72                              | 0.19 | 15 |  |
| <sup>b</sup> t                     | 0.38                       |      | 0.68                              |      |    |  |
| <sup>b</sup> t <sub>critical</sub> | 2.78                       |      |                                   |      |    |  |
| <sup>a</sup> Weighted<br>average   | 1.16                       | 0.10 | 1.70                              | 0.18 | 24 |  |
| Analyzed by                        | , CUG                      |      |                                   |      |    |  |
| 7                                  | 1.18                       | 0.02 | 1.77                              | 0.02 | 3  | with   |

Table S6 Fe isotopic composition of IGGCcp-2 measured by SN-MC-ICP-MS

| 8                                  | 1.15 | 0.08 | 1.74 | 0.14 | 3  | with     |
|------------------------------------|------|------|------|------|----|----------|
| <sup>a</sup> Weighted<br>average   | 1.17 | 0.07 | 1.75 | 0.11 | 6  |          |
| 9                                  | 1.22 | -    | 1.86 | -    | 1  | with not |
| 10                                 | 1.22 | -    | 1.69 | -    | 1  | with not |
| 11                                 | 1.17 | 0.05 | 1.73 | 0.08 | 3  | with not |
| 12                                 | 1.10 | 0.05 | 1.65 | 0.08 | 3  | with not |
| 13                                 | 1.12 | -    | 1.65 | -    | 1  | with not |
| 14                                 | 1.20 | -    | 1.73 | -    | 1  | with not |
| <sup>a</sup> Weighted<br>average   | 1.16 | 0.11 | 1.71 | 0.15 | 10 |          |
| <sup>b</sup> t                     | 0.21 |      | 0.79 |      |    |          |
| <sup>b</sup> t <sub>critical</sub> | 2.45 |      |      |      |    |          |
| <sup>a</sup> Weighted<br>average   | 1.16 | 0.09 | 1.72 | 0.13 | 16 |          |
| <sup>b</sup> t                     | 0.15 |      | 0.60 |      |    |          |
| <sup>b</sup> t <sub>critical</sub> | 2.18 |      |      |      |    |          |
| <sup>a</sup> Weighted<br>average   | 1.16 | 0.09 | 1.71 | 0.13 | 40 |          |

<sup>a</sup>: a weight average of Fe isotopic composition measurements ( $\delta^{56}$ Fe or  $\delta^{57}$ Fe) and the standard deviation for z parallel IGGCcp-2 chalcopyrite samples were calculated using the following formulas:

$$\bar{X} = \frac{\sum_{i=m}^{n} N_i \bar{X}_i}{\sum_{i=m}^{n} N_i} \qquad S = \sqrt{\frac{\sum_{i=m}^{n} (N_i - 1)S_i^2 + \sum_{i=m}^{n} N_i (\bar{X}_i - \bar{X})^2}{\sum_{i=m}^{n} N_i - z}}, \text{ respectively. Here, } N_i \text{ and } \bar{X}_i \text{ denoted the}}$$

times of measurement and the mean of  $N_i$  measured values for ith parallel sample correspondingly.  $S_i$  signified the standard deviation for  $X_i$  of  $N_i$  measured values for ith sample.

For the data analysis conducted at USTC on IGGCcp-2 chalcopyrite samples: when chemical chromatography was applied, m and n took the values 1 and 3 respectively; conversely, for those samples not treated with chemical chromatography, m and n were set to 4 and 6 respectively. Considering all data from USTC, regardless of treatment, m was assigned 1 and n was 6.

In the case of chalcopyrite samples analyzed at CUG, when chemical chromatography was used, m and n had the values 7 and 8 correspondingly; whereas for those without the chemical chromatography procedure, m and n were set to 9 and 14 respectively. For all data obtained from CUG, irrespective of the treatment method, m was assigned 7 and n was 14.

For all combined data from the 14 parallel IGGCcp-2 chalcopyrite samples analyzed at both USTC and CUG, m was set as 1 and n was 14.

<sup>b</sup>: the pooled standard deviation and *t*-values were calculated using the following formulas:

$$Pooled S = \sqrt{\frac{\sum_{i=n}^{m} (X_i - X_a)^2 + \sum_{i=o}^{p} (X_i - X_b)^2}{z_a + z_b - 2}} \quad \text{and} \quad t = \frac{|X_a - X_b|}{Pooled S} \sqrt{\frac{z_a z_b}{z_a + z_b}}, \text{ respectively. Here, } X_i$$

represented the mean of measured values for the Fe isotopic composition in the ith sample. Within the dataset analyzed at USTC,  $Z_a$  and  $Z_b$  indicated the quantities of parallel samples that underwent treatment with or without a chemical chromatography step, respectively. The weighted averages for these two groups were given as  $X_a$  for those treated with chromatography and  $X_b$  for those without. Specifically, in this case, m and n were set to 1 and 3, whereas o and p had values of 4 and 6, respectively.

For the data analyzed at CUG,  $z_a$  and  $z_b$  again represented the quantities of parallel samples subjected to either chemical chromatography or no such treatment. The respective weighted averages for these two

groups were given as  $\bar{X}_a$  and  $\bar{X}_b$ . Specifically, in this case, m and n were set to 7 and 8, whereas o and p had values of 9 and 14, respectively.

Considering all chalcopyrite sample data collectively from both USTC and CUG,  $^{Z_a}$  and  $^{Z_b}$  signified the total quantities of parallel samples analyzed across the two institutions. Their corresponding weighted

averages for each group were once more designated as  $\bar{X}_a$  and  $\bar{X}_b$ . In this comprehensive case, m and n values were established as 1 and 6, while o and p equated to 7 and 14, respectively.

The critical *t*-values were calculated using Excel's T.INV.2T function, applying a significance level of

0.05 under a two-tailed hypothesis.

|          |             |      |      |      | nent co |      | 1    |      |      |       |
|----------|-------------|------|------|------|---------|------|------|------|------|-------|
| Spot No. | Grain No.   | Cu   | Fe   | S    | Со      | Ni   | Zn   | As   | Pb   | Total |
| 1        | IGGCcp-2 1  | 34.1 | 29.7 | 34.8 | 0.93    | -    | -    | 0.02 | 0.06 | 99.7  |
| 2        | IGGCcp-2 2  | 34.1 | 29.6 | 34.5 | 0.93    | -    | -    | -    | 0.06 | 99.3  |
| 3        | IGGCcp-2 3  | 34.0 | 29.8 | 34.7 | 0.95    | 0.02 | -    | 0.02 | 0.06 | 99.6  |
| 4        | IGGCcp-2 4  | 33.9 | 29.7 | 34.7 | 0.95    | -    | -    | 0.04 | 0.05 | 99.4  |
| 5        | IGGCcp-2 5  | 33.6 | 29.8 | 34.5 | 0.93    | -    | -    | 0.04 | 0.07 | 99.0  |
| 6        | IGGCcp-2 6  | 33.7 | 29.8 | 34.5 | 0.92    | -    | -    | -    | 0.04 | 99.0  |
| 7        | IGGCcp-2 7  | 33.8 | 29.8 | 34.3 | 0.93    | -    | -    | 0.02 | 0.03 | 98.9  |
| 8        | IGGCcp-2 8  | 33.7 | 29.6 | 34.2 | 0.93    | -    | 0.02 | 0.04 | 0.03 | 98.5  |
| 9        | IGGCcp-2 9  | 33.5 | 29.6 | 34.4 | 0.93    | -    | -    | 0.02 | -    | 98.6  |
| 10       | IGGCcp-2 10 | 34.3 | 29.8 | 34.5 | 0.94    | -    | -    | -    | 0.03 | 99.5  |
| 11       | IGGCcp-2 11 | 34.3 | 29.8 | 34.5 | 0.93    | 0.03 | -    | 0.02 | 0.04 | 99.6  |
| Average  |             | 33.9 | 29.7 | 34.5 | 0.93    |      |      |      | 0.04 | 99.2  |
| 18       |             | 0.3  | 0.1  | 0.2  | 0.01    |      |      |      | 0.02 | 0.4   |
| 12       | IGGCcp-2 12 | 34.1 | 29.8 | 34.5 | 0.93    | -    | -    | -    | 0.07 | 99.4  |
| 13       |             | 34.1 | 29.9 | 34.7 | 0.94    | -    | -    | 0.02 | 0.06 | 99.7  |

Table S7 Elemental concentrations (wt%) of IGGCcp-2 by EPMA

| 14      |             | 34.4 | 30.0         | 34.5 | 0.94 | -    | -    | 0.02 | -    | 99.8  |
|---------|-------------|------|--------------|------|------|------|------|------|------|-------|
| 15      |             | 34.4 | 29.8         | 34.4 | 0.94 | -    | -    | -    | 0.11 | 99.6  |
| 16      |             | 34.2 | 29.8         | 34.7 | 0.94 | -    | -    | -    | 0.02 | 99.6  |
| 17      |             | 34.1 | 29.8         | 34.6 | 0.92 | -    | -    | 0.04 | 0.05 | 99.5  |
| 18      |             | 34.2 | 29.8         | 34.5 | 0.92 | -    | -    | 0.04 | 0.03 | 99.5  |
| 19      |             | 34.4 | 29.9         | 34.7 | 0.92 | -    | -    | -    | 0.07 | 100.0 |
| 20      |             | 34.2 | 29.8         | 34.5 | 0.93 | 0.03 | -    | 0.02 | 0.02 | 99.5  |
| 21      |             | 34.3 | 29.8         | 34.6 | 0.93 | -    | -    | 0.02 | -    | 99.7  |
| 22      |             | 34.0 | 29.8         | 34.3 | 0.94 | -    | -    | 0.03 | 0.04 | 99.1  |
| 23      |             | 34.3 | 29.9         | 34.7 | 0.92 | -    | -    | 0.03 | 0.03 | 99.9  |
| 24      |             | 34.2 | 29.9         | 34.4 | 0.92 | -    | -    | 0.03 | -    | 99.5  |
| 25      |             | 33.9 | 29.8         | 34.7 | 0.92 | -    | 0.35 | -    | 0.09 | 99.7  |
| 26      |             | 34.2 | 29.5         | 34.5 | 0.93 | -    | 0.06 | 0.02 | 0.04 | 99.2  |
| 27      |             | 34.1 | 29.9         | 34.5 | 0.93 | -    | -    | 0.02 | 0.06 | 99.5  |
| 28      |             | 34.2 | 30.0         | 34.5 | 0.92 | -    | -    | 0.05 | 0.02 | 99.7  |
| 29      |             | 34.2 | 29.8         | 34.4 | 0.93 | -    | -    | -    | -    | 99.3  |
| 30      |             | 34.3 | 29.6         | 34.5 | 0.93 | -    | -    | 0.02 | 0.02 | 99.4  |
| 31      |             | 34.2 | 29.7         | 34.7 | 0.93 | -    | -    | -    | 0.06 | 99.6  |
| 32      |             | 34.2 | 29.8         | 34.4 | 0.93 | -    | -    | -    | 0.05 | 99.4  |
| 33      |             | 34.2 | 29.9         | 34.6 | 0.92 | -    | -    | -    | 0.04 | 99.6  |
| 34      |             | 34.2 | 29.8         | 34.6 | 0.92 | -    | -    | -    | 0.05 | 99.5  |
| 35      |             | 34.1 | 29.9         | 34.7 | 0.92 | -    | -    | -    | 0.04 | 99.7  |
| 36      |             | 34.3 | 29.8         | 34.6 | 0.93 | -    | -    | -    | 0.03 | 99.6  |
| 37      |             | 34.3 | 29.8         | 34.4 | 0.95 | -    | 0.03 | 0.02 | 0.02 | 99.5  |
| 38      |             | 34.0 | 29.7         | 34.6 | 0.93 | -    | 0.21 | 0.03 | 0.04 | 99.5  |
| 39      |             | 34.1 | 29.7         | 34.6 | 0.91 | -    | -    | -    | -    | 99.4  |
| 40      |             | 34.0 | 29.8         | 34.5 | 0.94 | -    | -    | 0.03 | 0.04 | 99.3  |
| 41      |             | 34.2 | 29.8         | 34.6 | 0.93 | _    | 0.04 | 0.02 | _    | 99.6  |
| Average |             | 34.2 | 29.8         | 34.6 | 0.93 |      |      |      | 0.04 | 99.5  |
| 1S      |             | 0.1  | 0.1          | 0.1  | 0.01 |      |      |      | 0.03 | 0.2   |
| 42      | IGGCcp-2 13 | 34.0 | 29.8         | 34.5 | 0.93 | _    | _    | 0.02 | 0.10 | 99.3  |
| 43      |             | 34.0 | 29.6         | 34.4 | 0.95 | _    | _    | 0.02 | 0.05 | 99.1  |
| 44      |             | 34.3 | 29.7         | 34.5 | 0.92 | _    | 0.02 | 0.03 | 0.05 | 99.5  |
| 45      |             | 34.1 | 29.7         | 34.4 | 0.95 | _    | 0.04 | 0.04 | 0.02 | 99.3  |
| 46      |             | 34.1 | 29.9         | 34.6 | 0.93 | _    | _    | 0.03 | 0.03 | 99.5  |
| 47      |             | 34.2 | 29.7         | 34.6 | 0.93 | _    | _    | 0.03 | 0.06 | 99.5  |
| 48      |             | 34.2 | 29.9         | 34.6 | 0.93 | 0.02 | -    | -    | 0.05 | 99.7  |
| 49      |             | 34.1 | 30.0         | 34.6 | 0.93 | -    | _    | 0.05 | 0.02 | 99.7  |
| 50      |             | 33.9 | 29.7         | 34.4 | 0.92 | _    | 0.04 | -    | 0.02 | 99.1  |
| 51      |             | 34.3 | 29.9         | 34.6 | 0.92 | -    | -    | -    | 0.02 | 99.8  |
| 52      |             | 34.2 | 29.9         | 34.7 | 0.93 | -    | 0.02 | -    | 0.05 | 99.8  |
| 53      |             | 34.0 | 29.8         | 34.5 | 0.91 | _    | 0.02 | -    | 0.07 | 99.3  |
| 55      |             | 33.9 | 29.8<br>29.8 | 34.4 | 0.91 | _    | -    | _    | 0.07 | 99.2  |
| 55      |             |      | 29.8<br>29.8 |      |      | _    | _    |      |      |       |
| 22      |             | 34.2 | 29.8         | 34.5 | 0.92 | -    | -    | -    | 0.07 | 99.5  |

| 1 <b>S</b> | 0.1  | 0.1  | 0.1  | 0.01 |   |   |      | 0.03 | 0.2  |
|------------|------|------|------|------|---|---|------|------|------|
| Average    | 34.1 | 29.8 | 34.5 | 0.93 |   |   |      | 0.05 | 99.5 |
| 61         | 34.2 | 29.8 | 34.5 | 0.94 | - | - | 0.04 | 0.09 | 99.6 |
| 60         | 34.3 | 29.9 | 34.6 | 0.91 | - | - | 0.03 | -    | 99.8 |
| 59         | 34.1 | 29.7 | 34.5 | 0.91 | - | - | 0.02 | 0.05 | 99.3 |
| 58         | 34.3 | 29.9 | 34.6 | 0.93 | - | - | -    | 0.04 | 99.8 |
| 57         | 34.1 | 29.9 | 34.6 | 0.93 | - | - | -    | 0.02 | 99.6 |
| 56         | 34.0 | 29.8 | 34.6 | 0.94 | - | - | -    | 0.04 | 99.4 |

Description:

The symbol '-' signified 'Not Detected' within the presented data.

The elemental compositions, encompassing both major and minor constituents, of chalcopyrite grains derived from sample IGGCcp-2 were meticulously quantified through the application of Electron Probe Microanalysis (EPMA). To evaluate the consistency of major element concentrations, a systematic multi-point analysis was conducted on an arbitrarily chosen 11 grains. These grains were sequentially numbered from IGGCcp-2 G01 to IGGCcp-2 G11, with a single spot analysis performed on each distinct grain.

To delve deeper into the intra-grain compositional uniformity, two further grains, identified as IGGCcp G12 and IGGCcp G13, were subjected to an exhaustive examination. Grain IGGCcp G12 underwent 30 individual spot analyses, while grain IGGCcp G13 was analyzed at 20 distinct locations, thereby affording a thorough assessment of the heterogeneity or homogeneity of these compositions both interand intra-grain.