

Kinetics of iron–copper sulphides oxidation in relation to protohistoric copper smelting

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Abstract This article deals with one specific step of the copper extractive metallurgy process: the roasting of iron–copper sulphides. It aims at shedding light on an archaeological issue: the reconstruction of the copper extractive metallurgy processes during protohistory (IV^c–II^c millennium BC). Experimental simulations are performed at laboratory scale by modelizing the conditions of protohistoric furnaces. Kinetic of roasting is studied by thermogravimetry combined with the physico-chemical analysis of synthetic products. The influence of two parameters is studied: (i) the temperature (773, 973 and 1173 K) and (ii) the granularity of the roasted ores (1 mm and 100 μm). In each case, the chemical mechanism governing the oxidation of iron copper sulphide is proposed. Apart from one extreme case ($\varnothing = 1 \text{ mm}$; $T = 773 \text{ K}$), it is showed that kinetic is controlled by the transport of molecular oxygen (O_2) from the gas to the grain surface. Moreover, we prove that, in some cases where the diffusivity of gaseous oxygen is low, roasting can be accelerated by the presence of an oxide, which constitute an in-situ source of oxygen. Theses experiments support the hypothesis that such a technique could have allowed a roasting process where iron and sulfur were removed by the solid oxygen instead of the gaseous oxygen. These results allow to validate a one-step copper smelting process starting from sulphidic ores, and to identify the experimental parameters of this process.

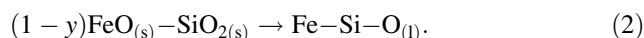
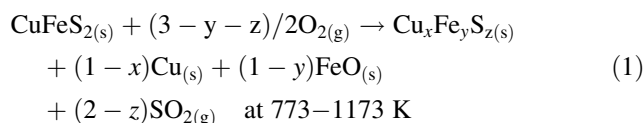
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Introduction

It is now well accepted [1] that copper–iron sulphides ores such as chalcopyrite (CuFeS_2) have been smelted in the Alps and South of France since the beginning of Metal ages (end of the 4th millennium BC). On the basis of Middle and Late Bronze Age smelting sites excavated in the Eastern Alps [2, 3], protohistoric copper sulphide smelting is traditionally described as a succession of at least two pyrometallurgical stages. First, the beneficiated ore is laid on top of an open charcoal burning bed, the so-called roasting bed, for air partial oxidation at the solid state (reaction 1). The process may last one day or more. Then, in order to separate iron and copper in two immiscible phases, the roasted ore is processed in charcoal-powered furnaces for smelting at the liquid state (reaction 2).



Because of the Boudouard equilibrium, the oxygen fugacity within the high temperature reactor is much too low for desulfurization. These are estimated to turn around 10^{-7} atm at the bottom of a 30 cm high protohistoric furnace [4]. Consequently, the roasting stage proves to be the only way to introduce enough oxygen in the system for further copper processing. However, no roasting structure has ever been found on any archaeological copper smelting

sites dated from Chalcolithic times/Early Bronze Age studied by the authors [5].

In order to solve this apparent paradox, we propose a model where roasting and smelting are carried out in the same reactor, with no interruption between the two stages [5]. First, sulphide grains are kept at solid state above the charcoal bed (ca. 1073 K) under the air flow, where they are partially roasted. Then, they sink at the bottom of the reactor where high temperatures (ca. 1473 K) ensure the co-smelting of sulphides and newly formed oxides. Since sulphide grains cannot be kept a long time at the solid state on top of the charcoal bed, the roasting kinetics appears to be a crucial parameter. In the last decades, kinetics of solid-state copper/iron sulphides have been widely investigated [6–15]. However, most studies refer to modern processes such as fluidized bed reactor, fine copper concentrate grains, preheated air jet. The associated working conditions are very different from the protohistoric conditions. In particular, in protohistoric conditions, the preliminary crushing and sieving may lead to grains size around 0.5 and 3 mm [5], whereas in modern process grains are kept under a critical grain size of 100 μm to avoid a blown out of the furnace. Based on thermogravimetric measurements, this study aims at investigating roasting kinetics of copper-iron sulphides under protohistoric-like working conditions (static air bed, millimetric size of grains). Two main parameters will be scanned, namely temperature and grain size. Also, the effect of tenorite (CuO) input on the kinetics of chalcocite (Cu_2S) oxidation will be investigated.

Experimentals

Methodology

This study is divided in two parts. The purpose of the first part is to elucidate the mechanisms involved in the chalcopyrite oxidation in air between 773 and 1173 K. The pathway of reactions is observed by combining thermogravimetry method in isothermal conditions and characterization of the intermediate products. In particular, correspondences between brutal changes on the TG curves and evolution of the microstructure of intermediate products help to propose hypotheses of a change of the rate limiting-step. These hypotheses are then confirmed by experimental measurement of the apparent diffusion coefficient (D_{app}). Finally, the evolution of the D_{app} with temperature helps to estimate apparent activation energy for each stage. In the second part, we focus on the kinetics of chalcocite (Cu_2S) oxidation at 973 K, by studying the possible effect of the introduction of CuO within the system, as a new reservoir of oxygen. The influence of CuO is

qualitatively observed by coupling thermogravimetric measurements and physico-chemical characterisation of intermediate products.

Thermogravimetry

Oxidation of chalcopyrite (CuFeS_2) in air

The overall kinetics was studied using an isothermal technique. Samples (ca. 10 mg) were heated in a Setaram TAG 24 thermobalance. Samples consisted of natural chalcopyrite, from Katanga mines (Congo). Powder X-Ray diffraction (XRD) investigation showed that the ore is made of more than 95 wt% chalcopyrite CuFeS_2 . The chalcopyrite was packed in a cylindrical alumina crucible ($\varnothing = 5 \text{ mm}$, $L = 1 \text{ cm}$), protected by a perforated alumina cover. Three temperatures (773, 973 and 1173 K) and two range of granularity ($800 \mu\text{m} < \varnothing < 1400 \mu\text{m}$ noted “1 mm”, $83 \mu\text{m} < \varnothing < 160 \mu\text{m}$ noted “100 μm ”) were tested. Isothermal conditions of oxidation were set by heating the grains up to the pre-determined temperature in an inert atmosphere (Argon; purity: 99.995%), with a heating rate of 20 K/min, and then blowing air ($p\text{O}_2 = 0.21 \text{ atm}$) that react with the solid. During the isotherms in air, the gas flow was 1 L/h. In some preliminary tests, the effect of the heat-up period was measured. Even though significant sulfur vaporization was observed (especially above 873 K [16]), no decomposition product was observed, meaning that the steady state had not been reached. At the beginning of the isotherm, the phase formed was CuFeS_{2-x} , x varying between 0.04 (at 773 K) and 0.50 (at 1173 K). All the experiments were carried out twice.

Oxidation of a mixture of chalcocite (Cu_2S) and tenorite (CuO) in air and inert atmosphere

The influence of the nature of the oxygen source on the kinetics of Cu_2S oxidation at 973 K was tested. Therefore, chalcocite (Alfa Aesar, 99.5% purity) was heated either in air alone, or in presence of tenorite CuO (Alpha Aesar, 99% purity) in an inert atmosphere (Argon), or in presence of tenorite CuO in air. A preliminary experimental determination has yield a local $p\text{O}_2$ ranging between 10^{-6} and 10^{-8} atm in Argon media under the operating conditions tested. The grain size of chalcocite and tenorite was $20 \mu\text{m} \pm 40$, as measured by a grain size analyser SILAS 1064. For the experiments with tenorite, the tenorite:chalcocite molar ratio was chosen in order to form SO_2 (O:S = 2). Samples were packed in a cylindrical alumina crucible ($\varnothing = 1 \text{ cm}$, $L = 3 \text{ cm}$) lided by a perforated alumina cover. Two different initial mass were tested,

namely 20 and 500 mg. The kinetics was studied using an isothermal thermogravimetric technique (973 K) in a Netzsch STA 409 thermobalance. All experiments were performed with a gaz flow of 1 L/h. The experiments at 773 K were carried out twice.

Analytical characterization

After crushing powders of grain size around 100 μm , XRD was carried out on intermediate products using a Brücker D5000 device in detector scan mode (Cobalt anticathode $\lambda = 1,79 \text{ \AA}$, $0,04 \text{ }^\circ\text{s}^{-1}$ step between 15° and 80° in an additive mode during $\sim 8 \text{ h}$). Observations of intermediate products sections as well as local elemental analysis were performed on polished sections by SEM-EDX with a Jeol JSM-80 and Philips XL30CP. (20 kV), both equipped with a Link Isis Oxford Instrument system. Moreover, elemental profiles in intermediate products cross sections were performed with help of an electronic microprobe, by using Cameca SX50 (10 kV, 40 nA), providing a spatial resolution of 5 μm and a maximal penetration depth of 2 μm .

Results and discussion

Oxidation of chalcopyrite (CuFeS_2) in air

General description

The variations of mass were converted into desulfurization evolution profile (Figs. 1, 2). The first derivative of these curves represents the local flux of sulfur across the surface of one grain of chalcopyrite, measured for stretch of curve considered as a straight line. A slight inflexion is visible on most curves shortly after the beginning of the air input (time 0). The sulfur lacunae within the chalcopyrite

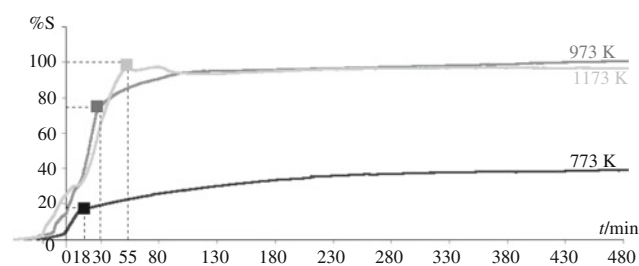


Fig. 1 Desulfurization evolution profile for the oxidation of 1-mm size chalcopyrite grains in air under isothermal conditions for three temperature (773, 973 and 1173 K). The grains are heating up to the pre-determinate temperature in Argon, with a heating rate of 20 K/min. The origin of the curve ($t = 0 \text{ min}$) corresponds to the moment when air is blowed. The desulfurization occurs in one or two stages, depending on the temperature. The *square* represents the end of Stage I

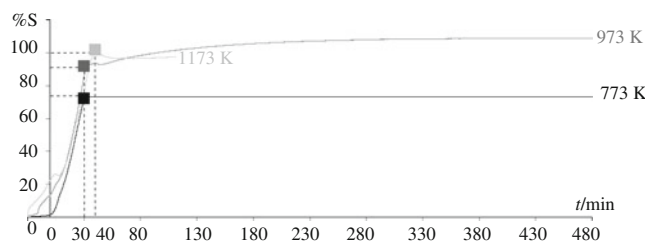


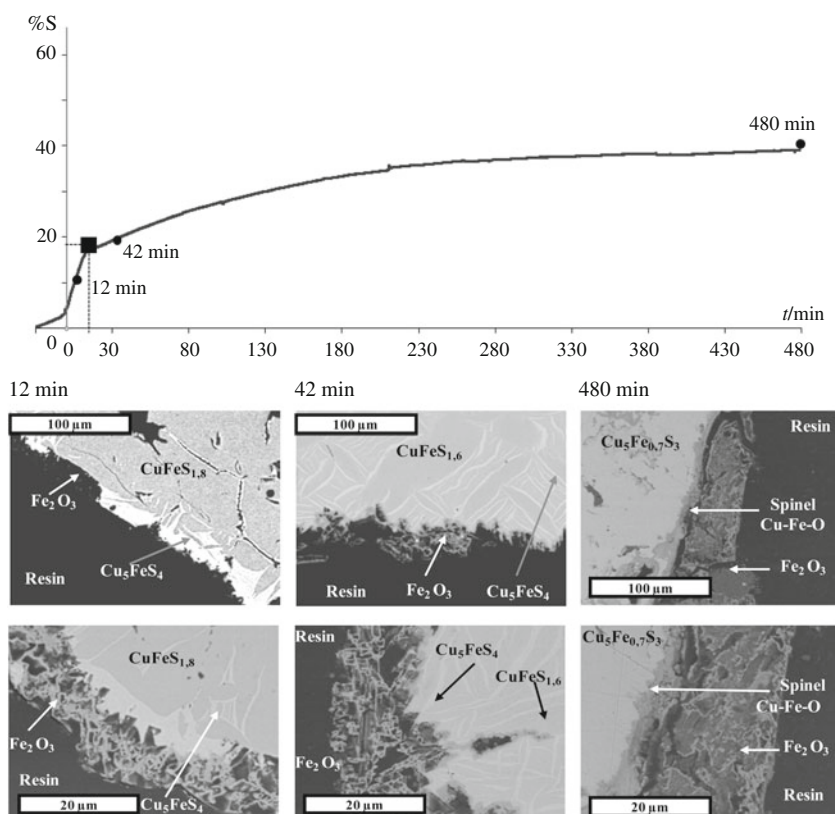
Fig. 2 Desulfurization evolution profile for the oxidation of 100- μm size chalcopyrite grains in air under isothermal conditions for three temperatures (773, 973 and 1173 K). The *square* represents the end of Stage I

generated by the pre-heating under inert gas are probably responsible for this. These lacunae may indeed induce a disequilibrium between iron and sulfur oxidation rate. Whatever the grain size, the desulfurization occurs in one or two stages, depending on the temperature. Stage I is common to all temperatures. During stage I, the local fluxes of sulfur strongly depend on the grain size (Table 1): fluxes are about six times lower for 100 μm grains (around $55 \text{ nmol cm}^{-2} \text{ s}^{-1}$) than for 1 mm grains (220 to $350 \text{ nmol cm}^{-2} \text{ s}^{-1}$). It also can be noted that kinetics depends on temperature for the 1 mm grains, but not for the 100 μm grains. Hence, for 1 mm grains at 500 $^\circ\text{C}$ (resp. 700 and 900 $^\circ\text{C}$), stage I lasts 18 min (resp. 30 and 55 min) and leads to a desulfurization rate of 18 wt% (resp. 75 and 100%). For 100 μm stage I lasts respectively 30 min (at 773 K and 973 K) and 40 min (at 1173 K), with a desulfurization rate of 100% except at 773 K because of metastable equilibrium (see hereafter). A second stage of desulfurization (Stage II) is only observed for 1 mm grains at 773 and 973 K. During this stage, the local fluxes of sulfur decrease drastically (Table 1) to around $10 \text{ nmol cm}^{-2} \text{ s}^{-1}$. Under the other operating conditions, one can consider at first approximation that the equilibrium has been reached directly at the end of stage I.

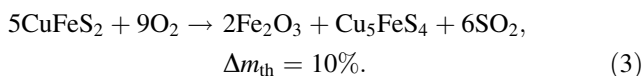
Whatever the grain size, the intermediate products before total oxidation or metastable equilibrium consist of an external layer of porous hematite $\alpha\text{-Fe}_2\text{O}_3$ and a sulphidic core made of a mixture of bornite Cu_5FeS_4 and desulfurized chalcopyrite CuFeS_{2-x} (Fig. 3). It can be noted that for the entire intermediate product investigated (12, 42 and 480 min), the thickness of the hematite layer ranges between 20 and 100 μm and does not seems to evolve markedly with time, whatever the temperature. SEM-EXD analysis indicates that iron preferentially oxidizes at the surface of the sample and that no copper is present in the outer oxide layers ($<1\%$ wt). A slight difference of core is observed at 773 K for the 100 μm grain, where main compound appears to be chalcocite (Cu_2S) with traces of chalcocyanite (CuSO_4). For most working

Table 1 Local fluxes of sulfur measured during the oxidation in air of (a) 1 mm grain size and (b) 100 μm grain size chalcopyrite at 773 K, 973 K and 1173 K

T/K	Stage I		Stage II	
	Time/min	Local flux of sulfur/nmol $\text{cm}^{-2} \text{s}^{-1}$	Time/min	Local flux of sulfur/nmol $\text{cm}^{-2} \text{s}^{-1}$
(a) $\varnothing = 1 \text{ mm}$				
773	0–18	220	18–480	11
973	0–30	260	30–480	10
1173	0–55	350	55–480	0
(b) $\varnothing = 100 \mu\text{m}$				
773	0–30	58	30–480	0
973	0–30	53	30–480	0
1173	0–40	55	40–480	0

Fig. 3 a Desulfurization evolution profile for the oxidation of 1-mm size chalcopyrite grains during 500 $^{\circ}\text{C}$ isotherm in air and **b** SEM micrographs (back scattered electron) of intermediate products cross sections after 12, 45 and 442 min of 773 K isotherm under air

conditions tested, the beginning of oxidation can be modeled by reaction (3):



For 1-mm size grains, the dramatic decrease of desulfurization rate after 18 min of 773 K isotherm coincides with the apparition of a continuous and compact bornite intermediate layer (Fig. 3).

Whatever the grain size, the total oxidation is reached at 973 and 1173 K. The final products consist of a tenorite (CuO) core bearing small amounts of spinelle ($(\text{Cu},\text{Fe})_3\text{O}_4$,

surrounded by a porous layer of hematite $\alpha\text{-Fe}_2\text{O}_3$. Small amounts of cuprite (Cu_2O) are also observed at 1173 K, thus explaining the slight differences of mass losses with the 973 K curves. The 773 K treatment leads, within the hematite layer, to metastable core products, the nature of which depends on the grain size. For 1 mm grains, the core consists of a homogeneous geerite-like (Cu_8S_5) sulphide core. Electronic microprobe profiling has revealed what seems to be a 10–20 μm layer of Cu-rich magnetite (2–6 Cu at%) near the hematite/sulphide interface. For the 100 μm grain, the core of the transformed grain consists mainly of two copper sulphates, namely chalcocyanite

(CuSO₄) and dolerophanite (Cu₂OSO₄). These metastable compounds do not evolve further until the end of the isothermal treatment (450 min).

Interpretation

Figure 4 features the proposed mechanism of chalcopyrite oxidation in air. Iron cations diffuse towards the surface of the sulphidic core where it is oxidized and form hematite Fe₂O₃. Simultaneously, sulfur anions react with oxygen to form gaseous SO₂, which is responsible for the formation of porosities within the layer of hematite. As a consequence, the external layer of hematite is not protective and one can assume that gaseous oxygen diffuses through this layer before it reacts at the interface sulphide/oxide. The cleavage and crumbling of the layer explain why its

thickness does not markedly increase during further oxidation. The depletion of chalcopyrite from sulfur and iron leads to the formation of the lamellar microstructure bornite (Cu₅FeS₄)/chalcopyrite (CuFeS₂) observed at the surface, which forms by demixtion during the cooling [17].

In the range of temperature studied (773–1173 K), the overall rate of reaction is controlled by mass transfer [18]. Two kinds of diffusion processes occur in series: (i) an external diffusion in gas medium, from the atmosphere to the gas–solid boundary layer and (ii) an internal diffusion in solid, through the sulphide (Fig. 4). At 773 and 973 K for the 1 mm grains, the dramatic decrease of desulfurization rate during the oxidation process (stage I/II) may be due to a change of rate-limiting step. At 973 K, this change occurs while 75% of sulfur has been removed. This testifies that reaction (3) is total, and this case will thus not be further discussed here. At 773 K, the dramatic decrease of desulfurization rate (18 min) occurs as soon as the intermediate bornite layer is formed. Hence, during stage I, the oxidation rate is controlled by the diffusion of gaseous oxygen through the external gas boundary layer (and the hematite layer) to the sulfur/oxide interface. During stage II, the oxidation rate is controlled by outward diffusion of iron cations and sulfur anions through the internal solid bornite layer. By comparing the local fluxes of sulfur, we can deduce that under all other working conditions, the desulfurization rate is controlled by gas diffusion through the external gas layer. In order to test this model, apparent diffusion coefficients (*D*_{app}) were estimated (Table 2). For the cases where the oxidation rate is controlled by the gas–gas diffusion, coefficients were estimated using the Fick’s first law (4):

$$J_i = -(D_{app})_i \cdot dC_i/dl \tag{4}$$

where *J*_{*i*} represents the diffusion flux of compound, and *dC_i/dl*, the gradient of concentration of *i*. The value of *dC_i/dl* was calculated according to the model of Ajersh and Toguri [19]. Stating in our case a thickness of laminar

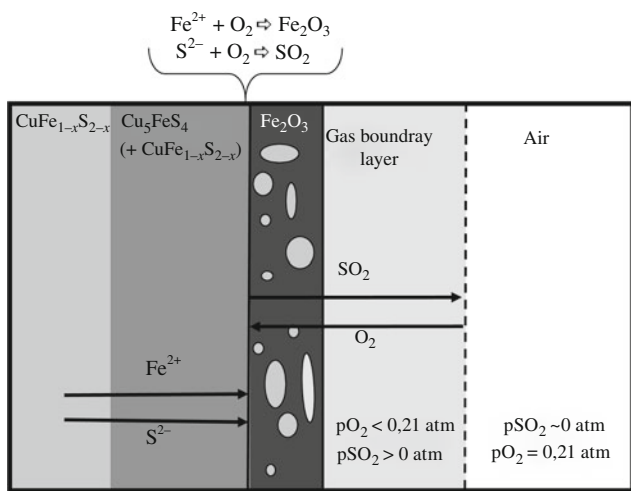


Fig. 4 Schematic representation of the mechanisms of chalcopyrite oxidation in air. Two steps occur in series: the diffusion of iron cations and sulfur anions towards the solid sulphidic core and the diffusion of O₂ and SO₂ gaz through the external gas boundary layer (including the porous hematite layer). The chemical reactions take place at sulfur/oxide interface

Table 2 Apparent diffusion coefficient and hypothesis of rate limiting step during the oxidation in air of (a) 1-mm size grains and (b) 100-µm size grains chalcopyrite at 773, 973 and 1173 K

<i>T</i> /°C	Stage I			Stage II		
	Time/min	Rate limiting step	<i>D</i> _{app} /m ² s ⁻¹	Time/min	Rate limiting step	<i>D</i> _{app} /m ² s ⁻¹
(a) Ø = 1 mm						
500	0–18	Gas diffusion	~ 10 ⁻²	18–480	Solid diffusion	~ 10 ⁻⁷
700	0–30	Gas diffusion	~ 10 ⁻²	30–480	Solid diffusion	~ 10 ⁻⁷
900	0–55	Gas diffusion	~ 10 ⁻²	–		
(b) Ø = 100 µm						
500	0–30	Gas diffusion	~ 10 ⁻²	30–480		
700	0–30	Gas diffusion	~ 10 ⁻²	30–480		
900	0–40	Gas diffusion	~ 10 ⁻²	10–480		

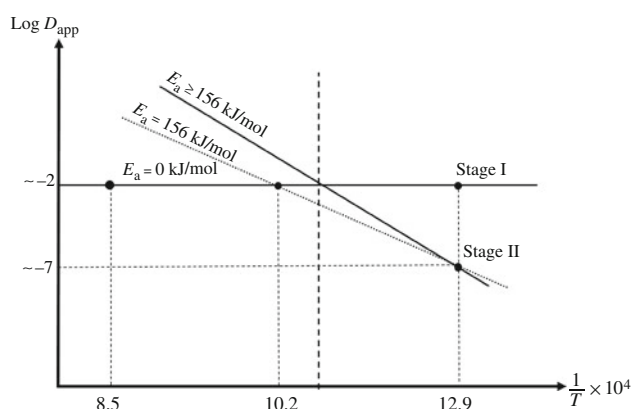


Fig. 5 Arrhenius diagram of the oxidation of 1-mm size chalcopyrite under air. Apparent activation energy has been approximated at 0 kJ/mol for the gaseous diffusion, and remains superior to 156 kJ/mol for the solid diffusion

gaseous layer equal to the height of the crucible yields to an apparent diffusion coefficient compatible with gaseous diffusion, namely ($10^{-2} \text{ m}^2 \text{ s}^{-1}$) [18] (Table 2). Note that at 773 K, the grain size has a remarkable influence on the oxidation rate. This can be explained by two phenomena. First, the length of diffusion path in solid decreases with the surface:volume ratio of the grains. Second, the mass transfer rate coefficient depends on the pore radii of the porous media, which decreases with granularity. For the specific case of diffusion through the solid sulphide (stage I of the 773 K/1 mm grain experiment), D_{app} was estimated by following the iso-concentrations lines (5):

$$\sqrt{(Dt)} = 1 \quad (5)$$

The thickness of the sulphide lamellar layer increases by 300 μm within 42 min. The apparent diffusion coefficient obtained ($10^{-7} \text{ m}^2 \text{ s}^{-1}$) lays within the order of magnitude of grain-boundary diffusivity [18] (Table 2). For the 1 mm-grains, the estimated D_{app} are plotted in an Arrhenius diagram (Fig. 5). The transition temperature towards a gaz diffusion-controlled mechanism is situated between 773 and 973 K. Below this transition, the desulfurization is limited by the diffusion of iron cations and sulfur anions through the solid sulphide, which is a thermally activated process. The apparent activation energy has been estimated to be superior to 156 kJ/mol. For the gas diffusion, the diffusion coefficients between 773 and 1173 K did not show any significant evolution, thus leading to an activation energy equal to 0 kJ/mol in this range of temperature.

Oxidation of a mixture of chalcocite (Cu_2S) and tenorite (CuO) in air and inert atmosphere

The influence of the nature of the oxygen source (air and/or tenorite) and the initial sample weight on the kinetics of

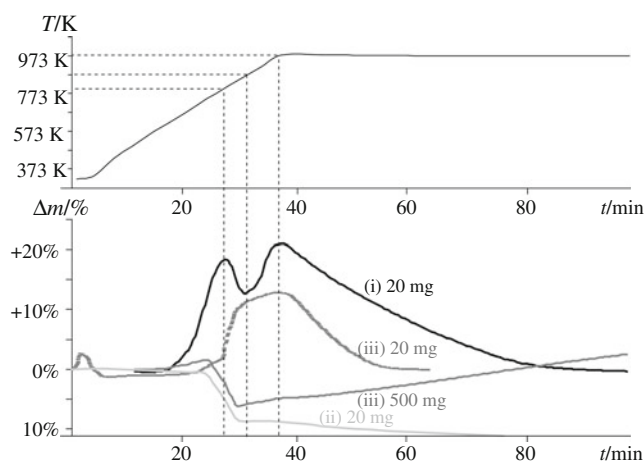
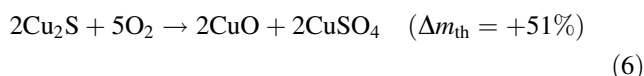


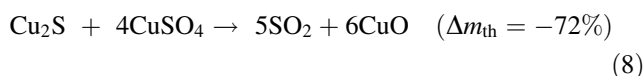
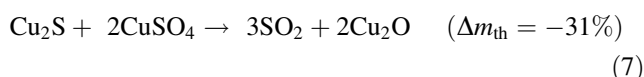
Fig. 6 Evolution of the temperature and mass variations during the oxidation of chalcocite (i) in air alone (at 20 mg), (ii) in presence of tenorite in Argon (20 mg) and (iii) in presence of tenorite in air (at 20 mg and 500 mg)

Cu_2S oxidation at 973 K is reported on Fig. 6. Two main different behaviours may be observed.

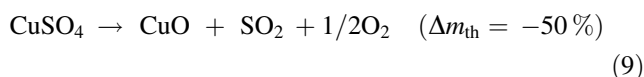
On one hand, oxidation of chalcocite in air (curve i) leads to a mass increase during heating and a mass decrease during the 973 K isotherm. Mass increase under 973 K is due to sulphatation (reaction 6), as predicted by thermodynamics [20, 21].



The marked dip between 773 and 973 K may be interpreted as a double decomposition between residual chalcocite and the neo-formed sulphate along the reactions 7 and 8:



At 973 K, the decomposition of the remaining sulphate (reaction 9) is responsible for the mass decrease.

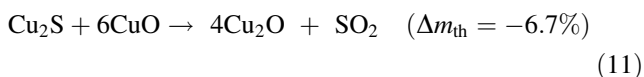


At the end of the isotherm, the final mass, which equals the initial mass, shows that the global reaction is a total oxidation of chalcocite into tenorite (reaction 10), as confirmed by XRD measurements.



On the other hand, in an inert atmosphere but with presence of CuO (curve ii), the thermogravimetric profile

shows only a brutal mass decrease starting at 743 K ($\Delta m = -7\%$), followed by a slight mass decrease until the end of the experiment. The brutal desulfurization at 743 K testifies for an oxidation of sulfur with solid oxygen, which can be modeled by reaction 11, assuming that no sulphatation takes place.



XRD patterns of intermediate products confirm the presence of cuprite Cu_2O immediately after the brutal decrease and suggest that the following slight mass decrease correspond to a slow reduction of cuprite (Cu_2O) into metallic copper along reaction 12:



The input of both sources of oxygen, namely tenorite and air yields a peculiar pattern (curve iii), which actually depends strongly on the initial sample mass. On one hand, the kinetics associated to the lower mass (20 mg) is similar to the kinetics of chalcocite oxidation in air. On the other hand, the oxidation of the heavier mixture (500 mg) behaves like the oxidation of chalcocite with tenorite in an inert atmosphere. Nevertheless, in both cases the presence of a solid source of oxygen increases markedly the global oxidation rate. Tenorite (CuO) is indeed a p-type semi-conductor. As such, it can chemisorb a considerable volume of oxygen on its surface and thus accelerate the reaction [22]. Moreover, the influence seems to be more important for the 500 mg sample than for 20 mg one. The main reason for this may be that the increase of initial weight which leads to a decrease of the gaseous oxygen concentration within the charge (because of the longer diffusion path within porosities). Note that for the 20 mg sample, the higher oxidation rate is a consequence of a slighter weight compensation during the double decomposition (Eqs. 7, 8), due to oxidative conditions as reported previously [23]. The slight weight increase at the end of the isotherm (from 27 to 90 min) may be interpreted as a slow oxidation of metallic copper in contact with air (which is more detectable with the heavier mixture).

Conclusions

By coupling thermogravimetric measurements and physico-chemical characterisation of intermediate products, this study enables to hypothesize the mechanisms that control the roasting of copper-iron sulphides under protohistoric-like working conditions. Kinetics of oxidation of chalcopyrite in air in protohistoric-like conditions at 773–1173 K is controlled by diffusion of dioxygen in laminar gaz layer. The lower the grain size, the more the solid sample behaves

as a porous medium thus impeding the diffusion of dioxygen. As a consequence, the effect of the decrease of the grain size is less than expected on the basis of a simple calculation of surface to volume ratio. For large grains (1 mm) and at low temperatures (773 and 973 K), this first rate-limiting stage is followed by a second stage before final stable or metastable equilibrium is reached. There, kinetics is controlled by the internal diffusion of iron cations and sulfur anions through the unreacted solid sulphides. Moreover, for the first time the effect of CuO on the oxidation of Cu_2S has been put into light. As a large reservoir of oxygen, CuO accelerates markedly the kinetics of oxidation.

The predominant role of dioxygen diffusion in gaz on the kinetics of oxidation of CuFeS_2 is particularly problematic for protohistoric copper smelting processes. Indeed, since the reactors are charcoal-powered, the atmosphere above the sulphides to be roasted is markedly rich in CO and poor in dioxygen, thus largely increasing the diffusion path. Hence, preliminary roasting experiments in charcoal-powered furnaces [1] have put into light rates of oxidation of CuFeS_2 which are several orders of magnitude lower than those obtained in laboratory in the present study. The temperature during the field experiments was maintained at 973 ± 100 K, which appeared to be an optimum since higher temperatures happened to agglomerate the grains and thus hinder the oxidation. Similarly, the decrease of grain size from 2 to 0.5 mm, though it significantly affected the rate of desulfurization, did not enable to overpass the simple decomposition of CuFeS_2 into Cu_2S . As a consequence, the only parameter that may be played with to promote sufficient chalcopyrite oxidation under protohistoric working conditions is the amount of initial CuO in the ore. Yet, such oxide is clearly absent from both the paragenesis of most ancient copper ore deposits studied by the authors [24] and from the associated archaeological assemblages. Iron-oxide ores are much more frequent: could they have constituted an oxygen reservoir as well?

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