**Preliminary**

**Product Information**

**Microanalytical Reference Material**

**Cu isotope analysis for chalcopyrites**

**Natural crystal**

**(14ZJ12-1, JGZ-29 and JGZ-78)**

***This certificate is valid for five years after purchase***

***Sales date:***

***The minimums amount of sample to be used is ~200mg***

***NOTE***

***These materials have been developed by xx ().***

***Latest revision: April 2024***

***Signed:***

***Prof. xxx***

***Xxx***

***Xxx***

***Xxx***

1. **Description**

Three natural chalcopyrites 14ZJ12-1, JGZ-29 and JGZ-78 were investigated in this study. The chalcopyrite 14ZJ12-1 is collected from Xiaseling Cu-W deposit at Linan County, Zhejiang Province, China. The main metallic minerals in the quartz-vein are wolframite, chalcopyrite, pyrite, etc. which are eutectoid to semi-euhedral crystals. The chalcopyrite JGZ-29 and JGZ-78 are collected from Jiguanzui copper-gold deposit at Hubei Province, China, in the middle and lower Yangtze metallogenic belt. The main metallic minerals are chalcopyrite and pyrite which are eutectoid to semi-euhedral crystals that are symbiotic with calcite. A great number of fresh chalcopyrite crystals were picked out from the three rock samples, such as 150g of 14ZJ12-1, 100g of JGZ-29 and 80g of JGZ-78 (Fig. 1).



**Fig. 1 Photographs of chalcopyrites 14ZJ12-1, JGZ-29 and JGZ-78**

**2. Analytical method**

**2.1 Sample preparation**

Samples were crushed with a steel mortar to 1–2 mm size. Any fragments with visible imperfections under a binocular microscope were removed. The clean fragments were selected randomly (30–40 fragments for each sample) and embedded in epoxy resin and carefully polished to obtained flat surfaces for microscopic observation, major and trace elements analyses by LA-ICP-MS, respectively, Cu isotope analyses by LA-MC-ICP-MS. Parts of the fragments were used for bulk analyses using MC-ICP-MS.

**2.2 Concentration of trace elements**

Trace element compositions in 14ZJ12-1, JGZ-29 and JGZ-78 were measured by using LA-ICP-MS. An Agilent 7900 quadrupole ICP-MS combined with a GeoLas Pro 193 nm excimer laser platforms were used. The laser ablation parameters were set at a spot size of 44 μm, a repetition rate of 5 Hz and a fluence of ~5 J cm-2. Each LA-ICP-MS analysis incorporated an approximately 20 s background acquisition followed by 50 s of data acquisition from the sample. Element mass fractions were calibrated against multiple-reference materials (NIST 610 and MASS-1). The analytical results were listed in Table 2.

**Table 1. The trace elements obtained from LA-ICP-MS**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Element** | **Isotope** | **Unit** | **14ZJ12-1** | **JGZ-29** | **JGZ-78** |
| **Mean** | **SD, K=1** | **Mean** | **SD, K=1** | **Mean** | **SD, K=1** |
| FeS | 57  | wt% | 45.7  | 1.01  | 46.1  | 0.92  | 45.6  | 0.51  |
| CuS | 63  | wt% | 53.1  | 0.84  | 53.1  | 0.99  | 53.6  | 0.55  |
| Li | 7  | μg g-1 | 0.16  | 0.31  | 0.10  | 0.16  | 0.14  | 0.15  |
| Be | 9  | μg g-1 | 0.10  | 0.14  | 0.06  | 0.12  | 0.11  | 0.15  |
| Na | 23  | μg g-1 | 20.2  | 56.0  | 13.3  | 19.7  | 11.9  | 28.2  |
| Mg | 24  | μg g-1 | 1.18  | 1.36  | 14.7  | 36.8  | 0.73  | 2.66  |
| Al | 27  | μg g-1 | 0.83  | 1.65  | 15.0  | 38.0  | 2.21  | 7.62  |
| Si | 29  | μg g-1 | 1803  | 207  | 1588  | 372  | 1586  | 215  |
| P | 31  | μg g-1 | 67.3  | 25.6  | 70.1  | 20.8  | 72.3  | 25.6  |
| K | 39  | μg g-1 | 2.62  | 4.28  | 6.07  | 15.2  | 7.67  | 28.9  |
| Ca | 43  | μg g-1 | 90.0  | 79.3  | 70.0  | 96.0  | 64.3  | 53.5  |
| Ti | 49  | μg g-1 | 3.79  | 0.72  | 3.73  | 1.51  | 3.30  | 0.58  |
| V | 51  | μg g-1 | 0.02  | 0.03  | 0.05  | 0.13  | 0.02  | 0.03  |
| Cr | 52  | μg g-1 | 0.80  | 0.61  | 0.90  | 0.76  | 0.73  | 0.68  |
| Mn | 55  | μg g-1 | 4.41  | 7.71  | 0.98  | 1.22  | 0.93  | 2.70  |
| Co | 59  | μg g-1 | 15.8  | 27.3  | 8.24  | 17.0  | 2.08  | 3.97  |
| Ni | 60  | μg g-1 | 3.75  | 0.49  | 53.84  | 6.35  | 0.46  | 0.74  |
| Zn | 66  | μg g-1 | 2067  | 6931  | 1442  | 489  | 988  | 882  |
| Ga | 71  | μg g-1 | 2.50  | 1.05  | 0.49  | 0.16  | 0.27  | 0.24  |
| Ge | 72  | μg g-1 | 2.01  | 0.82  | 1.43  | 0.81  | 1.68  | 2.07  |
| Rb | 85  | μg g-1 | 0.04  | 0.05  | 0.06  | 0.10  | 0.07  | 0.26  |
| Sr | 88  | μg g-1 | 0.07  | 0.16  | 0.15  | 0.30  | 0.27  | 1.03  |
| Y | 89  | μg g-1 | 0.00  | 0.01  | 0.18  | 0.95  | 0.00  | 0.00  |
| Zr | 90  | μg g-1 | 0.06  | 0.27  | 3.68  | 19.7  | 0.01  | 0.01  |
| Nb | 93  | μg g-1 | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| In | 115  | μg g-1 | 1039  | 629  | 0.12  | 0.07  | 38.3  | 15.7  |
| Sn | 118  | μg g-1 | 715  | 730  | 0.58  | 0.56  | 4.45  | 2.81  |
| La | 139  | μg g-1 | 0.00  | 0.00  | 0.06  | 0.13  | 0.00  | 0.00  |
| Ce | 140  | μg g-1 | 0.00  | 0.00  | 0.08  | 0.17  | 0.00  | 0.00  |
| Pr | 141  | μg g-1 | 0.00  | 0.00  | 0.01  | 0.02  | 0.00  | 0.00  |
| Nd | 146  | μg g-1 | 0.00  | 0.01  | 0.04  | 0.06  | 0.01  | 0.01  |
| Sm | 147  | μg g-1 | 0.01  | 0.01  | 0.01  | 0.02  | 0.01  | 0.02  |
| Eu | 153  | μg g-1 | 0.00  | 0.00  | 0.01  | 0.02  | 0.00  | 0.00  |
| Gd | 157  | μg g-1 | 0.01  | 0.01  | 0.02  | 0.04  | 0.01  | 0.01  |
| Tb | 159  | μg g-1 | 0.00  | 0.00  | 0.00  | 0.01  | 0.00  | 0.00  |
| Dy | 163  | μg g-1 | 0.01  | 0.01  | 0.04  | 0.14  | 0.00  | 0.01  |
| Ho | 165  | μg g-1 | 0.00  | 0.00  | 0.01  | 0.05  | 0.00  | 0.00  |
| Er | 166  | μg g-1 | 0.00  | 0.01  | 0.04  | 0.20  | 0.00  | 0.01  |
| Tm | 169  | μg g-1 | 0.00  | 0.00  | 0.01  | 0.03  | 0.00  | 0.00  |
| Yb | 172  | μg g-1 | 0.01  | 0.01  | 0.05  | 0.26  | 0.00  | 0.01  |
| Lu | 175  | μg g-1 | 0.00  | 0.00  | 0.01  | 0.06  | 0.00  | 0.00  |
| Hf | 178  | μg g-1 | 0.01  | 0.01  | 0.09  | 0.45  | 0.01  | 0.01  |
| Ta | 181  | μg g-1 | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| Pb | Total | μg g-1 | 25.3  | 19.7  | 2.92  | 2.87  | 8.37  | 5.93  |
| Th | 232  | μg g-1 | 0.00  | 0.00  | 0.02  | 0.09  | 0.00  | 0.00  |
| U | 238  | μg g-1 | 0.00  | 0.01  | 0.26  | 1.39  | 0.00  | 0.00  |

**2.4 Bulk Cu isotope analysis using MC-ICP-MS**

The δ65Cu for three chalcopyrites investigated in this study were determined using solution-MC-ICP-MS in two independent labs, GPMR lab in Wuhan and IGL lab in Beijing. In GPMR, each sample was divided into two parts and digested two times. After the digestion of all samples, Cu was separated from the matrix using an anion exchange resin (AG MP-1M). 0.5 ml of each purified Cu fraction was taken and diluted to 4 ml in 2% HNO3 (m/m), then was spiked with NIST SRM 994 Ga solution, yielding a concentration of 200 ng g-1 of Cu and Ga. Also, NIST SRM 3114 Cu solution in 2% HNO3 was prepared and spiked with the Ga solution to yield a concentration of 200 ng g-1 of Cu and Ga. Samples and standards were introduced into the MC-ICP-MS in the following sequence: NIST SRM 3114 Cu–sample–NIST SRM 3114 Cu. Six replicate measurements of each sample solution were performed.

In IGL analysis, the chemical purification method also used the AG-MP-1M anion exchange resin. The combination of the SSB method and Zn-doping was used to correct instrumental mass fractionation. During the analyses, samples and standards were diluted to produce 100 ng g-1 of Cu solution in 3% (m/m) HNO3 respectively. NIST SRM 976 Cu solution was used as an external standard. Three replicate measurements of each sample solution were performed.

All of the results from two labs were converted to NIST SRM 976 Cu using the δ65CuNIST976 of NIST SRM 3114 Cu = 0.18 ± 0.02 (2SD). The analytical results were listed in Table 2.

**Table 2 Cu isotope compositions (δ65CuNIST976) of three chalcopyrites measured by solution-MC-ICP-MS and LA-MC-ICP-MS**

|  |  |  |  |
| --- | --- | --- | --- |
| **Sample** | **Solu. Ana. in IGL** | **Solu. Ana. in GPMR** | **LA-MC-ICP-MS** |
| **Mean (n=3)** | **2SD** | **Mean (n=6)** | **2SD** | **Mean** | **2SD** | **n** |
| 14ZJ12-1 | -0.22 | 0.02 | -0.21 | 0.04 | -0.21 | 0.07 | 150 |
| JGZ-29 | 0.44 | 0.01 | 0.47 | 0.04 | 0.49 | 0.08 | 152 |
| JGZ-78 | -0.05 | 0.02 | -0.07 | 0.04 | -0.02 | 0.08 | 152 |

**2.5 Micro analysis of Cu isotope using LA-MC-ICP-MS**

For in situ Cu isotope measurements, a high sensitivity X skimmer cone and a Jet sample cone were mounted in the Neptune Plus interface. The mass spectrometer was operated in the low mass resolution mode. The routine data acquisition consisted of one block of 120 cycles (0.524 second integration time per cycle): the first 30 cycles were measured to determine the background, while the remaining 90 cycles were measured as the sample signal intensities. The laser was run with an energy density on the sample of approximately ~1.5 J cm-2. Cu isotope analyses were completed with laser spot sizes of 16-32 μm and a low laser frequency of 2-4 Hz. These conditions were sufficient to produce the signal intensities of 6-15 V on the mass of 65Cu, while the blank was producing average values of ~0.01 V on the mass of 65Cu. No interference correction was implemented in this study. Chalcopyrite JGZ-78 was employed as matrix-matching standard reference materials. Finally, all δ values were converted to NIST SRM 976 for interlaboratory comparison. The analytical results were listed in Table 2.

**3. Intended Use**

This series of samples are mainly used for Cu isotope analysis of micro analysis in chalcopyrite, which are suitable for LA-MC-ICP-MS. They can be used as calibration standards or unknown samples to monitor data quality (secondary reference material). Please note that each sample can only be used for a single purpose, for example, each sample cannot be used as both a calibration standard and an unknown sample during the same test.

**4. Storage and Handling**

Samples are recommended to be stored in a dry environment. Natural chalcopyrite is stable at normal temperature and pressure. Do not contact dilute acid, chalcopyrite is easily oxidated in dilute acid.

**5. Safety Instructions**

Natural chalcopyrite is sulfide, stable at room temperature and pressure, can be in contact with the skin, but can not be ingested into the body.

**6. Other Information**

The chalcopyrite reference materials have been published in the SCI journal. Because samples are natural crystals, a small number of inclusions or cracks may appear. If users observe these inclusions or cracks during microanalysis, please avoid them.

This series of samples is sold exclusively through xx.

**7. Legal Notice**

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**8. References**

Development of three chalcopyrites and one copper metal as potential reference materials for copper isotopic analysis by LA-MC-ICP-MS. Yang WenWu, Wen Zhang, Zhou, Lian, Liu, Sheng-Ao, Qiu, Xiaofei, Tong, Xirun. Rapid Communications in Mass Spectrometry. 2023; 37(15): e9538. doi:10.1002/rcm.9538

**9. Revision History**

(a): 3 April 2024, First publication Version 1.0.