



Considerations on Copper Smelting from Fahlores and the Metallurgy of Cu-As Bronzes

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Abstract: The copper production in the Alps began three thousand years BC, usually near ore deposits in Austria and Switzerland. For copper smelting, sulphidic ores like chalcopyrite and fahlores were used. Copper produced from fahlores was widely used in the Alps resulting in As and Sb contents in the metallic copper. Such copper alloys were generally referred to as arsenical bronzes. However, in ancient bronze objects, a wide range of arsenic content was observed. One question relates to how much arsenic is transferred into the bronze alloy during smelting. By thermodynamic equilibrium calculations, the roasting and smelting processes are simulated and show that As reacts already to gaseous As compounds before Cu_2S is attacked and metallic Cu is formed. In case of Sb liquid, Sb_2O_3 is formed quickly during roasting and is finally enriched in the slag.

These results have been confirmed by the investigation of an ancient copper ingot containing 4 wt. % As and 2.5 wt. % S as well as smaller quantities of Sb, Ni, Fe, and Ag. The main phases apart from metallic copper are Cu_3As , Cu_2S , and Sb oxide. In a slag sample, an inclusion was characterized containing chalcopyrite, FeO, and Sb oxide. This result is in accordance with the thermodynamic calculations where Sb_2O_3 was obtained.

Another interesting point is the As loss of arsenical bronzes during remelting. Thermodynamic equilibrium calculations reveal that Cu_3As is very stable and during remelting no evaporation of As is observed. Moreover, during oxidation of metallic Cu-As, the formation of Cu_2O is favoured from Cu and not from Cu_3As . Consequently during melting of Cu-As for casting, at first Cu_2O is formed resulting in an As enrichment in the melt and in the casted object, respectively. These effects are superimposed and, if recycled Cu alloys are used, the starting concentration of As is unknown.

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Überlegungen zur Kupfergewinnung aus Fahlerzen und zur Metallurgie von Cu-As-Bronzen

Zusammenfassung: Die Kupferproduktion in den Alpen begann dreitausend Jahre vor Christus, meist in der Nähe von Erzvorkommen in Österreich und der Schweiz. Für die Kupferverhüttung wurden sulfidische Erze wie Chalkopyrit und Fahlerze verwendet. Kupfer wurde in den Alpen häufig aus Fahlerzen hergestellt, was zu As- und Sb-Gehalten im metallischen Kupfer führte. Solche Kupferlegierungen werden allgemein als Arsenbronzes bezeichnet. In antiken Bronzegegenständen wurde jedoch ein breites Spektrum an Arsengehalten beobachtet. Die Frage dazu lautet, wieviel Arsen bei der Kupfergewinnung in die Bronzelegierung überführt wird. Durch thermodynamische Gleichgewichtsrechnungen werden Röst- und Schmelzprozesse simuliert und gezeigt, dass As bereits zu gasförmigen As-Verbindungen reagieren, bevor Cu_2S angegriffen wird und metallisches Cu entsteht. Im Fall von Sb wird bereits beim Rösten flüssiges Sb_2O_3 gebildet und reichert sich schließlich in der Schlacke an.

Diese Ergebnisse wurden durch die Untersuchung eines alten Kupfergusskuchens mit 4 Gew.-% As und 2,5 Gew. % S sowie kleinere Mengen Sb, Ni, Fe und Ag, bestätigt. Die Hauptphasen neben metallischem Kupfer sind Cu_3As , Cu_2S und Sb-Oxid. In einer Schlackenprobe wurde ein Einschluss charakterisiert, der Chalkopyrit, FeO und Sb-Oxid enthielt. Dieses Ergebnis stimmt mit den thermodynamischen Berechnungen überein, bei denen Sb_2O_3 erhalten wurde. Ein weiterer interessanter Punkt ist der As-Verlust von arsenhaltigen Bronzen beim Umschmelzen bzw. Recycling. Die thermodynamischen Berechnungen zeigen, dass Cu_3As sehr stabil ist und während des Umschmelzens keine Verdampfung von As erfolgt. Außerdem wird bei der Oxidation von metallischem Cu-As die Bildung von Cu_2O aus Cu und nicht aus Cu_3As begünstigt. Folglich entsteht beim Schmelzen von Cu-As zum Gießen zunächst Cu_2O , was zu einer As-Anreicherung in der Schmelze bzw. im Gussobjekt

führt. Diese Effekte überlagern sich und bei der Verwendung von recycelten Cu-Legierungen sind auch die Ausgangskonzentration von As unbekannt.

Schlüsselwörter: Kupfergewinnung, Fahlerz, Arsen, Antimon, Metallographie, Thermodynamische Gleichgewichtsberechnungen

1. Introduction

In the Alps the copper production started at the end of the 3rd millennium BC, especially at the ore deposits in Salzburg and Graubünden. For copper smelting the main ores were sulphides like chalcopyrite CuFeS_2 (Fig. 1a,b) and fahlores, e.g. tetraedrite $(\text{Cu, Fe})_{12}\text{Sb}_4\text{S}_{13}$ (Fig. 1c,d) or tennantite $(\text{Cu, Fe})_{12}\text{As}_4\text{S}_{13}$. The copper smelting metallurgy was extensively described by Tylecote [1–3].

Ernst Pernicka and co-workers analyzed many copper ore samples and prehistoric metal artefacts to find correlations between ores and artefacts on the basis of impurity patterns from fahlore according to fahlore deposits in Schwaz and Brixlegg. During the end of the Early Bronze Age, the impurity patterns in metal artefacts changed to the ores from the Mitterberg region where chalcopyrite was found. Copper from the Middle Bronze Age was almost completely produced from chalcopyrite. Later on the fahlore signature reappeared, indicating that, during the Late Bronze Age, fahlores as well as chalcopyrite were used for copper production [5].

For the ancient copper metallurgy, arsenical bronze is of higher interest than antimony bronze because most of the artefacts contain more As than Sb. Additionally it is well known that metallic As has a low sublimation temperature (613°C), but also As_2O_3 has a rather low boiling point (465°C). From a chemical point of view, it should be verified which compounds are formed during the metallurgical processes and if an As loss by evaporation is possible.

It is well known that sulphidic ores cannot be reduced by coal or carbon monoxide. Thus the copper metallurgy is a two-step process: at first, the ore is roasted to form oxides and the sulphur is eliminated as gaseous SO_2 , subsequently the cupreous oxides are reduced by coal [3, 6, 7].

At the end three or more steps were used because it was not so easy to form pure oxides during roasting. In such a case, the second step was melting and accumulation of Cu sulphides, followed by a second roasting step and a final reduction step to metallic copper. In principle this final reduction step needs no coal because Cu oxide is reduced by the present Cu sulphide.

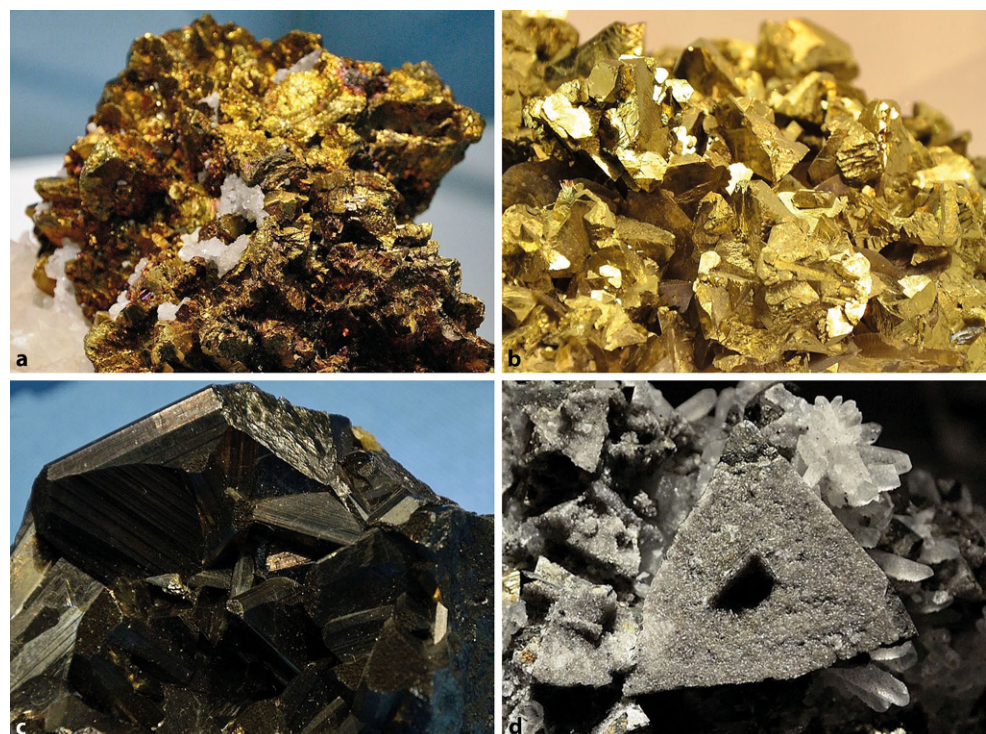
From archaeological investigations of fahlore smelting sites, it is well known that high As pollution is locally present. It is assumed that this pollution is caused by the evaporation of As_2O_3 [8–10].

Several reports describe experiments in which various copper ores were smelted to copper-arsenic alloys [2, 3, 11].

A mixture of malachite and synthetic copper arsenate directly reduced with charcoal resulted in a copper alloy with 4.2 wt.% As [12]. Tylecote [3] suggested that copper-arsenic alloys with high arsenic concentration are produced through addition of high-arsenic minerals to the crucible.

Co-smelting experiments of various Cu and As containing compounds resulted in a wide range of copper-arsenic

Fig. 1: Photos of copper ores: a chalcopyrite, France, b chalcopyrite, China, c tetraedrite, France, d tetraedrite, Peru



alloy ingots [13]. For example, in an ancient bronze ingot melted from fahlore, 4wt.% As, 2.5wt.% S, and little Sb were observed [14, 15]. In this ingot the inhomogeneous distribution of As, Sb, and trace elements like Ni makes it difficult to describe the elemental composition of large objects. Finally, it is difficult to give a clear correlation between the As content in the ore and the amount of As in the final arsenical bronze. For antimony, nearly no data are available.

Velem in Hungary is an outstanding site, and it became known in the 19th century that it was a centre of late Bronze Age metalworking [16]. After chemical analyses of two depot finds, it was already clear that the copper alloys from Velem contain increased concentrations of antimony [17, 18]. Tylecote suspected that in Velem Sb was added to the bronze due to the increased Sb content compared to As [19].

The metallographic examination of a cast cake from Velem showed that antimonite (Sb_2S_3) was probably added to the molten copper, which would explain the high Sb content in the copper [20]. From this point of view, it also seems worth mentioning that cast cakes with high Sb contents were also detected in a hoard from Rannersdorf, located nearby in Lower Austria [21].

During the last years, the theory of ancient copper recycling has come up [22–24]. The idea was that there is a linear decrease of elements during remelting of arsenical copper alloys. Such an effect was already described for the zinc loss during recasting of copper coins in Roman Britain [25, 26]. To confirm this theory, the thermodynamic of metal alloys was studied [27] and the processes during solidification of Cu-As alloys as well [28, 29]. More detailed experiments by differential thermal analysis (DTA) and simultaneous thermal gravimetric analysis (TGA) gave no hint for the evaporation of As during melting of Cu-As alloys [30]. To get more information about the Cu-As alloys, the eutectic and the Cu_3As phase compositions were synthesized and described [31].

2. Experimental Procedure

2.1 Thermodynamic Equilibrium Calculation

For calculations of the thermodynamic equilibrium conditions during the metallurgical processes, the software EKVIVALC was used [32]. To get adequate results, all available thermodynamic data of the potentially involved compounds were considered by the software (see list below). A disadvantage is that metastable phases which are formed intermediately and missing phases in the program database are not taken into account.

The list of compounds used for the thermodynamic calculations is as follows:

$\text{O}(\text{g})$, $\text{O}_2(\text{g})$, $\text{O}_3(\text{g})$, $\text{C}(\text{s})$, $\text{C}(\text{g})$, $\text{C}(\text{diamond})$, $\text{C}_2(\text{g})$, $\text{C}_3(\text{g})$, $\text{CO}(\text{g})$, $\text{CO}_2(\text{g})$, $\text{C}_2\text{O}(\text{g})$, $\text{C}_3\text{O}_2(\text{g})$, $\text{COS}(\text{g})$, $\text{CS}(\text{g})$, $\text{S}(\text{s})$, $\text{S}(\text{l})$, $\text{S}(\text{g})$, $\text{S}_2(\text{g})$, $\text{S}_3(\text{g})$, $\text{S}_4(\text{g})$, $\text{S}_5(\text{g})$, $\text{S}_6(\text{g})$, $\text{S}_7(\text{g})$, $\text{S}_8(\text{g})$, $\text{SO}(\text{g})$, $\text{SO}_2(\text{g})$, $\text{SO}_3(\text{g})$, $\text{S}_2\text{O}(\text{g})$, $\text{Cu}(\text{s})$, $\text{Cu}(\text{l})$, $\text{Cu}(\text{g})$, $\text{Cu}_2(\text{g})$, $\text{CuCO}_3(\text{s})$, $\text{CuO}(\text{s})$, $\text{CuO}(\text{g})$, $\text{Cu}_2\text{O}(\text{s})$, $\text{CuS}(\text{s})$, $\text{Cu}_2\text{S}(\text{l})$, $\text{CuSO}_4(\text{s})$, $\text{Cu}_2\text{SO}_5(\text{s})$, $\text{Cu}_3\text{As}(\text{s})$, $\text{As}(\text{s})$, $\text{As}(\text{g})$, $\text{As}_2(\text{g})$, $\text{As}_3(\text{g})$, $\text{As}_4(\text{g})$, $\text{As}_2\text{O}_3(\text{s})$, $\text{As}_2\text{O}_3(\text{l})$, $\text{As}_2\text{O}_5(\text{s})$, $\text{As}_4\text{O}_6(\text{g})$, $\text{AsS}(\text{g})$, $\text{As}_2\text{S}_2(\text{s})$, $\text{As}_2\text{S}_2(\text{l})$, $\text{As}_2\text{S}_3(\text{s})$, $\text{As}_2\text{S}_3(\text{l})$, $\text{Sb}(\text{s})$, $\text{Sb}(\text{l})$, $\text{Sb}(\text{g})$, $\text{Sb}_2(\text{g})$, $\text{Sb}_4(\text{g})$, $\text{Sb}_2\text{O}_3(\text{s})$, $\text{Sb}_2\text{O}_3(\text{l})$, $\text{Sb}_2\text{S}_3(\text{s})$.

2.2 Metallography

Large samples were sectioned by a cut off machine to obtain samples with a proper dimension for metallographic preparation.

Metallic samples were hot mounted in Bakelite, and slags were cold mounted with Araldite in vacuum to infiltrate the porous materials. After plane grinding, the samples were gradually polished using 9, 3, and 1 μm diamond suspensions. Final polishing was performed partially using a 0.05 μm Al_2O_3 suspension. To reveal the

Fig. 2: Thermodynamic calculation for the composition Cu 12 mol, S 13 mol, As 4 mol, C 10 mol at 800 °C with increasing oxygen content. Due to the logarithmic scale, it is rather confusing

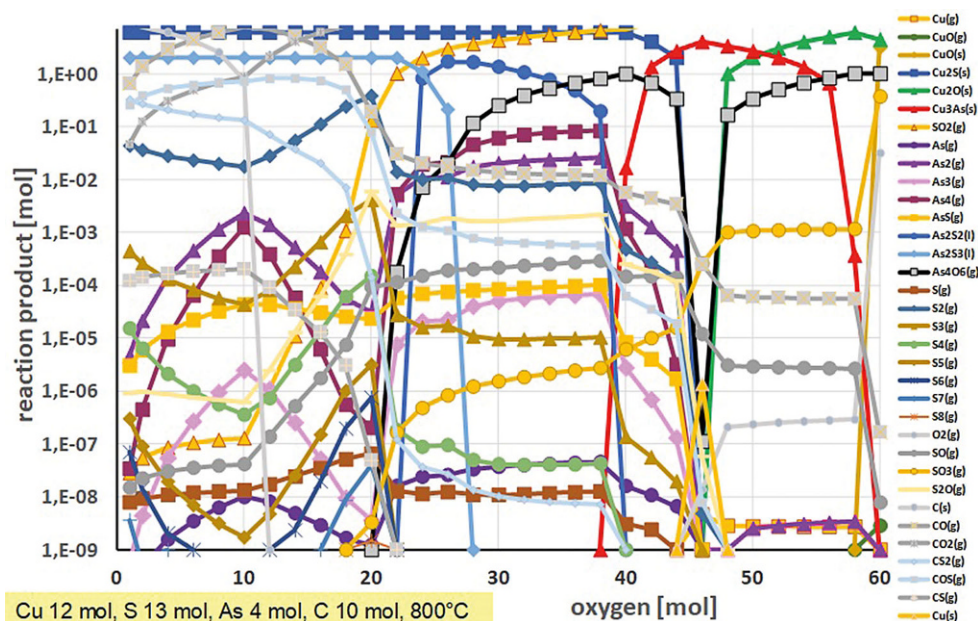
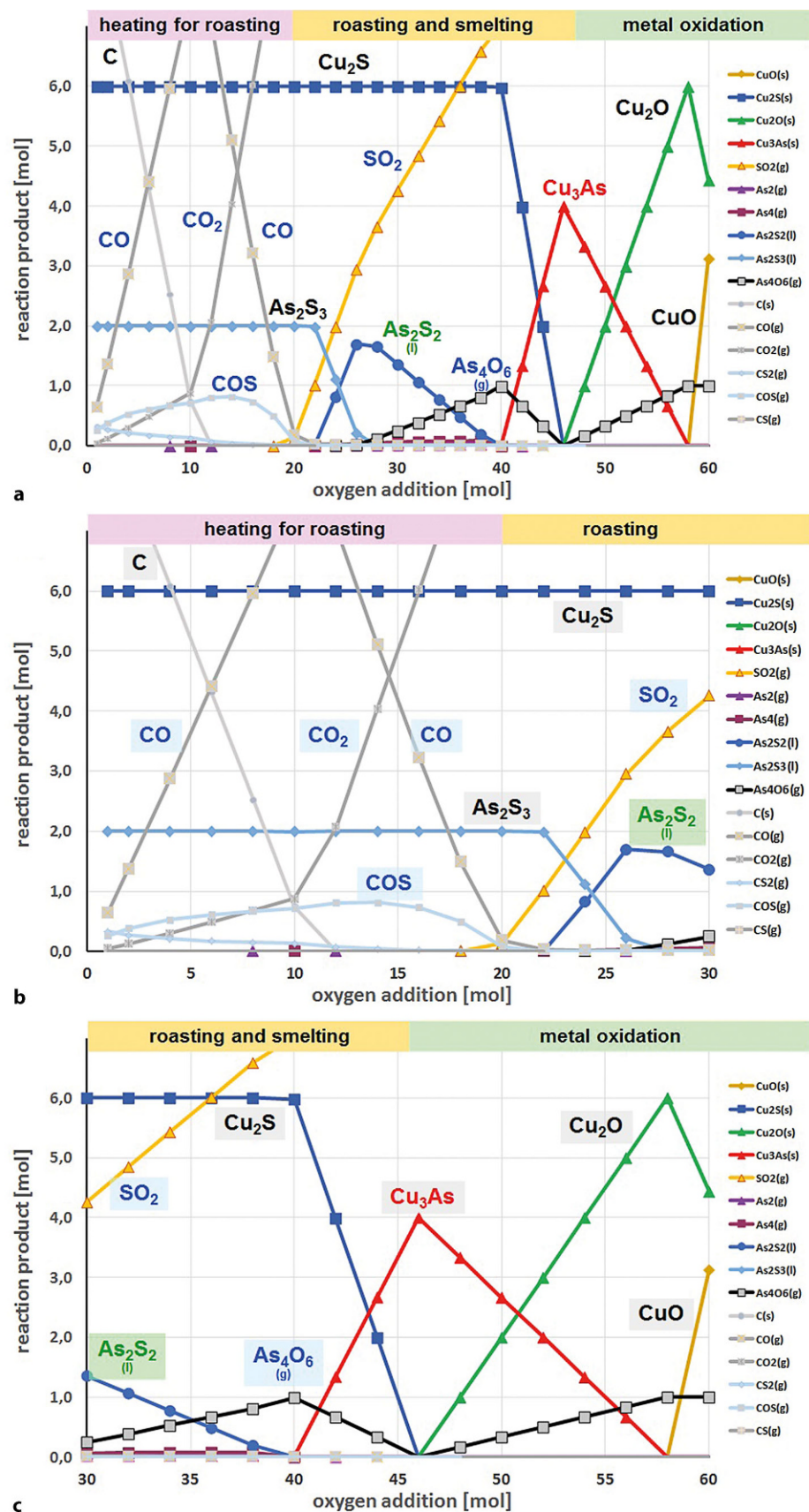


Fig. 3: Thermodynamic calculation for the composition Cu 12 mol, S 13 mol, As 4 mol, C 10 mol at 800 °C. **a** whole range from ore roasting to metal oxidation; **b** detailed section from heating (burning charcoal) to beginning of roasting; **c** detailed section from roasting to oxidation of metallic Cu



metallic microstructure, typical etchants for Cu alloys such as FeCl₃, Klemm 1, and (NH₄)₂CuCl₄·2H₂O were used [33].

The microstructures were examined by using a light optical microscope (LOM) and a scanning electron microscope (SEM, SE, and BSE mode). The elemental composition was determined by energy dispersive X-ray analysis (EDX) and X-ray fluorescence analysis (XRF).

3. Results and Discussion

3.1 Thermodynamic Equilibrium Calculations to Simulate the Metallurgy of Fahlores

For the calculations various compositions containing copper, arsenic, and sulphur in stoichiometric ratio were determined (the EKVICALC software searched all compounds containing these elements), a temperature was selected, and the equilibrium composition was calculated for increasing oxygen levels. This procedure simulates the reactions during roasting and smelting of the copper ores.

We have to keep in mind that these equilibrium calculations are thermodynamic. During practical smelting processes, the chemical reactions are overlaid by the reaction kinetics. For example, if one compound is evaporating during roasting, it is lost for the metallurgical process, but in our calculations the elements remain in the system and the concentrations are constant.

Fig. 2 shows the raw data for a calculation in logarithmic scale, and it is rather complex. For a better understanding, we changed to the decimal scale and used the relevant sector for presentation and discussion.

3.1.1 Behaviour of As during Smelting Arsenical Cu Ores

In Fig. 3a the simulation of the whole process is shown, starting from pure sulphide and adding oxygen till CuO is

formed. To simulate the chemical reactions of roasting, carbon was added to the system. The calculations confirm the already known fact that sulphides cannot be reduced by carbon. As can be seen in Fig. 3b, at first the carbon reacts with oxygen to CO and, in the next step, CO reacts to CO₂. During this process step, some COS can be formed additionally. When the carbon has been totally consumed, SO₂ formation starts. In practice the used charcoal for roasting is necessary to increase the temperature to a value that oxygen can react with the sulphidic ore. For the roasting reaction itself, an adequacy of oxygen has to be available, which can be carried out in roasting beds but not in shaft furnaces.

At 800 °C roasting starts with the reaction of As₂S₃ to liquid As₂S₂ and gaseous SO₂. In the next step, the As₂S₂ reacts with oxygen forming gaseous As₄O₆ (Fig. 3c). Cu₂S reaction with O starts after the total conversion of As₂S₂ into As₄O₆. For the metallurgical process, this means that As can evaporate completely during roasting, even at 800 °C.

Since there is no Cu excess in relation to the Cu₃As in these calculations, the formation of Cu₃As begins with the decomposition of Cu₂S, whereby metallic Cu would arise without the presence of As. In practice, the As could already have evaporated as As₄O₆ by this point in time, which means that, at the point in time when Cu is formed, As is no longer available for the reaction to form Cu₃As.

With a further increase of oxygen, Cu₃As reacts at first to Cu₂O followed by CuO formation. As forms As₄O₆, which can evaporate.

Another calculation was performed at 1100 °C (Fig. 4). In contrast to 800 °C, the As₂S₃ directly reacts to gaseous As₂ and As₄, respectively. At higher O contents, Cu₃As is formed and decomposes to Cu₂O and As₄O₆.

In metallurgical practice fahlore smelting means that, during roasting at lower temperatures, As evaporates as As₂O₆ and at higher temperatures as As₂–As₄ mixtures. The Cu₃As formation starts not before Cu₂S is decomposed. Thus As evaporates partially on the roasting bed, and, in

Fig. 4: Thermodynamic calculation for the composition Cu 12 mol, S 13 mol, As 4 mol, at 1100 °C

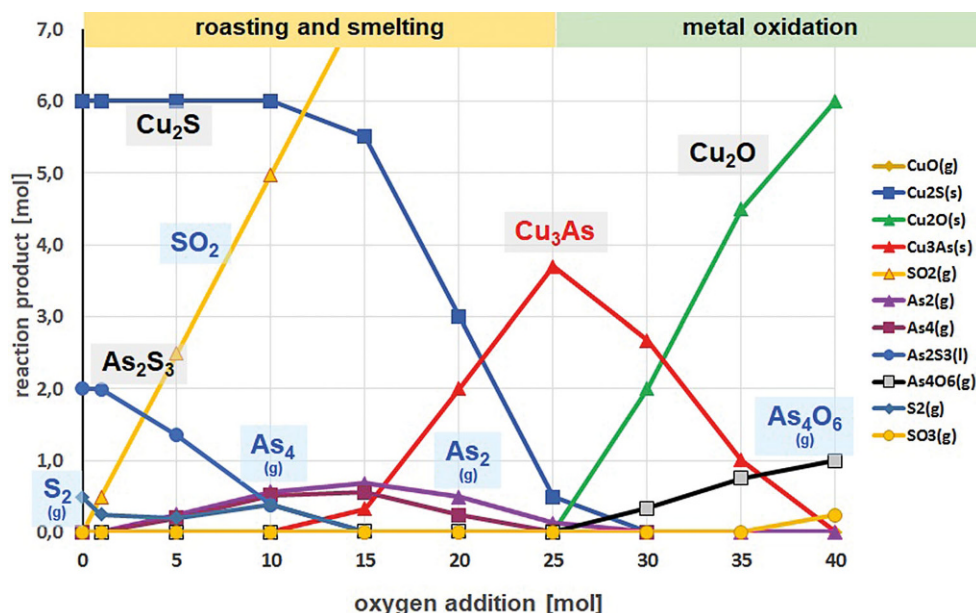
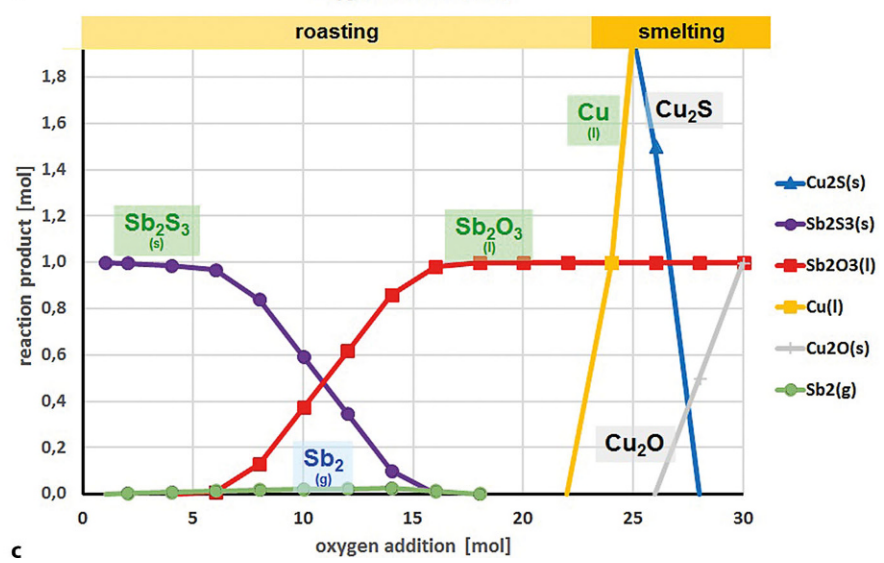
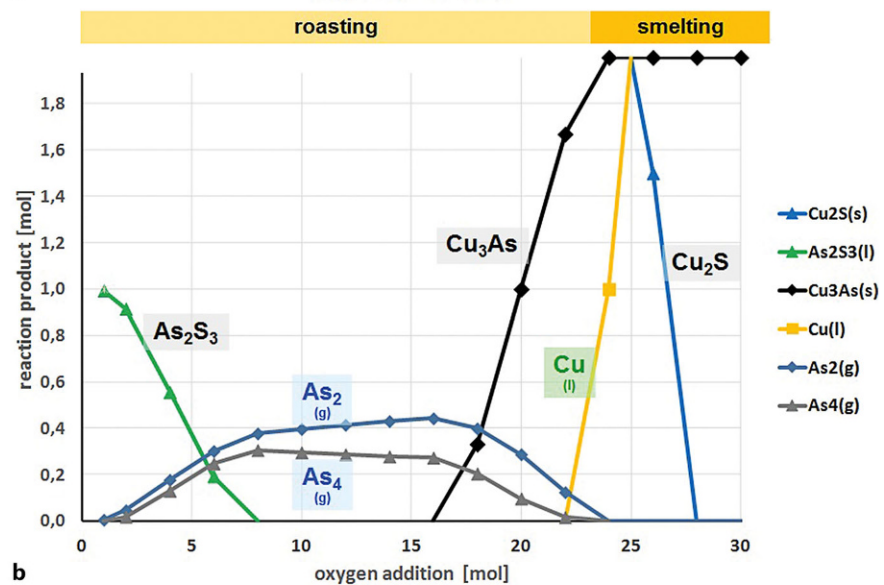
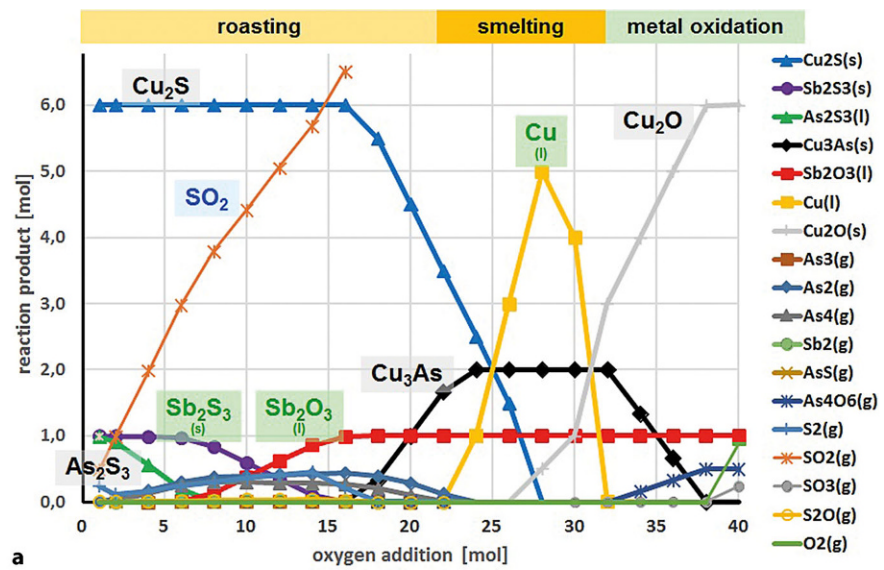


Fig. 5: Thermodynamic calculation for the composition Cu 12 mol, S 13 mol, As 2 mol, Sb 2 mol at 1100°C. a whole range from ore roasting to metal oxidation; b detailed section for As reactions during roasting; c detailed section for Sb reactions during roasting



the following shaft furnace process, the remaining As can react to Cu_3As . Cu_3As is a very stable intermetallic phase and remains in the alloy until Cu_2O formation takes place.

3.1.2 Behaviour of Sb during Smelting Fahlors

The simultaneous presence of As and Sb was calculated at 1100°C (Fig. 5a). In this case As_2S_3 reacts at first with oxygen and volatile As_2 and As_4 (Fig. 5b). The Cu_3As formation starts when metallic Cu is available for the reaction. The gap between the As_2S_3 decomposition and Cu_3As formation is caused by the reaction of Sb_2S_3 to liquid Sb_3O_3 (Fig. 5c). On the one hand, before metallic Cu is present Cu_3As is formed. On the other hand, the metallic Cu is oxidized before Cu_3As reacts.

The summary for the chemical reactions in Cu-As-Sb-S-containing ores is:

- As_2S_3 reacts to gaseous As_2 and As_4 , which evaporate during roasting.
- Sb_2S_3 reacts to liquid Sb_3O_3 , which will remain in the roasted ore.
- If metallic Cu is present, Cu_3As is immediately formed.
- After Cu_3As formation, metallic Cu is formed from Cu_2S .
- Metallic Cu reacts with O at first to Cu_2O .
- Finally, the Cu_3As is oxidized, and Cu_2O , CuO , and As_4O_6 are formed.

3.2 Example of Sb in a Slag Inclusion

A stray find slag from Prigglitz-Gasteil was investigated to describe its nature and to find out the process step where it comes from. From its appearance this slag shows a rough

mainly dark brown surface and some spots in a beige colour (Fig. 6a). This indicates that the sample is a mixture of quartz (beige) and slag (dark brown) from an earlier production step of copper smelting [34, 35]. This mixture occurs probably when molten slag flows out of a furnace or crucible and is mixed with sand because no reaction zone on the quartz surface is visible.

Metallographic investigations confirm that quartz grains are surrounded by slag (Fig. 6b). The quartz shows many cracks, which can be explained by a contact of cold quartz with molten slag (Fig. 6b,c). The slag microstructure shown in Fig. 6d reveals large fayalite (Fe_2SiO_4) dendrites which primarily crystallized. In the interdendritic areas, a glass phase is present, containing all elements which cannot crystallize with fayalite, e.g. Al, Ca [36]. Due to its complex composition, the glass phase is amorphous. As can be seen in the SEM-BSE image (Fig. 6d), there are many bright fine spots in the glass phase. Bright spots in BSE indicate the presence of massive atoms like Cu which are available metallic or as compounds. In the present case, the spots were not analyzed, but we can assume that they are not converted chalcopryrite or copper.

Additionally a spherical inclusion with 1 mm in diameter was observed in the slag containing various Cu compounds (Fig. 6e). The different levels of grey in the SEM-BSE image show that this inclusion is an intense mixture of different compounds and by EDX measurements the main elements Cu, Fe, S and O were observed (Fig. 6f). Surprisingly, small amounts of Sb were observed locally. To localize Sb in the microstructure an EDX mapping was executed (Fig. 7).

From the mapping of the particle shown in Fig. 6e,f we can summarize:

This particle is a partially roasted chalcopryrite ore because it contains S as well as O.

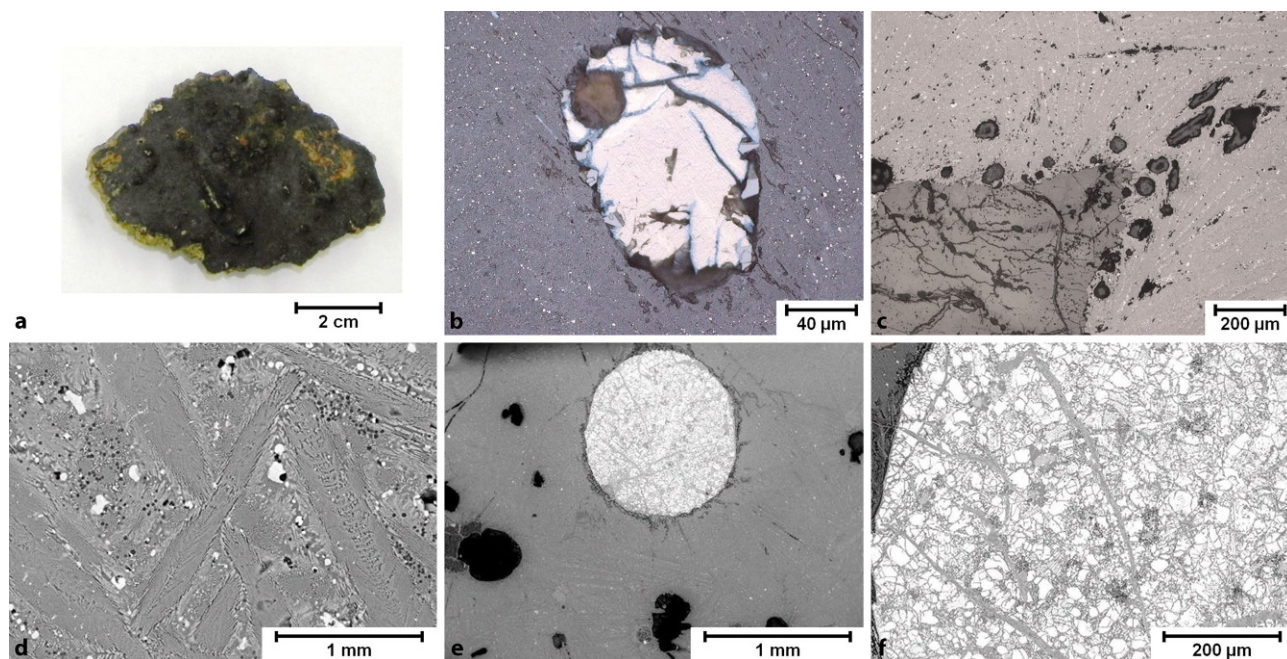


Fig. 6: Metallography of a slag. a photo of the original slag; b,c quartz inclusions in the slag (LOM); d slag microstructure in SEM-BSE, e,f inclusion of roasted ore in the slag (SEM-BSE)

The bright regions consist of chalcopyrite with a grain size smaller than $20\ \mu\text{m}$ surrounded by a grey phase containing O. In these grey areas, the chalcopyrite was already transformed into oxides. Large oxygen enriched cracks in the particle were observed additionally.

In oxide containing regions, mainly in the cracks, Sb is enriched. This confirms the thermodynamic calculations that Sb-S compounds are firstly roasted and that Sb forms Sb oxides, which remain in the slag.

3.3 Example of a Copper Ingot Produced from Fahlore

We were able to investigate an ancient copper ingot with 4 wt.% As, 0.4 wt.% Sb, and 2 wt.% S (Fig. 8a; [14, 15]). We assume that this ingot is the final product of copper smelting before it is used for casting artefacts.

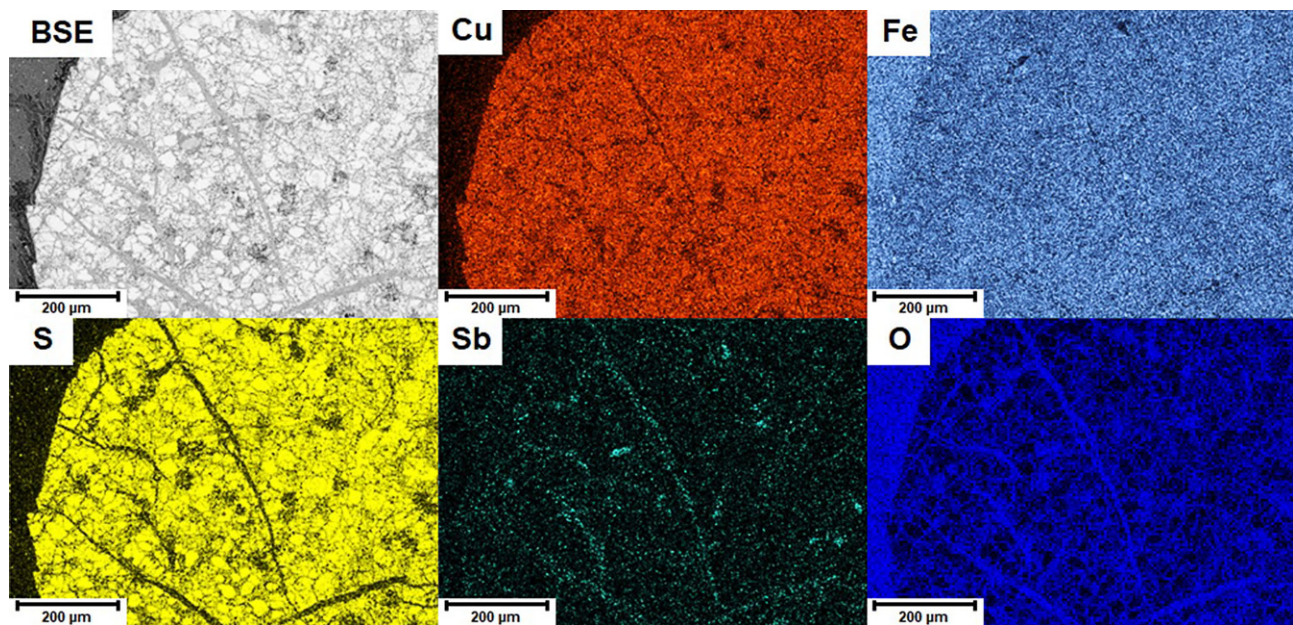


Fig. 7: SEM-EDX mapping of a slag inclusion consisting of roasted ore (see Fig. 5e,f)

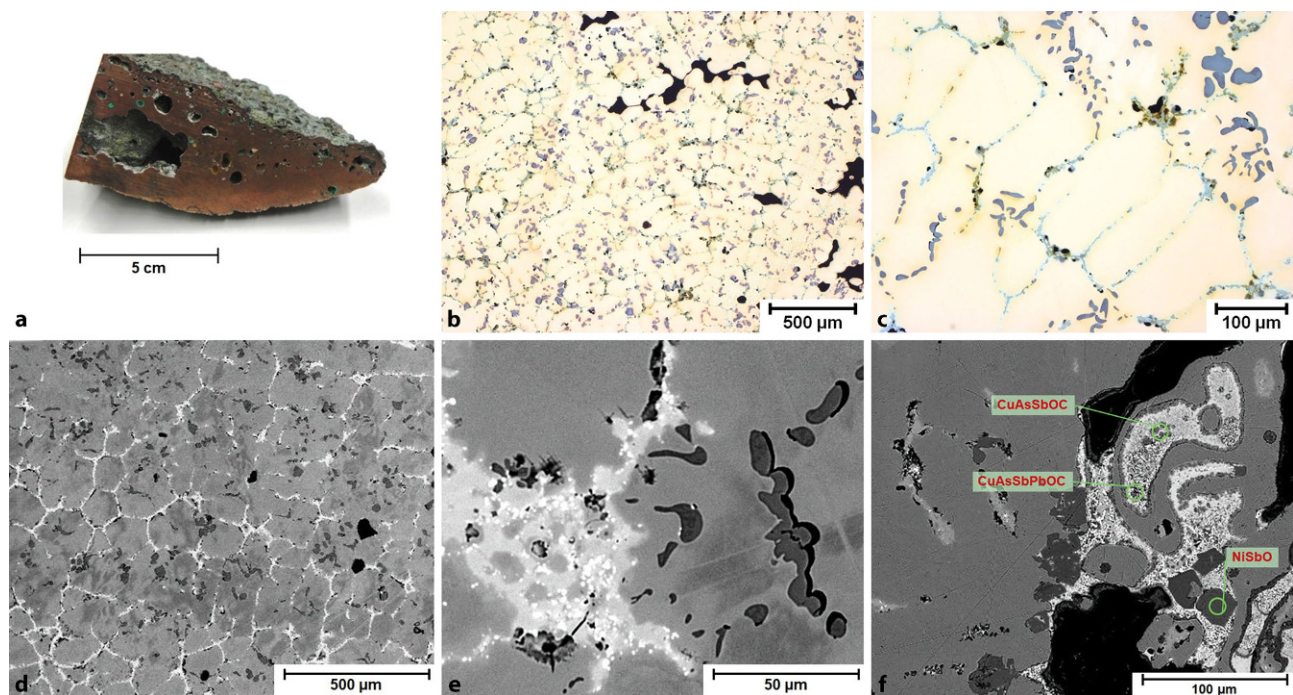


Fig. 8: Metallography of the Cu ingot. **a** photo of the original Cu ingot; **b,c** typical microstructures observed in the Cu ingot (LOM); **d** microstructure in SEM-BSE; **e** interdendritic area at higher magnification (SEM-BSE); **f** microstructures from regions with higher oxygen content (SEM-BSE)

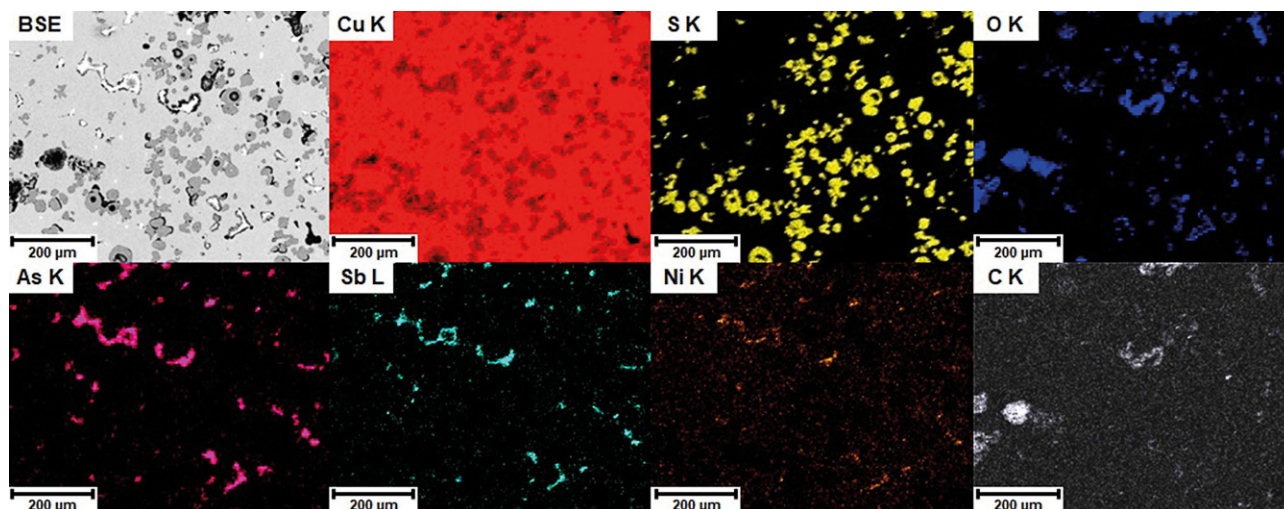


Fig. 9: SEM-EDX mapping of the Cu ingot microstructure

The setting of the ingot can be divided into the sections bulk-bottom and top-surface. The most important difference is the access of oxygen during ingot production.

At the bulk and bottom of the ingot, there is nearly no oxygen present and no oxides were observed consequently.

Almost impurity-free copper dendrites were firstly built during solidification of the ingot (Fig. 8b). The interdendritic areas are enriched with As, Sb, and S (Fig. 8c). In addition, some carbon was observed, which probably was introduced by stirring the alloy with a branch. In some regions, spherical Cu_2S or Cu_2As inclusions are detected. This indicates that during roasting some S and Sb remained in the ore and, during smelting in a charcoal heated shaft furnace, both elements cannot be eliminated and remain in the copper ingot (Fig. 8d).

On the top side of the ingot, oxygen access is easier resulting in the presence of oxides and small holes (Fig. 8e,f). Again, copper-rich dendrites had been formed surrounded by interdendritic areas containing the alloying elements (Fig. 8e). For detailed information about the element distribution, a SEM-EDX mapping was performed (Fig. 9). It can be seen that O, As, and Sb are enriched in some regions. Sulphur is concentrated in spherical spots, but there is no clear correlation with another element except Cu, suggesting the presence of Cu_2S . Less but similar As-containing particles were observed corresponding to the Cu_3As phase.

Moreover, the SEM-EDX mapping discloses a clear correlation between Sb, O, and Ni (Fig. 9). As it has been shown by the thermodynamic calculations, Sb can easily form a liquid oxide which remains in the Cu melt. When Ni is present, the Sb oxide reacts with Ni and Cu to $\text{Cu}_3\text{Ni}_2\text{SbO}_6$, which corresponds with the mineral delafossite [37]. In the thermodynamic calculations, this compound was not found because, on the one hand, Ni was not included to the calculations and, on the other hand, no thermodynamic data for delafossite are available.

4. Discussion of the Copper Metallurgy from Fahlores

4.1 Roasting

For sulphide roasting, heat and oxygen are necessary to start sulphur oxidation and consequently SO_2 formation. In ancient times the roasting was executed on a roasting bed by burning charcoal. The combustion heat of the charcoal heats up ore and air to roasting temperature. Anyway, an access of oxygen is necessary for the roasting reaction because the reaction of carbon with oxygen is preferred compared to the reaction oxygen with As, Sb, and S, respectively. To remove S, an open roasting bed is necessary and a closed system like a shaft furnace is useless. Nevertheless, the roasting reaction is exothermal and is a continuous process after initiation.

During roasting, at first the reaction of As_2S_3 to liquid As_2S_2 starts, followed by the formation of gaseous As_4O_6 at 800°C . At 1100°C the As_2S_3 directly reacts to gaseous As_2 and As_4 , respectively. We can conclude that at both temperatures As will evaporate from the roasted ore. This volatile As is contaminating the surrounding of the smelting site [9, 10].

If Sb is present in the fahlore, its reaction starts after the As_2S_3 reaction is finished. Sb_2S_3 reacts to liquid Sb_3O_3 , which remains in the roasted ore.

Cu_2S reaction with O starts after the full conversion of As_2S_3 and Sb_2S_3 , respectively. During this reaction step, Cu_2O will be formed intermediately, but, if the O ratio is low, the already formed Cu_2O can react with Cu_2S to metallic Cu. Depending on the starting grain size of the ore, unchanged material remains in the core of the roasted particles. Finally, the roasted ore may contain not only Cu_2O , Cu_2S , metallic Cu, but also As and Sb.

In practice, Fe and Si compounds are present additionally in the ore, but they were not considered for the thermodynamic calculations.

4.2 Smelting

The next production step is smelting of the roasted ore in a charcoal fired shaft furnace. As the thermodynamic calculations for roasting showed, there should be no reactions of As_2S_2 and Sb_2S_3 if C is present.

The starting composition of the roasted ore may contain Cu_2O , metallic Cu, Cu_2S , As_2S_3 , Sb_2O_3 , and silicates for slag formation. In principle the oxides may react with the sulphides forming metallic Cu and SO_2 . The As compounds should react with metallic Cu to Cu_3As . From a thermodynamic point of view, a Cu ingot should also contain Cu_2S and Cu_3As in addition to metallic Cu, which could be confirmed by the investigated Cu ingot [14, 15]. Due to the fact that metallic Cu is necessary to form Cu_3As , the amount of As in a Cu ingot depends on the remaining amount of As in the roasted ore. Another method to increase the As content in a Cu ingot is the co-smelting of Cu ores and As ores [13, 38].

Moreover, the fact that Cu metallurgy may run over several steps has to be considered, e.g. 1st roasting—smelting to mate—2nd roasting—smelting to black Cu—casting. If, during smelting to mate, metallic Cu is present, As can form Cu_3As , which will not be removed during the 2nd roasting process and is present in the final As bronze.

The role of Sb during smelting could not be explained by our thermodynamic calculations. It is not clear what is happening with Sb_2O_3 if metallic Cu and carbon are present. According to the Cu-Sb phase diagram, the intermetallic phases Cu_4Sb or Cu_6Sb can be formed [39]. In the investigated Cu ingot, Sb is often arranged together with As, Ni, O, and Cu. Only the mineral delafossite ($\text{Cu}_3\text{Ni}_2\text{SbO}_6$) could be identified but no other phases.

In slags from the smelting process, often sulphidic inclusions (chalcopyrite) are observed and it was shown that in such inclusions also Sb oxides are present, confirming the thermodynamic calculations that during roasting Sb_2O_3 is formed (Fig. 5 and 7).

4.3 Melting before Casting

By melting Cu for casting, there should be no evaporation of As and Sb. Cu_3As is a very stable phase which is already formed during smelting and its reaction starts after metallic Cu was completely oxidized to Cu_2O .

Sabatini [27] suggested that arsenic evaporation from a Cu-As melt is low because of intense arsenic-copper bonding. Differential thermal analyses (DTA) and thermal gravimetric analyses (TGA) by Mödlinger et al. [30] showed no decrease in the As concentration during melting, respectively no As evaporation.

However, in ancient bronze objects, a wide range of arsenic contents was observed. As described above, the As content in Cu depend on the reactions during roasting and smelting.

If Cu-As alloys are oxidized, the metallic Cu will form at first Cu_2O due to the stability of Cu_3As , resulting in an As enrichment in the Cu melt, respectively the final bronze.

The often described phenomenon of “arsenic loss” during ancient recycling of Cu seems to be a simple As decrease by attenuation because recycled Cu parts contain different amounts of As [29, 40].

5. Conclusion

Thermodynamic equilibrium calculations were performed to explain the reactions during copper smelting from fahlores. Additionally, material investigations of a slag from a copper smelting process and a copper ingot produced from fahlore were performed.

The main question relates to what happens with As and Sb during roasting of fahlore, smelting of copper and casting of copper and bronze, respectively.

During roasting, As can evaporate as As_4O_6 or As_2 and As_4 , respectively. Sb will form Sb_2O_3 and remains in the roasted ore.

During smelting in a shaft furnace, the amounts of As and Sb cannot be reduced due to the presence of carbon. All three elements can be observed in metallic Cu ingots. A smaller part of impurities can be included in the slag. Metallic As or As compounds still present in the roasted ore can react with metallic Cu to form Cu_3As . Available Cu_3As will not react during an optionally performed second roasting step. The reactions of Sb_2O_3 during smelting are not clear till now.

During bronze melting for casting, As will not evaporate. Sb_2O_3 remains mainly in the slag.

The As decreases during recycling seems to be an effect of attenuation.

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References

1. Tylecote, R.F.: A History of Metallurgy. The Metals Society, Mid County Press, London (1976)
2. Tylecote, R.F., Ghaznavi, H.A., Boydell, P.J.: Partitioning of trace elements between the ores, fluxes, slags and metal during the smelting of copper. *J. Archaeol. Sci.* **4**, 305–333 (1977)
3. Tylecote, R.F.: Summary of results of experimental work on early copper smelting. In: Oddy, W.A. (ed.) *Aspects of Early Metallurgy*, pp. 5–12. British Museum, London (1980)

4. Pernicka, E., Lutz, J., Stöllner, T.: Bronze Age Copper Produced at Mitterberg, Austria, and its Distribution. *Archaeologia Austriaca*, vol. 100. Österreichische Akademie der Wissenschaften, Wien, pp 19–55 (2016)
5. Haubner, R.: Die prähistorische Kupfermetallurgie – allgemeine Betrachtungen. *Berg Huettenmaenn. Monatsh.* **166**, 343–351 (2021)
6. Zwicker, U., Greiner, H., Hofmann, K.-H., Reithinger, M.: Smelting, refining, and alloying of copper and copper alloys in crucible furnaces during prehistoric up to Roman times. In: Craddock, P.T., Hughes, M.J. (eds.) *Furnaces and Smelting Technology in Antiquity*, pp. 103–115. British Museum, London (1985)
7. Rapp Jr., G.: Determining the origins of sulfide smelting. In: Hauptmann, Pernicka, Wagner (eds.) *Old World Archaeometallurgy*, pp. 107–110. Selbstverlag des Deutschen Bergbau-Museums, Bochum (1989)
8. Harrison, A.P., Cattani, I., Turfa, J.M.: Metallurgy, environmental pollution and the decline of Etruscan civilization. *Environ. Sci. Pollut. Res.* **17**, 165–180 (2010)
9. Costagliola, P., Benvenuti, M., Chiarantini, L., Bianchi, S., Benedetto, F., Paolieri, M., Rossato, L.: Impact of ancient metal smelting on arsenic pollution in the Pecora River Valley, Southern Tuscany, Italy. *Appl. Geochem.* **23**, 1241–1259 (2008)
10. Dallai, L.: Influence of ancient mining settlements on arsenic pollution in the southwest of Tuscany. In: Donati, A., Rossi, C., Brebbia, C.A. (eds.) *Brownfield Sites II*, pp. 183–189. (2004)
11. Lorenzen, W.: *Helgoland und das früheste Kupfer des Nordens*. Otterndorfer Verlagsdruckerei, Otterndorf (1965)
12. Rostoker, W., Dvorak, J.R.: Some experiments with co-smelting to copper alloys. *Archaeometallurgy* **5**, 5–20 (1991)
13. Lechtman, H., Klein, S.: The production of copper-arsenic alloys (arsenic bronze) by cosmelting: modern experiment, ancient practice. *J. Archaeol. Sci.* **26**, 497–526 (1999)
14. Ertl, F., Strobl, S., Haubner, R.: An ancient bronze ingot smelted from fahllore. *MSF* **891**, 613–617 (2017)
15. Haubner, R., Ertl, F., Strobl, S.: Examinations of a bronze ingot made of Fahlor. *Pract. Metallogr.* **54**, 107–117 (2017)
16. Miske, K.: Die Bedeutung Velem St. Veits als prähistorische Gussstätte mit Berücksichtigung der Antimon-Bronzefrage. *Arch. Anthropol.* **2**, 124–138 (1904)
17. Helm, O.: Chemische Analyse vorgeschichtlicher Bronzen aus Velem St. Veit in Ungarn. *Z. Ethnol.* **25**, 359–365 (1900)
18. Költő, L., Varga, K.M., McLaen, P.: Analysis of high antimony concentration finds with various methods XRF analysis os antimony bronzes. In: Jerem, E., Bíró, T.K., Rudner, E. (eds.) *Archaeometry*, 98. Proceedings of the 31st Symposium Budapest I–II, BAR, 1, Budapest, April 26–May 3 1998. pp. 405–408. (2002)
19. Tylecote, R.F.: *The Early History of Metallurgy London-New York* (1987)
20. Haubner, R., Strobl, S., Thurner, M., Herdits, H.: A copper ingot with high antimony content from Velem / Western Hungary. *Berg Huettenmaenn. Monatsh.* **165**, 453–460 (2020)
21. Reiter, V., Linke, R.: Ein Werkplatz mit Brucherzdepot der ausgehenden Bronzezeit aus Rannersdorf, Niederösterreich. *Fundber. Österreich* **55**, 144–182 (2016)
22. Bray, P.J., Pollard, A.M.: A new interpretative approach to the chemistry of copper-alloy objects: source, recycling and technology. *Antiquity* **86**, 853–867 (2012)
23. Pollard, A.M., Bray, P.J., Gosden, C.: Is there something missing in scientific provenance studies of prehistoric artefacts? *Antiquity* **88**, 625–631 (2014)
24. Pollard, A.M., Bray, P.J.: A new method for combining lead isotope and lead abundance data to characterise archaeological copper alloys. *Archaeometry* **57**, 996–1008 (2015)
25. Caley, E.R.: *Orichalcum and Related Ancient Alloys: Origin, Composition and Manufacture with Special Reference to the Coinage of the Roman Empire*. Numismatic Notes and Monographs, vol. 151. The American Numismatic Society, New York (1964)
26. Dungworth, D.B.: Caley's "zinc decline" reconsidered. *Numis. Chron.* **156**, 228–234 (1996)
27. Sabatini, B.: The Cu-As-Ni system: a chemical thermodynamic model for ancient recycling. *JOM* **67**(12), 2984–2992 (2015)
28. Mödlinger, M., Sabatini, B.: A Re-evaluation of inverse segregation in prehistoric Cu-As objects. *J. Archaeol. Sci.* **74**, 60–74 (2016)
29. Mödlinger, M., Cziegler, A., Macció, D., Schnideritsch, H., Sabatini, B.: Archaeological arsenical bronzes and equilibrium in the As-Cu system. *Metall. Mater. Trans. B* **49**, 2505–2513 (2018)
30. Mödlinger, M., Oro Calderon, R., Haubner, R.: Arsenic loss during metallurgical processing of arsenical bronze. *Archaeol. Anthropol. Sci.* **11**, 133–140 (2019)
31. Haubner, R., Strobl, S.: The copper-arsenic eutectic and the Cu₃As phase. *Defect Diffusion Forum* **405**, 19–25 (2020)
32. Noläng, B.: EQUICALC 1.21: Svensk EnergiData Agersta, Bälänge, Sweden. In: Proceedings of the Fifth European Conference on Chemical Vapour Deposition Uppsala, 1985. pp. 107–114. (1986)
33. Vander Voort, G.F.: *Metallography—Principles and Practice*, 3rd edn. ASM International (2004)
34. Haubner, R., Strobl, S., Klemm, S., Trebsche, P.: Prähistorische Kupfergewinnung im südöstlichen Niederösterreich – archäometallurgische Untersuchungen an alten und neuen Fundstücken. In: Lauerermann, E., Trebsche, P. (eds.) *Beiträge zum Tag der Niederösterreichischen Landesarchäologie 2015*. Katalog des Niederösterreichischen Landesmuseums N.F. 521, Asparn/Zaya, pp. 26–33. (2015)
35. Haubner, R., Strobl, S.: Slag investigations from Bronze Age copper smelting sites. *MSF* **891**, 608–612 (2017)
36. Haubner, R., Strobl, S., Klemm, S.: Investigations of a slag from copper smelting discovered at the Bronze Age site Prein VII/Cu in Lower Austria. In: Montero-Ruiz, I., Perea, A. (eds.) *Archaeometallurgy in Europe IV*. Bibliotheca Praehistorica Hispana, vol. 33, pp. 135–142. Editorial CSIC, Madrid (2017)
37. Roudebush, J.H., Andersen, N.H., Ramlau, R., Garlea, V.O., Toft-Petersen, R., Norby, P., Schneider, R., Hay, J.N., Cava, R.J.: Structure and magnetic properties of Cu₃Ni₂SbO₆ and Cu₃Co₂SbO₆ delafossites with honeycomb lattices. *Inorg. Chem.* **52**, 6083–6095 (2013)
38. Rehren, T., Boscher, L., Pernicka, E.: Large scale smelting of speiss and arsenical copper at Early Bronze Age Arisman, Iran. *J. Archaeol. Sci.* **39**, 1717–1727 (2012)
39. Massalski, T.B.: *Binary Alloy Phase Diagrams*. ASM International, Metals Park OH (1990)
40. Radivojević, M., Roberts, B.W., Pernicka, E., Stos-Gale, Z., Martínón-Torres, M., Rehren, T., Bray, P., Brandherm, D., Ling, J., Mei, J., Vandkilde, H., Kristiansen, K., Shennan, S.J., Broodbank, C.: The provenance, use, and circulation of metals in the European Bronze Age: the state of debate. *J. Archaeol. Res.* **27**, 131–185 (2019)

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