

RESEARCH ARTICLE

Thermal and Spectroscopic Feature of the Cu_3AsS_4 Enargite Oxidation Up To 800°C . Implications in the Arsenic Evolution

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ABSTRACT:

The thermal oxidation of enargite (Cu_3AsS_4) from Chuquicamata (Chile), has been studied between RT and 800°C . Enargite samples were heated in air atmosphere and analyzed by means of several physicochemical techniques such as XRPD, SEM-EDS, FTIR, XPS and chemical analysis. A surface digenite formation was observed in a first step. The XPS technique was particularly useful to correlate the copper oxidation with the As-O-Cu interaction, responsible for the continuous and slow As evolution up to temperatures higher than 600°C . These results must be considered of interest to reduce the negative environmental impact of the technological copper production from valuable Cu-ores where enargite is present.

KEYWORDS: Enargite, oxidation, As-O-Cu interaction, arsenic evolution.

1. INTRODUCTION:

Arsenic is a trace element with an earth's crust abundance of 5 mg/Kg, which can be considered one of the most dangerous inorganic pollutants¹. Transition metal arsenic sulphides, particularly arsenopyrite (FeAsS) and enargite (Cu_3AsS_4) are the most common As-mineral sources. These sulphides are usually present in the valuable Cu-ores. So, the copper production by thermal oxidation is a potential risk to the environment².

The North-western of Argentina and the North of Chile are rich metal-sulphide geological regions and the main copper source. In these regions, enargite and arsenopyrite are the dominant arsenic minerals^{3,4}.

Arsenic is thermodynamically stable under oxidic conditions. However, As_2O_5 decomposes at about 300°C with oxygen and As_2O_3 evolution. The arsenopyrite thermal oxidation shows a mechanism governed by the sorption of As(V) on remains metal oxides. It is particularly retained as $\text{AsO}_4\text{Fe}(\text{s})$ up to 600°C ⁵. On the other hand, CuO nanoparticles are proved to be very effective adsorbent in the removal of arsenic species⁶.

Unlike to that observed for the arsenopyrite mineral species and other metal sulphides⁷, studies on thermal oxidation of enargite were scarce². No representative results related to the roasting process of Cu-As-S system are reported.

It is also known that chalcogenide minerals show a thin layer of oxidation products covering the surface of the minerals in natural conditions². In this sense, comparative surface behaviour between enargite fresh fracture and that exposed to air was analyzed by means of X-ray Photoelectron Spectroscopy (XPS)^{8,9,10}. Likewise, the thermal decomposition of enargite in inert atmosphere was studied and the intermediate formation of tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{12}$) – cuprite (Cu_2S) - orpiment (As_2S_3) was sequentially stated, following a topochemical reaction model¹¹.

The aim of the present work is the study of bulk and surface changes of natural enargite resulting from the exposure to oxidative conditions (air atmosphere) between room temperature (RT) and 800°C . The oxidation was analyzed by means of different physicochemical techniques such as "in situ" X-ray powder diffraction (XRPD), scanning electron microscopy (SEM-EDS (EDAX)), X-ray photoelectron spectroscopy (XPS) and infrared (FTIR) spectroscopies. The enargite samples, selected for the study,

proceed from the Chuquicamata (Chile), the world's greatest copper ore deposit³.

2. MATERIAL AND METHODS

Enargite mineral species, attributed to a strong supergene effect overimposed to the main hypogenic event in Chuquicamata deposit is present in the principal vein assemblage associated with pyrite-chalcopyrite-bornite and pyrite-bornite-digenite³. So, the studied specimens were selected by hand picked method.

Chemical analyses for the main Cu, S and As elements were performed by means of ICP-AES technique (ALS Chemex Argentina).

Samples with a particle size below 200 μm were thermally treated in air in a furnace with automatic control of temperature ($\pm 10^\circ\text{C}$) from room temperature to 800°C. Thermal steps of 50 and 100°C for 1 h each were carried out. The SEM-EDS (EDAX) surface studies were performed by a scanning electron microscope provided with dispersive X-ray energy EDS accessory (EDAX 9100).

X-ray powder diffraction (XRPD) patterns, $\text{CuK}\alpha$ (Ni-filtered) radiation, were recorded in the 2θ angular range from 10° to 60° (scanning speed, $1^\circ/\text{minute}$) using a PW-1729 diffractometer equipped with a high temperature camera (Antón PAAR [HTK-10]) for "in situ" treatments in controlled atmosphere of air from RT to 800°C.

FTIR spectra were recorded with an Equinox 55 Bruker spectrophotometer in the frequency range 4000 cm^{-1} - 400 cm^{-1} .

XPS spectra were recorded on a Leybold-Heraeus LHS10 spectrometer in FAT mode (50 eV) using $\text{Al K}\alpha$ radiation (1486.6 eV; 12 kV, 20 mA). The pressure inside the analysis chamber was lower than 10^{-9} Torr. The following regions were acquired by a computer in a sequential manner: Cu 2p, O 1s, C 1s, S 2p and As 3d. Binding Energy (BE) values were referenced to C1s at 285.0 eV. Data analysis included smoothing, X-ray satellite removal, background subtraction and curve fitting. Decomposition of the spectral shape by curve fitting was performed with fixed spectroscopic parameters, the position, the intensity and FWHMH were optimized by the computer. Surface composition was obtained from the peak area ratios, using the sensitivity factor values proposed by Wagner et al (1979)¹².

3. RESULTS AND DISCUSSION:

Enargite (Cu_3AsS_4) can be structurally described as a hcp superstructure ZnS wurtzite-type where the Zn atoms are replaced by Cu ($\frac{3}{4}$) and As ($\frac{1}{4}$). This factor leads to an orthorhombic lattice¹³, with $a_e = \sqrt{3}a_w$; $b_e = 2 a_w$ and $c_e = c_w$ lattice constant ratios (w= wurtzite and e= enargite respectively). Enargite is a high temperature modification of Cu_3AsS_4 and the inversion to luzonite polytype occurs

below 300 °C, although both phases can coexist² between 215 and 315°C.

Bulk and surface chemical compositions of samples were obtained by ICP-AES and EDS-EDAX respectively (Table 1), where theoretical Cu, As and S stoichiometric values were included for comparison.

Table 1: Bulk and surface chemical composition of enargite specimens

	Cu (% w/w)	S (% w/w)	As (% w/w)
ICP-AES	48.50	32.54	18.96
EDS (EDAX) *	49.28	33.66	17.06
Theoretical data	48.40	32.56	19.04

• Value average of 10 EDS-measurements.

Occasionally, oxygen and silicon were observed as trace elements. Figure 1 shows the typical SEM morphology of enargite. In some specimens, it was also possible to observe a weathering effect through eventual thin layers of small green crystals as it can be observed in Figure 2.

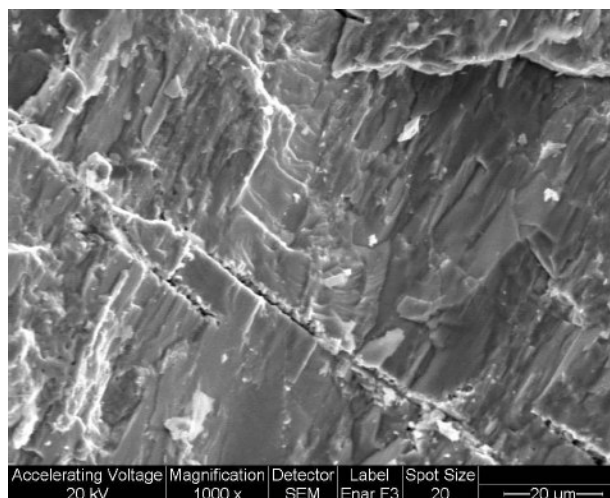


Figure 1: SEM of enargite, x 1000, scale bar 20 μm

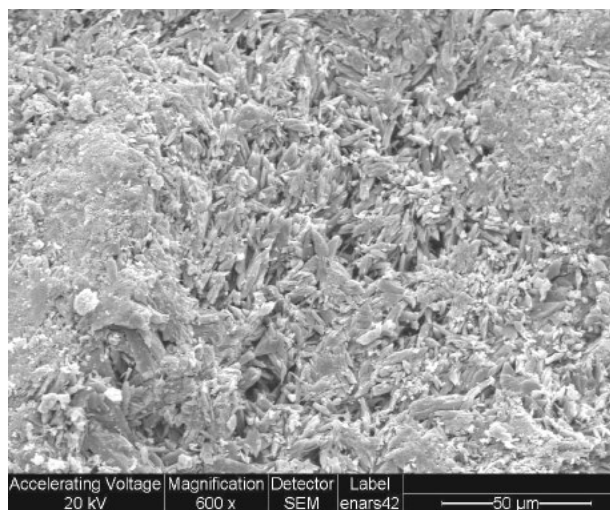


Figure 2: SEM of green surface alteration product, x 600, scale bar 50 μm

Cu- and S-EDS surface values were higher than the bulk results, suggesting the presence of a thin layer of Cu-S species on the surface, although it is difficult to assign the adequate formulation of the phase. Binary copper sulphides such as covellite, CuS, and calcosite, Cu₂S, usually appear as Cu_{2-x}S intermediate oxidation states. Metastable and non stoichiometric phases, such as digenite Cu_{1.80}S, Cu_{1.96}S djurleite are observed¹⁴ in the range RT- 500 °C.

Digenite phase, presenting about 9/10 of copper atoms in distorted tetrahedral coordination, can also be described as a wurtzite related structure. The presence of copper and sulphur in “quasi” trigonal and octahedral coordination can be associated to a very high copper mobility in the anionic arrangement. On the other hand, there is a structural ratio between CuS and Cu₂S lattices, which also allows the presence of Cu₂S micro-domains in a CuS matrix¹⁴.

Figure 3 show XRPD spectra collected on fresh and “in situ” treated samples. The treatments were performed in air atmosphere in the temperature range of RT – 800°C. The starting sample (curve a) mainly consists of enargite (PDF 85-1603) with typical signals in the 30° 2θ zone and a medium intensity peak at 2θ about 49°, in agreement with the results reported in the study of the Cu-As-S system⁷. Additional weak peaks can be clearly attributed to the most intense reflections of digenite phase (PDF 47-1748). The peaks at about 20.9° and 26.6° are attributed to quartz (PDF 87-2096). It is interesting to remark that digenite, in which Cu(II) and Cu(I) species coexist, is a binary phase commonly observed in mineral assemblages of Chuquicamata and other similar sub-volcanic copper sulphide deposits^{3,15}. This structural arrangement remains unchanged up to 400°C (curves b-e).

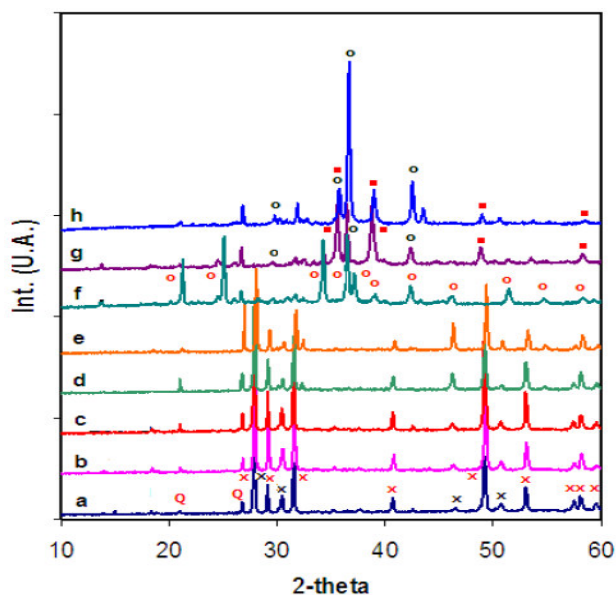


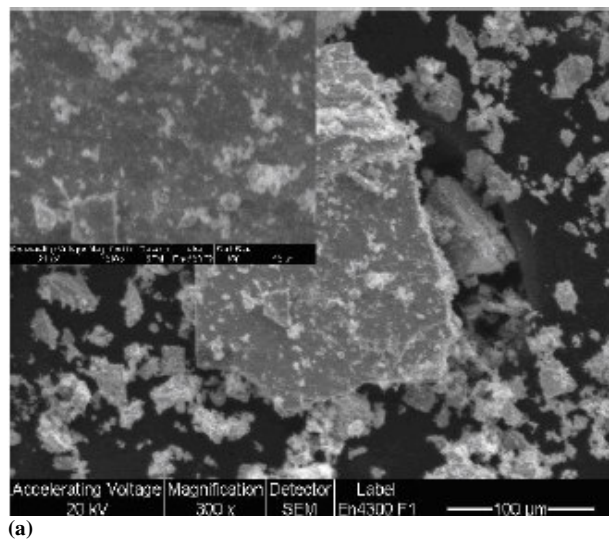
Figure 3: Comparative XRPD patterns of fresh and “in situ” thermally treated enargite sample. a)original, b) 110°C, c) 200°C, d) 300°C, e) 400°C, f) 500°C, g) 600°C, h) 800°C
x, enargite; x, digenite; Q, quartz; o, CuSO₄; ▪, tenorite ; o, cuprite

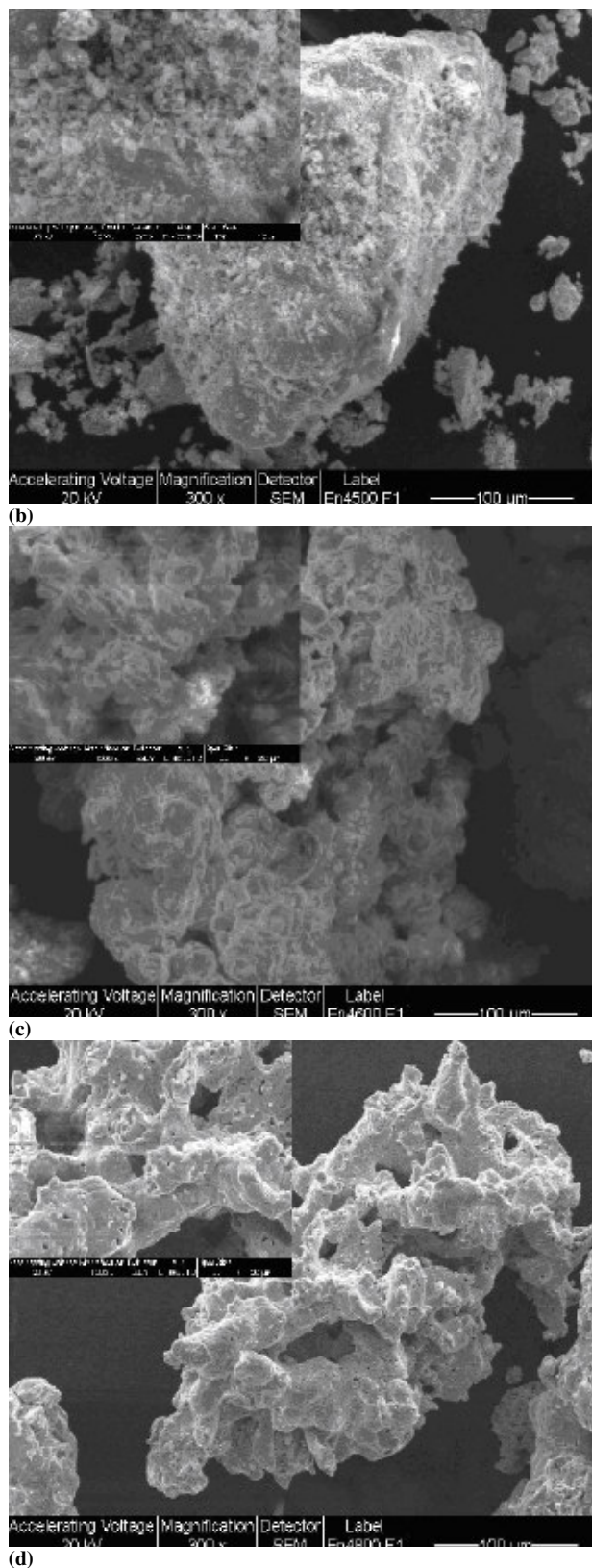
However, the enargite lattice collapses at about 500°C (curve f), yielding to the formation of CuSO₄ (PDF 72-0090) with their principal diffraction lines at 28.21° and 33.27°, although the presence of copper oxides cannot be disregarded. This behaviour is different from that observed when the thermal treatments were performed in an inert atmosphere or under very low oxygen pressure (below 1%) where enargite and tennantite are the predominant phases^{7,11,16,17} up to 600°C.

In an inert atmosphere, arsenic volatilizes as sulphide whereas a mixture of arsenic sulphide and oxide is formed at low oxygen pressure². According to Fig. 3, digenite grows at the expense of enargite, surely through a topochemical process favoured by the formation of a lacunary lattice⁷.

Comparative copper surface oxidation at low temperature suggests that copper sulphides are thermally more stable than the arsenic-copper sulphide⁷. The lower stability can be related to structural aspects of binary and ternary systems. On the other hand, thermodynamic data (formation free energy of oxides and sulphides) reveal that the oxides prevail on the respective sulphides^{7,17,18}. In this context, enargite exposed to an exogenous environment reveals that the surface is covered with a rich As- oxidized layer².

After treatment at 600°C, the XRPD pattern (Fig. 3, curve g) is dominated by the tenorite CuO species, as revealed by the appearance of the most intense signal at 2θ 38.5° (PDF 72- 0629). When increasing the treatment temperature up to 800°, it gave as result the incipient formation of Cu₂O cuprite with the most intense line at 36.44° of 2θ (PDF 78-2076), Fig. 3 curve h. This finding is in agreement with the stabilization of the Cu (I) at high temperature, although copper sulphate is still observed. In fact, it is well known that copper metal reacts with oxygen yielding first black CuO, which is converted to red Cu₂O for long reaction times at high temperature¹⁹. During the XRPD study no crystal phases containing arsenic were detected.





(d)
Figure 4: Micrographs of enargite at different temperatures x300 (Left upper corner x1000) a: 300°C, b: 500°C, c: 600°C, d: 800°C.

Surface changes in the sample morphology with thermal treatments were monitored also by SEM / EDX analysis. SEM micrographs at different magnification clearly revealed morphological changes above 500°C and suggested an incipient sintering at 800°C, Fig. 4.

The variations of chemical composition, obtained from EDS-EDAX analysis for the thermally treated samples, are compared with thermogravimetric data in RT-800°C, temperature range, Fig. 5.

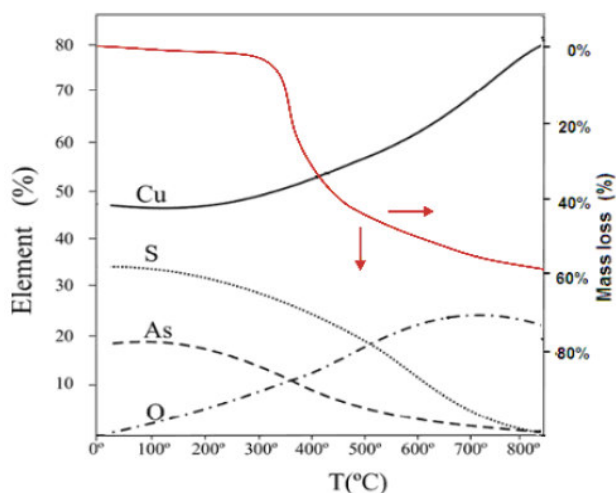


Figure 5: EDS data (% element) and mass loss (wt%) as a function of treatment temperature (°C)

The slight mass loss up to 300°C contrasts with the abrupt change observed from 400°C. The topochemical process observed in the decomposition in inert conditions can be also suggested in the oxidative process at low temperature (150-200°C) with the formation of an enargite lacunary phase as first step. The behaviour between 200 and 400°C can be attributed to various simultaneous processes including formation of digenite, copper oxidation, volatilization of covalent oxides, and incipient formation of copper sulphate (this last not detected yet by XRPD). The intense mass-loss starting from 400°C is associated with structural disorder related to non stoichiometric phases and high mobility of copper atoms, leading to the lattice collapse. In this context it is interesting to remark that the pure As_2O_5 decomposes at about 300°C. Hence, the thermal behaviour of these mineral species is different to that observed for As-O free oxides²⁰, suggesting the formation of As-O-Cu surface clusters.

The relative increase of copper from 600°C, evidenced by EDS, can be associated to the CuSO_4 decomposition to give copper oxides whereas the decrease in oxygen content at about 800°C can be attributed to the Cu(II)-Cu(I) reduction process.

FTIR spectroscopy allowed us to follow the thermal transformation of enargite by monitoring the vibrational modes of the sulphate group: anti-symmetric stretching (ν_3 ,

1105 cm^{-1}) and the bending mode (ν_4 , 611 cm^{-1}) for Td symmetry²¹. Figure 6, corresponding to FTIR spectrum of enargite after thermal treatment at 600°C in air for 2h, showed the presence of two bands centred at 1100 and 600 cm^{-1} typical of anhydrous copper sulphates. These bands, splitted by crystal field effect, appear at 1211, 1150, 1075 cm^{-1} and 702, 606, 585 cm^{-1} respectively²². A weak and not defined signal centred at 865 cm^{-1} can be associated to the arsenic oxide surface clusters. All these signals are practically inexistent above 800°C.

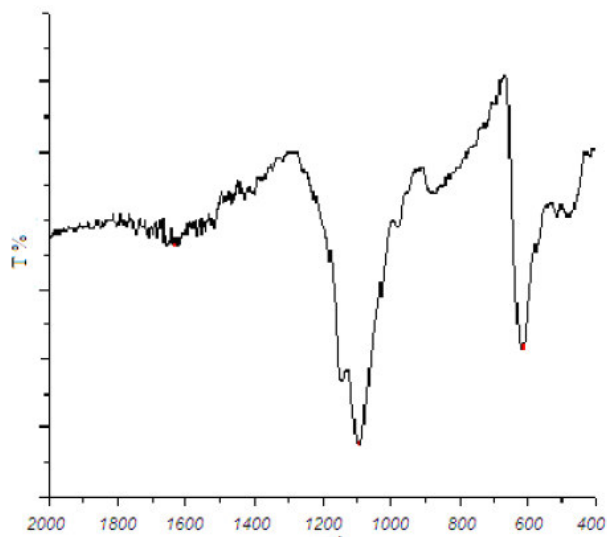


Figure 6: FTIR spectrum of enargite at 600°C

The FTIR spectrum of Figure 7 corresponds to the alteration product of natural enargite (observed in Fig. 2) and assigned to the $\text{Cu}_4(\text{OH})_6\text{SO}_4(\text{H}_2\text{O})$ copper oxidized alteration product XRD (PDF 43-0671). The intense bands at about 3500 cm^{-1} are attributed to OH vibrations of water molecules as well as hydroxyl groups. Likewise, additional OH librations are observed in the 800 cm^{-1} region^{22,23}.

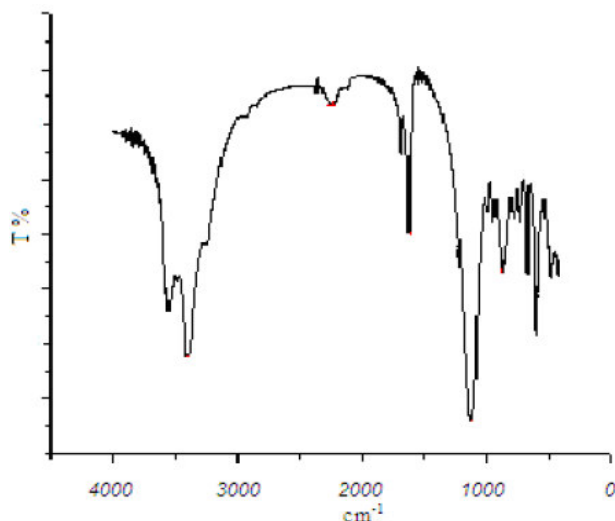


Figure 7: FTIR spectrum of enargite alteration product $\text{Cu}_4(\text{OH})_6\text{SO}_4(\text{H}_2\text{O})$, langite

The surface enargite properties, submitted to heat treatments in air, were also investigated using XPS. The evolution with temperature of the shape of the Cu 2p and As 3d regions is depicted in Fig. 8 and Fig.9, respectively. The binding energies, BE, for the various surface species, obtained from curve fitting, are summarized in Table 2.

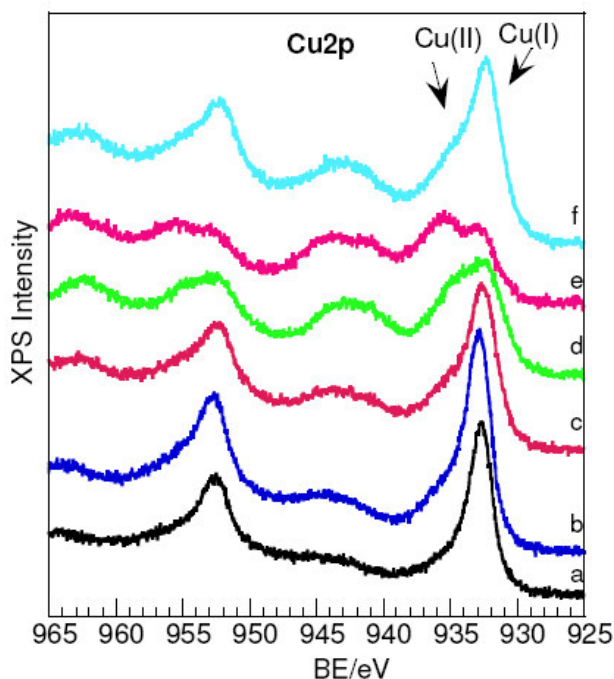


Figure 8: Cu 2p XPS spectra recorded from enargite samples submitted to heat treatments in air for 2 h: a, fresh sample; b, 200°C; c, 450°C; d, 500°C; e, 600°C; f, 800°C.

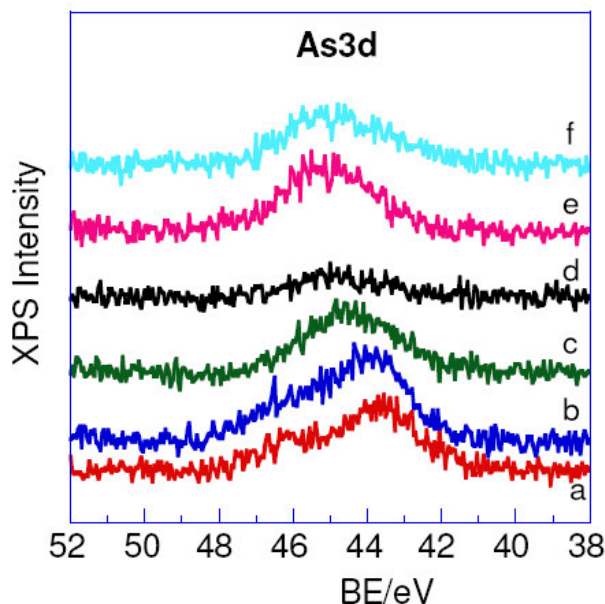


Figure 9: As 3d XPS spectra recorded from enargite samples submitted to heat treatments in air for 2 h: a, fresh sample; b, 200°C; c, 450°C; d, 500°C; e, 600°C; f, 800°C.

Table 2: XPS results. Oxygen, copper, sulphur and arsenic BE (e.V.)

Element line	RT	T= 200°C	T= 450°C	T= 500°C	T= 600°C	T= 800°C
O1s	531.2 (20%)	531.7 (55%)	530.8 (45%)	530.6 (30%)	530.5 (35%)	530.5 (60%)
	532.9 (80%)	533.1 (45%)	532.6 (65%)	532.2 (70%)	532.5 (65%)	532.3 (40%)
Cu2p _{3/2}	932.8 (80%)	932.8 (70%)	932.5 (65%)	932.4 (35%)	932.4 (25%)	932.3 (60%)
	934.1 (20%)	935.0 (30%)	935.1 (35%)	935.2 (65%)	935.6 (75%)	935.1 (40%)
S2p _{3/2}	162.2	162.1	162.5 (90%)	162.5 (45%)	168.3	168.2
			168.3 (10%)	168.4 (65%)		
As3d _{5/2}	43.8 (60%)	43.6 (80%)	43.5 (70%)	43.3 (48%)	44.2 (85%)	43.8 (80%)
	45.6 (40%)	45.8 (20%)	44.7 (30%)	45.1 (52%)	45.6 (25%)	45.4 (20%)

O1s signals, at the different heating steps, were broad and could be resolved by two components with binding energies in the range 530.5– 531.8 eV and 532.5– 533.3 eV. The component at lower BE is attributed to the presence of oxide species and sulphur-oxy species and, at higher BE, to chemisorbed water and/or OH groups²⁴. Both of the oxygen components could, however, be associated with oxidic species having metal-oxygen bond with different covalent character, as for Cu and As oxides²⁵.

The contribution at higher BE decreased after heating at 200°C, and then it remained practically constant.

The copper Cu2p region always exhibits a composite structure (Fig. 8). In the fresh sample (curve a) the low intensity shake-up features, about 10 eV away from the Cu2p_{3/2} and Cu2p_{1/2} spin-orbit splitting components, indicate that the surface species are mainly in the Cu(I) state. The Cu2p_{3/2} region was reproduced by two components at about 932.8 and at about 934.1 eV, assigned to Cu(I) and Cu(II) species. These findings suggest that the sulphide species (as for Cu₂S) are covered by a thin layer of CuO. Also, the binding energy of the S2p_{3/2} peak at 162.2 eV corresponds to that of sulphur in the sulphide chemical state. The As3d region (Fig. 9, curve a) clearly shows the presence of two components at 43.8 eV and at 45.6 eV, indicating the formation of As₂S₃ and As₂O₅. The observed shift is consistent with the concept given by Lattanzi² that the first reaction step in oxidizing environments is the creation of As-O bonds with protruding surface As atoms.

When heating at 200°C all surface species were left practically unchanged (Fig. 8, curve b), whereas changes were detected starting from 450°C. The Cu2p region became broad with the appearance of shake-up features, whose intensity increased while increasing treatment temperature up to 600°C, Figure 8 curves c-e. Curve fitting of the Cu2p_{3/2} region resulted in components at 932.5 and at 935.2 eV attributed to oxo sulphate species, Table II. Concomitantly, the S2p peak showed a new component at 168.3 eV due to sulphate formation. The two sulphur species (S2p_{3/2} peaks at 162.2 and 168.3 eV) merged in one component at 168.4 eV (sulphate species) in the temperature range 600°C - 800°C. Furthermore, after treatment at 800°C, the intensity decrease of both, the shake up feature associated with the Cu2p spectral shape (Fig 8, curve f) and the S2p signal suggest that sulphur has been lost from the surface.

The As3d region, for the same temperature interval, showed a more marked component due to sulphide species with respect to the oxide form (Fig. 9 and Table 2). However the As signal practically disappeared at 500°C, surely due to the abundant copper sulphate formation over the particle surface. Later, at 600°C As-signal reappeared by the sulphate decomposition.

Figure 10 shows graphically the results of thermal treatments by comparing the experimentally derived atomic ratios R_{exp} , with the values calculated by the stoichiometric formula of enargite, R_{st} . This shows more clearly the surface morphology variations.

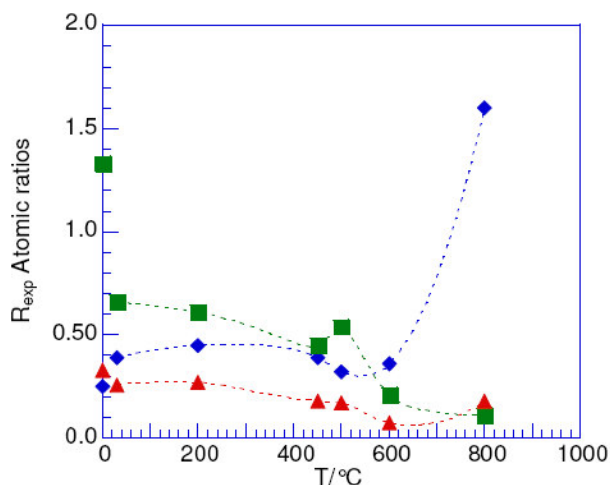


Figure 10: XPS atomic ratios, R_{exp} , obtained from integrated peak areas corrected for the appropriate sensitivity factors, as a function of the treatment temperature in air for 2 h. The atomic ratio values at T = 0

were calculated according to stoichiometric values. ■, nS/nCu; ◆, nAs/nS; ▲, nAs/nCu

In the starting sample, a surface copper enrichment with respect to As and S species is present. In addition, the arsenic enrichment increases with respect to sulphur points to the presence of oxide species onto the surface. The anomalous value for 500°C can be attributed to the Cu(I) sulphide -Cu(II) sulphate oxidation. By increasing the treatment temperature the lowering in the atomic ratio As/Cu could be indicative of agglomeration of As species. Yet, the decrease of the nS/nCu atomic ratio paralleled by the strong increase of the nAs/nS atomic ratios supports the agglomeration of sulphate species, the loss of sulphur

species during the oxidation process or both effects. However it is interesting to remark that the stability of As species in the residue is relatively higher than the S ones, suggesting a strong affinity between As-metal oxide.

4. CONCLUSIONS:

In the reported oxidative thermal study, the XRPD and chemical techniques revealed that digenite is the first product of the enargite surface alteration, favoured by a topotactic process and associated with the Cu(I)-Cu(II) incipient reaction. The XPS analysis was useful to understand the surface phenomena: the copper oxidation is correlated to the presence of surface As-O species, which reveals a higher thermal stability to that observed for free-As oxides. This can be explained by the As affinity towards metal oxides which is responsible for the permanence of the As surface clusters at temperatures close of the CuSO₄ decomposition, phase obtained in the course of the oxidative process. The copper-oxygen-arsenic interaction can be also related to the good performance of copper oxides in the As removal in polluted waters. The continuous and slow As evolution up to temperatures higher than 600°C must be considered to avoid the negative environmental impact of roasting process.

5. ACKNOWLEDGEMENTS:

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