Copper isotope fractionation during prehistoric smelting of copper sulfides: experimental and analytical data
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Contents

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3. Data Description

The project from which the data derived aimed to establish the first systematic study of Cu isotope fractionation during the prehistoric smelting and refining process. For this reason, an experimental approach was used to smelt sulfide copper ore according to reconstructed prehistoric smelting models. The ore was collected by E. Hanning as part of her PhD thesis work from a Bronze Age mining site, the Mitterberg region, Austria (Hanning and Pils 2011) and was made available for the experiments. All starting materials for the experiments such as the natural ore, roasted ore, construction clay, flux, dung (used for the roasting), wood and charcoal (fuel) were natural materials. All firing conditions including the amount of fuel or charging material and the temperatures in the furnaces were recorded, and the experimental procedures were documented in the very detail. In total, 30 experiments were carried out in 4 experimental series. The smelting products, both intermediate products and final products were sampled during or after the respective experiment. Slag, matte and copper metal were the major smelting products. All other materials used in and

produced by the experiments were sampled, too. Materials used and produced in the two most promising experimental series with regard to potential Cu isotope fractionation were analyzed. Based on the analytical results, the potential of Cu isotopes as a tool in archaeometallurgical research was systematically evaluated and consequences for the copper isotope application as a provenance tool in archaeometry were identified.

The data include the documentation of the experiments, laboratory procedures and analytical methods. An experimental outline was previously published in Rose et al. (2019). Analytical methods applied were ICP-MS (elemental analysis, 80 samples), MC-ICP-MS (copper isotopes, 98 samples), and XRD (phase analysis, 25 samples). The experiments were carried out at the Römisch-Germanisches Zentralmuseum, Labor für Experimentelle Archäologie, Mayen, Germany. Laboratories used for the analytical part of the project were the research laboratories at the Deutsches Bergbau-Museum Bochum and FIERCE (Frankfurt Isotope and Element Research Center), Goethe-University Frankfurt, both Germany. Data were processed and plots created with R (R Core Team 2019) in RStudio®. Data are provided as data tables or text files, the R scripts used to create the time-temperature plots of the smelting experiments are also included.

3.1. Smelting experiments

Experiments were carried out at the Römisch-Germanisches Zentralmuseum, Labor für Experimentelle Archäologie in Mayen, Germany. Only a general description of the experiments is given here. For detailed information about the experiment and the materials used and produced in the experiments, the reader is referred to the catalogue of the experiments (see file 2020-03_Rose-et-al_Experiments-catalogue).

3.1.1. Roasting (sample nomenclature R)

The crude ore was crushed to chestnut size and subsequently roasted in a clay lined roasting bed. The layout of the roasting pile and of the following experimental setups is given in Rose et al. (2019). Hard wood was used as fuel for the roasting experiment. The temperature was measured with a thermocouple at the center of the roasting pile. The roasting reaction had to be terminated before its end. To cool the roasted ore down, it was quenched in large buckets filled with water.

3.1.2. Shaft furnace experiments (sample nomenclature: f)

The roasted ore was crushed to a grain size between hazelnut and peas for the smelting in the shaft furnace. The shaft furnace was reconstructed according to the archaeological record from the east alpine Bonze Age (Hanning et al. 2015; Hanning and Pils 2011). To avoid contamination of the smelt with chalcopyrite inclusions from natural stone, schamotte tiles were used to build the furnace wall and lined with clay. Soft wood was used as fuel. The thermocouples were placed in one of the side walls in a height of about 12 cm (T1), 25 cm (T2), and 40 cm (T3) above the furnace bottom, and next to the tuyères (T4). In total, 4 shaft furnace experiments were carried out (experimental series S1 to S4, Fig. 1) and their smelting products were kept separated to avoid contamination between different experimental series.

Figure 1: Succession of the different experimental set ups. (S1-S4: 4 experimental series)

3.1.1. Pellet roasting/smelting experiments (sample nomenclature: r1)

The matte and some of the slag produced in the shaft furnace experiment were crushed with hammers and ground with basalt ground stones. Subsequently it was mixed with dung. The mixture was formed to pellets of about 10 cm length. The pellets were placed on a flat roasting pile made from soft wood and roasted overnight in the roasting bed. The temperature was recorded at the center of the roasting pile.

3.1.2. Pit furnace experiments (sample nomenclature: p)

Pit furnace experiments were carried out in a pit lined with clay. The originally dug pit was too deep for successful smelting experiments, hence it was filled with charcoal dust and either a large crucible covering the entire bottom of the pit was inserted or larger charcoal pieces inserted up to a suitable
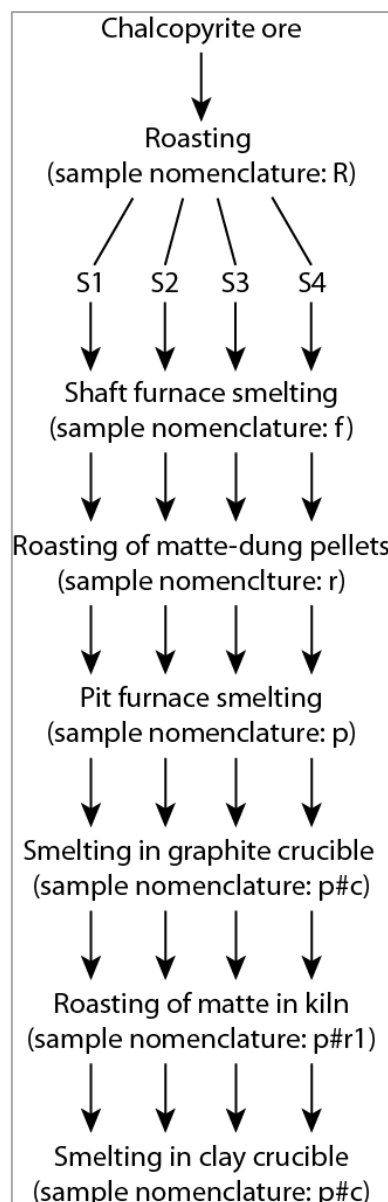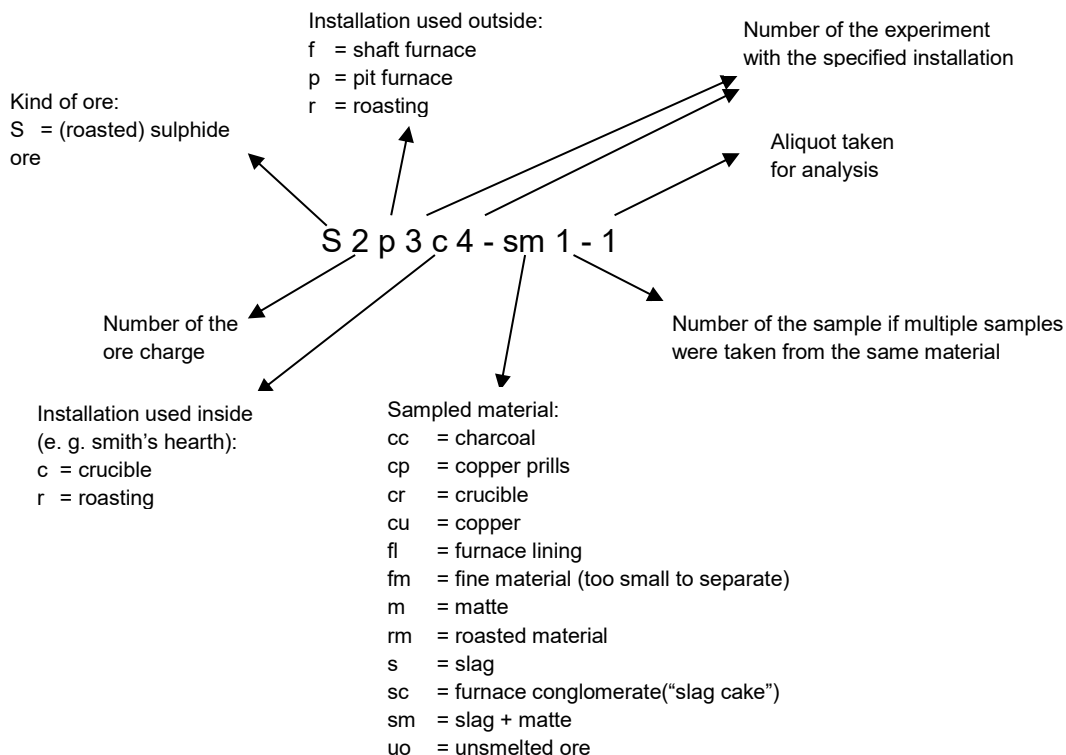
depth of the pit was achieved. The arrangement of the two tuyères changed between the experiments. The thermocouple for the temperature measurement was placed between the tuyères and the tip was on a similar position like the tuyères concerning height and distance from the furnace wall.

3.1.3. Crucible smelting experiments (sample nomenclature: c)

The matte from the pit furnace experiments was crushed with steel hammer and smelted in closed graphite crucibles in a smithing hearth. The melt was cast into foundry sand.

Because these experiments did not resulted in the production of metallic copper, additional experiments were carried out in clay crucibles. In them the matte was roasted for several hours in an electric kiln (sample nomenclature: p#r2) and subsequently molten in a flat clay lined pit inside the smithing hearth. In the experiment of the experimental series S4, no copper was produced, thus it was repeated once.

3.2. Nomenclature of experiments and samples

Installation used outside:
f = shaft furnace
p = pit furnace
r = roasting

Number of the experiment
with the specified installation

Kind of ore:
S   = (roasted) sulphide ore

Aliquot taken
for analysis

S 2 p 3 c 4 - sm 1 - 1

Number of the
ore charge

Number of the sample if multiple samples
were taken from the same material

Installation used inside
(e. g. smith's hearth):
c = crucible
r = roasting

Sampled material:
cc   = charcoal
cp   = copper prills
cr   = crucible
cu   = copper
fl   = furnace lining
fm   = fine material (too small to separate)
m   = matte
rm   = roasted material
s   = slag
sc   = furnace conglomerate("slag cake")
sm   = slag + matte
uo   = unsmelted ore

3.3. Sampling: methods and deviating nomenclature of samples

Out of four experimental series, samples from S2 and S4 were chosen for analysis. S2 is the experimental series with the highest number of experiments and S4 was regarded as the most successful one because it was the only one with a considerable amount of copper produced during a pit furnace experiment. Additionally, only in these both series a liquid slag was achieved in the pit furnace experiments.

Sampling methods were adapted to the material of the sample. From each material used or produced in the smelting experiments, representative samples were taken at the experimental site. From this material, samples were taken for the analytical procedures. Some samples were already

ground (matte, slag, charcoal dust), plastic (dung, clay) or fine grained (roasted material, sand, charcoal) and material was taken with a steel spatula from them. For the wood, small pieces left behind from chopping were collected and chopped into small pieces in the lab. The sample of the chalcopyrite ore consisted of small flakes of the ore collected after all of it (166 kg) was crushed.

Roasted ore pieces were collected from 27 areas of the roasting pile before quenching. From each location, one piece of roasted ore was crushed in a steel mortar (sample code: R-bulk). Another piece from each location was crushed and separated by color into more oxidized material and more unroasted material (sample codes: R-bulk-ox and R-bulk-red). Additionally, the water used for quenching was sampled after quenching was finished (sample code: R28). At two locations (sample codes: R11, R21), additional samples were taken to evaluate/monitor the influence of the quenching procedure on the Cu isotopic composition. Larger pieces were cooled down slowly, without quenching like the other samples from the roasting pile (R11c, R21c) and small pieces from the same location (R11f, R21f) that were quenched in water in separate glass vials. Six months later, the small pieces and the water were separated and both were sampled (water samples: R11l, R21l).

In case the slag and matte samples collected at the experimental site consisted pieces < 2 cm, several of them were used for the analysis. If they consisted only of one piece, this piece was crushed and either a single large fragment or several smaller fragments were used for the analysis. Samples from sintered materials were taken either by scraping the sintered material with a big steel spatula to extract the grains or by extracting aggregates of sintered grains with tweezers.

Copper prills were either extracted during crushing at the experimental site or tweezers were used to extract them in the lab. Larger metallic copper aggregates were sampled by drilling with a steel drill, the larger of them on different spots. In one experiment, spongy copper was produced, which was separated from the matte with a small steel chisel and hammer as well as possible.

From the furnace lining, parts were crushed in a steel mortar and the glazed area separated from the underlying clay by handpicking with tweezers.

Furnace conglomerate from two experiments was sampled to check for Cu isotopic homogeneity. Samples were extracted from spots scattered all over the cross section of the furnace conglomerate by drilling with a steel drill.

3.4. Sample preparation

3.4.1. Solid sample preparation and homogenisation

Powdered ore samples and powdered smelting products withdrawn during the experiments (matte, slag, copper metal) were produced by standard procedure applied in geochemistry by crushing, grinding in an agate mortar, and parting (Ney 1986).

3.4.2. Acid digestion of samples (DBM procedure)

Samples for chemical and isotope analysis were brought to solution. Millipore® water with a resistivity of 18.2 MΩ·cm, quartz distilled and double distilled acids and bleached PTFE beakers were used throughout the analytical processes.

Pure metals were dissolved directly in 2 ml H_2O, 1 ml conc. (65 %) HNO_3, and 1 ml conc. (32 %) HCl. Ores, slags, and matte, which are potentially silicate-containing, were broken down with acids in a

laboratory microwave. 100 mg of sample material were placed in teflon microwave vessels and a mixture of different acids was added. While conc. (48 %) HF and 50 g/l H_3BO_3 were always used, the addition of conc. (32 %) HCl and conc. (65 %) HNO_3 depended on the presence of considerable amounts of lead or tin in the sample (must be known beforehand):

without Pb	1.2 g HF + 5 g HNO_3 + 5 g HCl
with Pb	1.2 g HF + 9 g HNO_3 (to avoid reaction: $Pb + Cl^- \rightarrow PbCl_2 \downarrow$)
with Sn	1.2 g HF + 9 g HCl (to avoid reaction: $Sn + 2NO_3^- \rightarrow SnO_2 \downarrow\ +2NO_2$)

The microwave was operated with a maximum temperature of 250 °C, and a heating phase of 40 min. The total time of the program was 1.2 hours.

After the dissolution step, the solution was evaporated and adjusted to a defined volume of 2 % HNO_3. The sample solution was produced by diluting the dissolved sample to a concentration of 1000 mg/l (e.g. 100 mg of an undissolved sampled in 100 ml). The sample solution was split in half to have two aliquot solutions available for elemental and isotope analysis, respectively.

3.5. Analytical procedures

3.5.1. Elemental analysis

Elemental analyses were done with an ICP-SFMS ThermoScientific Element XR at the Deutsches Bergbau-Museum Bochum (Germany). External calibration was used for quantification. Sample solutions were diluted with 5 % HNO_3 by the factor 100 for main elements and the factor 10 for trace element analyses. The analyses are carried out with a FAST SC-system autosampler, a ST 5532 PFA μ-FLOW nebulizer, a Peltier-cooled PFA spray chamber and a 1.8 mm sapphire injector in triple detector mode at all three different mass resolutions (m/Δm), depending on the elements of interest. Measurements were controlled with comparable standard materials.

3.5.2. Copper isotope analysis

3.5.2.1. Ion exchange chromatography (IEC)

3.5.2.1.1. Establishment of the IEC protocol

The protocol developed by Maréchal et al. (1999) for geological materials to separate copper with an ion exchange resin was modified to match with the special sample matrices of the smelting products and the specific conditions at FIERCE.

Samples from different natural materials, smelting products and also artificial samples were processed to identify the different elution behavior of them compared to the protocol published by Maréchal et al. (1999). Exemplary elution curves of copper and iron are given in Fig. 2. Copper started to elute after 9 ml of 7 N HCl + 0.001 % H_2O_2. After 43 ml of acid, copper reached background level, but after switching to 2 N HCl + 0.001 % H_2O_2, another small amount of copper was eluted with the 2nd ml of 2 N HCl + 0.001 % H_2O_2, i.e. 45 ml in total. This small amount had an intensity of about 10 % compared to the main elution peak of copper. After another 2 ml, iron started to elute with a steep rise towards its elution peak. Although this is a very small gap between the elution of the two elements, the collection of this last portion of copper is crucial because copper isotopes strongly fractionate during IEC and incomplete recovery of the copper might result in measuring a wrong Cu isotope composition (Maréchal and Albarède 2002).

An explanation for this very rest of copper eluted with 2N HCl presumably lies in the differences in the collection of dissolved species of Cu and their dependency from acid molarity as investigated
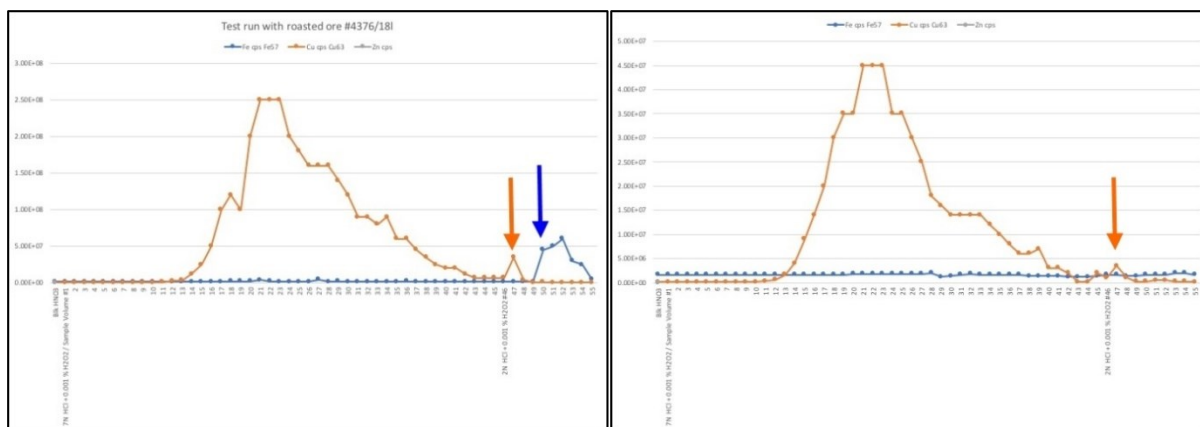
Figure 2: Elution curves for copper and iron. Two representative tests were selected for demonstration here. Left: Roasted chalcopyrite ore from Mitterberg. Right: iron-free copper solution. Arrows indicate the very last portion of copper (orange) with the 2nd ml of 2 N HCl and the starting volume of iron (blue) with the 4th ml of 2 N HCl.

earlier (Borrok et al. 2007; Maréchal et al. 1999; Maréchal and Albarède 2002; Ramette 1986). According to Sato and Kato (1977) and Borrok et al. (2007), the copper eluted with 2 N HCl + 0.001% H_2O_2 must comprise of the neutral to electro-positive species ($CuCl_2$, $CuCl^+$, Cu^{2+}), which could in contrary to the negative species not be eluted quantitatively with the stronger acid.

3.5.2.1.2. IEC protocol

All steps were carried out in a clean lab under a laminar flow hood at FIERCE, Goethe-University Frankfurt (Germany). PTFE beakers were bleached with double distilled 6 N HCl for several hours prior to use.

The ion exchange resin Bio-Rad® AG MP-1M was used. To clean the resin prior to any use, it is repeatedly mixed with Millipore® water, shaken for a few minutes and the water decanted. The so cleaned resin was covered with Millipore® water and stored for future use.

Single-use Bio-Rad® Polyprep chromatography columns (catalogue Nr. 731-1550) with a 10 ml reservoir and a 2 ml bed are used.

Step	ml	Solvent
Cleaning	7	0.5 N HNO_3
	2	H_2O
	7	2 N HCl
	2	H_2O
	7	7 N HCl
	2	H_2O
	7	7 N HCl
	2	H_2O
Conditioning	7	7 N HCl + 0.001 % H_2O_2
Sample load	1	7 N HCl + 0.001 % H_2O_2
Matrix elution (discarded)	9	7 N HCl + 0.001 % H_2O_2
Cu elution (collected)	36	7 N HCl + 0.001 % H_2O_2
	2	2 N HCl + 0.001 % H_2O_2

They are equipped with frits, caps and tip closures. A suspension of AG-MP-1M in Millipore® water was filled into the columns until the settled resin achieved the sub-edge of the funnel. The addition of H_2O_2 keeps Cu and Fe in their reduced forms.

The sample solution was evaporated to dryness at ca. 80 °C. The evaporated sample was dissolved in 7 N HCl + 0.001 H_2O_2 for IEC and insoluble residues separated in a centrifuge. The applied protocol is given in the table.

With each separation batch, a blind was run parallel to the samples (including procedural blinds) to identify any possible contamination or mistakes from the separation process.

The collected copper solutions were stepwise evaporated at 70 to 80 °C on a hot plate.

3.5.2.2. Copper isotope measurements

Isotopic analysis was carried out at FIERCE, Goethe-University Frankfurt (Germany) with a ThermoScientific NeptunePlus MC-ICP-MS equipped with a quartz glass nebuliser and a cyclonic spray chamber. The dried and column separated copper is diluted in 1 ml double distilled 2 % HNO_3 with 250 ppb Ni (NIST SRM-986) for internal mass bias correction (Ehrlich et al. 2004). Chemical blanks are measured at the beginning of each sequence and after each 20 samples. Measurement of the blanks shows that they range within 10 to 100 times lower in intensity than the measurements of the standard. Measurements of units with three samples each are bracketed by measurements of the copper standard NIST SRM-976 diluted in the Ni-doped solution like the samples to correct for mass bias and machine drift (sample-standard bracketing method). The internal background is corrected using the chemical blank measurements.

3.5.2.2.1. Instrument settings

Detector (cup) configuration				
Cup configuration file:	Cu-Ni-HR, High resolution			
Detectors:	Faraday			
Instrumental amplifiers:	#1-6 = 10^{11} (for isotopes with high intensities) #7-10 = 10^{13} (for isotopes with low intensities)			
Cup settings	Species	Target position (mm)	Actual position (mm)	Amplifier positions used:
L3-F	^{60}Ni	64.550	64.551	#6
L2-F	^{61}Ni	42.100	42.101	#5
L1-F	^{62}Ni	18.880	18.881	#8
Center-F	^{63}Cu (62.92 u)			#2
H1-F	^{64}Ni	19.430	19.431	#4
H2-F	64.5 u	32.834	32.832	#1
H3-F	^{65}Cu	46.110	46.112	#3
	Integration time (s)	Number of integration	Idle time	
Main	8.389	1	1.000	
lowres	0.008	1.000	0.000	

Instrument parameters	
Gas flows (exemplary)/RF	Auxilliary gas: 1.095 l/min. Sample gas: 0.94 l/min. RF power: 1000
Vacuum (exemplary)	Fore: 1.3 E-3 High: 1.54 E-7 Ion getter: 1.79 E-8
Cones	Vendor: ICP cones LTD Sample cone: Al 58272 Skimmer cone: Al 58266
Spray chamber	Small
Autosampler	ESI SC series, Capillary diameter: 0.25 mm, Graphite reinforced tip

Measurement settings	
Take-up time	1 min
Wash time	4 min
Background measurement	On 1st position, After sequence of 20 samples each
Measurements	10 sec. each 4 blocks 5 cycles

Standard reference material and correction of internal mass fractionation	
Standards reference materials	Cu: SRM-976 Ni: SRM-986
Cu Standard solution: Cu + Ni in 2 % HNO_3	150 ppb Cu-Standard 250 ppb Ni-Standard
Typical intensities of Cu standard solution	^{60}Ni=12 V, ^{63}Cu=8 V, ^{65}Cu=3 V, ^{62}Ni=0.5 V, ^{60}Ni=0.5 V
Ni standard reference solution in 2% HNO_3	Certified value: $^{62}Ni/^{60}Ni$ = 0.1386
Normalisation ratios	$^{61}Ni/^{60}Ni$, true value: 0.043469 $^{62}Ni/^{60}Ni$, true value: 0.1386
Correction law	exponential
Outlier test	2 sigma, Between cycles and blocks
Drift correction	Cu standard reference solution in 2% HNO_3 as unknown sample

3.5.2.2.2.   Calculation of δ^{65}Cu

The mean of the individual measurements is used to calculate the copper isotope ratios in the notation of δ^{65}Cu values. The formula used for the sample-bracketing correction is (Peel et al. 2008; Zhu et al. 2000):

$$\delta^{65}Cu\ [‰] = \left[\frac{\left(\frac{^{65}Cu}{^{63}Cu}\right)_{Sample}}{\frac{1}{2}\left[\left(\frac{^{65}Cu}{^{63}Cu}\right)_{Standard\ 1} + \left(\frac{^{65}Cu}{^{63}Cu}\right)_{Standard\ 2}\right]} - 1 \right] \cdot 1000$$

Because three samples (at the end of sequences sometimes two samples) were measured between each standard bracket, the formula was modified and the weighted average of the bracketing standards was calculated to have a better correction of instrumental drift:

$$\delta^{65}Cu\ [‰] = \left[\frac{\left(\frac{^{65}Cu}{^{63}Cu}\right)_{Sample}}{\frac{1}{x+1}\left[(x-n)\cdot\left(\frac{^{65}Cu}{^{63}Cu}\right)_{Standard\ 1} + n\left(\frac{^{65}Cu}{^{63}Cu}\right)_{Standard\ 2}\right]} - 1 \right] \cdot 1000,$$

where x gives the number of samples between the bracketing standards and n denotes the position of a sample within the standard bracket.

The δ-notation defines the deviation of the isotope ratio measurement of a sample within the standard bracket in ‰. Positive $\delta^{65}Cu$ values represent an enrichment of the heavier isotope ^{65}Cu, negative ones represent an enrichment of ^{63}Cu compared to the standard. As commonly used for the isotope measurement of copper, the certified standard NIST SRM-976 was utilised. The precision (external reproducibility) of the data is < 0.16 ‰ (2σ).

3.5.3. X-ray diffraction analysis

The ground sample material was analysed with Powder X-ray diffraction analysis (XRD) at the Deutsches Bergbau-Museum Bochum (Germany) using a PANalytical X'Pert Pro instrument equipped with a Cu anode operated at 45 kV and 40 mA. The diffraction patterns were recorded between 5° and 70° 2θ with a step size of 0.0170° 2θ and a step time of 10.1600 s in continuous mode and converted to fixed aperture afterwards. The obtained diffraction patterns underwent Rietveld refinement with GSAS II (Toby and Dreele 2013) using crystal structures from the American Mineralogist Crystal Structure Database (Downs and Hall-Wallace 2003) and the Crystallography Open Database (Gražulis et al. 2009; Gražulis et al. 2012) to identify not only the phases but also to give a semi-quantitative estimate of their proportions. The data base IDs of the minerals phases used for the Rietveld refinement are given in the keys of the diffractograms.

Unfortunately, crystal structures of some of the identified phases were not listed in the databases. This is probably due to the fact that the Cu-Fe-S system has an extensive range of solid solutions and the synthetically produced phases from the smelting experiments do not always have an equivalent in the databases at hand. Although the smelting products are anthropogenic materials and thus by definition not minerals (Nickel 1995), the mineral names of the equivalent phases are used to ease readability.

3.6. Data processing

All data were further processed with Microsoft Excel and the statistical programming language R (R Core Team 2019) using functions provided in the package bundle "tidyverse" (Wickham 2017) and the packages "readxl" (Wickham and Bryan 2019), "ggthemes" (Arnold 2017), "gridextra" (Auguie 2017), and "lubridate" (Grolemund and Wickham 2011). The R scripts used to plot the time-temperature plots of the experiments are part of this data publication.

4. File description

4.1. File inventory

Folder	File name	File format	Content
Experiments-t-T-data.zip	Temp_R Temp_S2f1 Temp_S2p1 Temp_S2p2 Temp_S2p3 Temp_S2p3c1 Temp_S2p3c2 Temp_S2p3c3 Temp_S2p3c4 Temp_S2p3r1 Temp_S2r1 Temp_S4f1 Temp_S4p1 Temp_S4p2 Temp_S4p2c1 Temp_S4p2c2 Temp_S4p2c3 Temp_S4p2r1 Temp_S4r1	.txt	Records of temperature and events during the respective experiments
	Temp_plot	.R	R script for drawing the t-T-plots
	Temp_plot_ready	.R	R script to prepare temperature data recorded with thermologger for plotting.
XRD-raw data.zip	Cpy6 R-bulk-ox R-bulk-red R-bulk S2f1-m S2f1-s S2p1a-m S2p1a-sm S2p3c2-m S2p3c3-m S2p3c4-m S2p3c4-s	.gpx	GSAS II project files of the respective experiments.

	S2r1-rm S4f1-sm S4f1-uo S4p1-fm S4p1-m S4p1-sm S4p2-m S4p2c1-m S4p2c2-s S4p2c3-s S4p2c3-sm S4p2r1-rm S4r1-rm	.lst	GSAS II summaries of the final Rietveld refinements of the respective experiments.
	Cpy6_4342-18 R-bulk-ox_4376-18 R-bulk-red_4377-18 R-bulk_4375-18 S2f1-m_4378-18 S2f1-s_4379-18 S2p1a-m_4392-18 S2p1a-sm_4395-18 S2p3c2-m_4409-18 S2p3c3-m_4419-18 S2p3c4-m_4412-18 S2p3c4-s_4413-18 S2r1-rm_4422-18 S4f1-sm_4437-18 S4f1-uo_4438-18 S4p1-fm_4441-18 S4p1-m_4442-18 S4p1-sm_4448-18 S4p2-m_4460-18 S4p2c1-m_4451-18 S4p2c2-s_4453-18 S4p2c3-s_4457-18 S4p2c3-sm_4458-18 S4p2r1-rm_4461-18 S4r1-rm_4463-18	.FXYE	Raw diffraction data of the respective experiments.
	Cu_isotopes	.txt	Copper isotope compositions
	Elements	.txt	Chemical compositions. Elements not measured: "nd"
	Experiments_catalogue	.pdf	Fact sheets for each experiment undertaken
	Sample_catalogue	.txt	Overview over the sample material
	XRD_Diffraktograms	.pdf	Diffractograms of the final Rietveld refinement.
	XRD_results	.txt	Concentrations derived from the Rietveld refined XRD data

4.2. Description of data tables

4.2.1. Temp_###.txt (### = Experiment ID)

Column header	Unit	Description
Place		Serial number of the measurement
Date	yyyy-mm-dd	Date of the measurement
Time	hh:mm:ss	Time of the measurement
T1_TempC	°C	Temperature measured; For shaft furnace experiments: Temperature measured at position T1; For crucible experiments: Top of charcoal
T2_TempC	°C	For shaft furnace experiments: Temperature measured at position T2; For crucible experiments: Side of crucible; Only S2p3c4, S4p2c3, S4p2c4: In front of the tuyères
T3_TempC	°C	For furnace experiments (type f): Temperature measured at position T3; For crucible experiments: Top of crucible
T4_TempC	°C	For furnace experiments (type f): Temperature measured by thermocouple T4
Remarks	°C	Any additional events in the course of the experiment

4.2.2. Cu-isotopes.txt

Column header	Unit	Description
Sample_ID		Sample identifier
DBM ID		Identifier of the sample at the German Mining Museum Bochum
Material		Short description of the sample material
d65Cu	‰	$\delta^{65}Cu$ value
2sd	‰	Standard deviation on the 2σ confidence level

4.2.3. Elements.txt

Column header	Unit	Description
Sample_ID		Sample identifier
DBM ID		Identifier of the sample at the German Mining Museum Bochum
Material		Short description of the sample material
#_%	wt%	Concentration of element #
Sum	wt%	Sum of major elements
#_ppm	ppm	Concentration of element #

4.2.4. Samples-catalogue.txt

Column header	Unit	Description
Sample_ID		Sample identifier
DBM-ID		Identifier of the sample at the German Mining Museum Bochum
Material		Short description of the sample material
Sampling procedure		Procedure of sampling
Elemental analysis		Samples with analysed chemical composition are marked with X
Cu isotopes		Samples with analysed Cu isotope composition are marked with X
XRD		Samples analysed by XRD are marked with X

4.2.5. XRD-results.txt

Column header	Unit	Description
Sample_ID		Sample identifier
DBM ID		Identifier of the sample at the German Mining Museum Bochum
wR_%	%	weighted profile R value of the Rietveld refined diffractogram
mineral		Identified mineral phases
percentage	wt%	weight percent of the identified mineral phase
amount		weight fraction (percentage / 100%) of the identified mineral phase
sigma		estimated standard deviation of the weight fraction
remarks		Comments about unidentified or unrefined phases

4.3. Other file types

4.3.1. Experiments-catalogue.pdf

The file provides a fact sheet for each experiment carried out. In the fact sheet, basic information about the experiment (Experiment ID, date, experimental setup), and the materials used (kind and amount of educts and products, sample ID) are given. It further provides a plot of the temperatures measured during the experiment and up to four pictures of the experimental set-up, the ongoing experiment and the smelting products. The first page of the file provides a detailed explanation of the nomenclature used for the experiment and sample IDs.

4.3.2. XRD-Diffractograms.pdf

This file provides all the Rietveld refined diffractograms of the samples analysed with XRD after their last refinement. The plots were exported from GSAS II. In the key of each diffractogram, the respective catalogue ID of the phases used for the Rietveld refinement is given behind its name. The first page of the file provides an explanation of the elements in the plot and the chemical compositions for each identified phase.

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