Mineralogy and chemical compositions of ancient slags from Volubilis archaeological site and Awam ancient mine (Morocco)

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ABSTRACT
Six slags from Volubilis archaeological site roman period (II-III centuries AC) and Jabal Awam ancient mine have been examined for their mineral and chemical compositions by a multi-technique approach (Optical and metallographical microscopies, XRD, ICP-AES and XRF). Mineralogical analyses have emphasised the occurrence of iron oxi-hydroxide, quartz, pyroxene and calcite. The bulk chemical compositions of slags are similar and related to a refining of a homogeneous ore. The very low contents of metals plead for well mastered pyrometallurgical methods. The metal composition of the treated ore is close to a polymetallic ore deposit probably similar to that of Awam mine (Lead and Silver).

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1. Introduction
In ancient times, the mines of Morocco were exploited by the natives and their products were exported by the Phoenicians of Lixus and the Punics to the Mediterranean countries. The mines were located in the middle Atlas (Jabal Awam) and in the south, in the Anti-Atlas (Jabal Addana) (Rosenberger 1964). The research and exploitation of silver mines is explained partly because of the monetary needs of successive powers since the 9th to the 14th-15th centuries and beyond. In Morocco, the medieval texts mention four big silver mines: Jabal Awam, Zgounder, Todgha and Tamdoult. The analyses of slags have confirmed that medieval metallurgists knew very well the smelting processes. This was confirmed also by the occurrence of huge quantities of slags in many ancient mining areas (El Ajlaoui 2008). Also, not far from Rabat, in the archaeological site of Thamusida, ancient items dated from the first to the third century AD, have been investigated. Chemical analyses of these items show that the choice of alloy is heterogeneous, mainly depending on availability and costs of raw and/or scrap materials and on technological constraints (Gliozzo et al. 2011).

In Volubilis archaeological site, several findings such as pyro-metallurgical slags and metal artefacts have been studied also from stratigraphy, suggesting that this area was also dedicated to the processing and smelting of ores to obtain metal. A hemispherical fusion lens of bronze has been found with a diameter of 32 cm gives an idea of the size of the crucible used (Piccot-Boube 1960). Other lens in Iron and Lead stored in Volubilis give an idea of the industrial activity of the city (Piccot-Boube 1960). In Roman period, most metals were imported from Spain but this does not exclude, that neighbouring mines were explored. Indeed, the Jabal Awam mine is located in south of Volubilis, in the middle Atlas. It is a Lead, Zinc and Silver mine. The ancient remains walls of the Ighrem Aousser fortress as well as the slag deposits found in the south of the mine reflect the importance of the ancient mining activity in this area. It has been decided to carry out the whole study of these findings with the application of an archaeometrical procedure, consisting of the use of petrographical analysis, x-ray diffraction, ICP-AES and x-ray fluorescence to allow the interpretation of the type and technological level of the forgery herein settled (Rosenberger 1964).
2. Materials and methods

2.1. Stratigraphy and chronology of studied slags

2.2. Materials

In Volubilis, a set of four archaeometallurgical samples were selected for this study. Informations regarding the samples are provided in Table 1. Samples of the slag were selected from the closed stratigraphic units (SU) excavated in the south of the capitol (Figure 1). Thus, the slags from the stratigraphic units that were determined as antique (i.e. SU 00, SU 14, SU 46) and the layers contained finds (from the recent periods, i.e. Vol.03.5606) were sampled and compared.

| N° | Slags       | Stratigraphic Unit | Location  | age       | Description                                      |
|----|-------------|--------------------|-----------|-----------|--------------------------------------------------|
| Vol.03.4198 (V3) | 46          | Wsp. 1- Sp.2      | 1-2 II century | The slag is red-brown in the outside but the fracture surface shows a blackish colour |
| Vol.03.2186(V2)   | 00          | Wsp. 2- Sp.1      | –         |          | This slag shows a porous appearance with gray colour outside and blackish inside |
| Vol.02.4824 (V1)  | 14          | Wsp. 4            | III century | This slag is rusty-red coloured, also on the fracture surface (in the inside). |
| Vol.03.5606 (V4)  | 00          | Wsp. 3- Sp.2      | 150-250   |          | This slag has a rusty-red surface and inside shows black and brilliant spots. |
| Awam. A6          |             | Collected on surface | South of Ighrm Aousser | n.id | This slag is rusty-red |
| Awam. A7          |             | Collected on surface | South of Ighrm Aousser | n.id | This slag shows a black colour in surface and inside |
Additionally, other two slags were sampled in Jabal Awam mine close to the ancient city of Ighrem Aoussar (Figure 2) (Table 2).

2.3. Methods

The performed polished cross-sections were observed under light microscopy using Olympus equipped with camera. For mineralogical analysis, the slags were cleaned and crushed in agate mortar. The powder was analysed by x-ray diffraction using Shimadzu 6100, equipped with Cu-Kα. Data were collected at 40 KV with a resolution of 0.04 2Θ. Spectra were acquired in the range from 2 to 80 2Θ and stripped using X-pert High Score Plus software. The mineral indexation was done using ICDD PDF2 library. For bulk chemical analysis, the slag’s samples were analysed for major chemical components (SiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, P₂O₅, and TiO₂) after digestion with ICP-AES equipped with sequential spectrometer with a spectrum from 120 to 800 nm. Jabal Awam Slags were analysed by x-ray fluorescence.

Figure 1. (a) Map of the Volubilis site (Aalil et al. 2016, modified) and location of the excavated area; (b-c) plan and view of the excavated area.
3. Results and discussion

3.1. Petrography of slags

The investigated polish cross-sections of the slag V1 under light microscopy show the presence of quartz wrapped in a red Fe-rich matrix with some remnants of wood particles. The observations of these thin sections under metallographic microscope show the dominance of iron oxi-hydroxides like hematite and goethite and iron-sulfide (pyrite) (Figure 3(a–d)). The samples show the presence of quartz with calcite and some pyroxene minerals (Figure 3(e and f)). The occurrence of some little amount of pyrite shows that the smelted ore contain metallic sulphides like pyrite, galena etc. (Figure 3(h)). Calcite can be added as lime influx or originated from furnace linings. Vesicles are filled with secondary clay minerals due to weathering. The two studied slag samples from Awam mine show a very close mineralogy to those of Volubilis archaeological site.

3.2. X-ray diffraction patterns of Volubilis and Jabal Awam slags

The x-ray diffraction patterns of slags from Volubilis show very close spectra with the same mineralogical phases. They contain mainly calcite, quartz and pyroxene (hedenbergite) with iron oxi-hydroxides such as hematite, goethite, magnetite and wustite. The presence of olivine (forsterite) was not confirmed under microscopy (Figure 4). The occurrence of wustite in these slags testifies that the temperature of the furnace was over 1200°C. Conversely, goethite occurs as a weathering product of magnetite. The pyroxene such as hedenbergite was crystallised from the melt in the presence of Ca, Si and Fe. Calcite and quartz were originated from the ore or added as influx (Figure 5).

The Awam slags have similar x-ray diffraction patterns. The slag A6 (red colour) shows more quartz than iron ox-hydroxides while the sample A7 exhibits a large dominance of goethite, magnetite with some traces of muscovite. The quartz and muscovite minerals are probably inherited from ore deposit hosted in granite rock. So, in this case, the original ore correspond may be to gossans developed by weathering on ore deposit.

3.3. Bulk chemical of slags

The bulk chemical analysis of the studied slags shows very similar chemical compositions for all elements (Ag, Al, Cu, Fe, Pb, Sb, Sn and Zn) (Table 3). This can be explained by a homogeneous nature of the starting ore and a common method of processing and refining mastered on these ores (Tsaimou, Tsakiridis, and Oustadakis 2015). The high iron contents of these slags are mostly associated with different types of iron
Figure 3. Volubilis and Jabal Awam thin sections observed under microscope. (a-d: sample V1, e-f: sample V5, g: sample V3, h: sample V6, i: sample A6, j: sample A7).

Note: Ca: calcite, Cpx: pyroxene, G: goethite, H: hematite, Q: quartz, P: pyrite, W: wood traces.
The presence of little amounts of Pb, Zn, Sb and Sn confirms the polymetallic nature of the exploited ore deposit (Table 3).

Figure 4. X-ray powder diffraction patterns of Volubilis slags.
Note: C: calcite, Cpx: hedenbergite, F: forsterite, G: goethite, H: hematite, M: magnetite, Q: quartz, R: rutile, W: wustite

Figure 5. X-ray powder diffraction patterns of the Jabal Awam slags.
Note: G: goethite, M: magnetite, Mu: muscovite, Q: quartz

Table 3. Bulk-chemical composition of Volubilis (AES-ICP) and Awam slags (XRF).

| Volubilis | \(\text{Ag}_2\text{O}\) | \(\text{Al}_2\text{O}_3\) | \(\text{CuO}\) | \(\text{Fe}_2\text{O}_3\) | PbO | \(\text{Sb}_2\text{O}_3\) | \(\text{SnO}_2\) | ZnO |
|-----------|-----------------|-----------------|--------------|-----------------|-----|-----------------|--------------|-----|
| Vol.02.4824 (V1) | 0,01 | 0,30 | 0,01 | 98,32 | 0,01 | 0,01 | 1,33 | 0,02 |
| Vol.03.2186 (V2) | 0,01 | 0,51 | 0,01 | 97,77 | 0,01 | 0,00 | 1,67 | 0,02 |
| Vol.03.4198 (V3) | 0,01 | 0,14 | 0,01 | 98,38 | 0,02 | 0,00 | 1,43 | 0,01 |
| Vol.03.5606 (V4) | 0,01 | 0,78 | 0,01 | 98,24 | 0,02 | 0,01 | 0,92 | 0,01 |

| Awam     | \(\text{SiO}_2\) | \(\text{Al}_2\text{O}_3\) | \(\text{Fe}_2\text{O}_3\) | MgO  | CaO  | K_2O  | TiO_2 | MnO_2 | SO_3  | ZnO  | PbO  | P_2O_5 |
|-----------|-----------------|-----------------|--------------|------|------|-------|-------|-------|-------|------|------|--------|
| Awam. A6  | 52,5 | 7,76 | 27,1 | 0,58 | 0,11 | 1,22  | 0,71  | 0,94  | 0,63  | 0,82 | 0,49 |
| Awam. A7  | 8,63 | 2,94 | 66,3 | 0,49 | 0,26 | 0,36  | 0,06  | 6,79  | 0,10  | 0,59 | 0,17 | 0,49  |

The chemical compositions of two slags from Awam mine (A6 and A7) show higher iron and siliceous contents with low amount of Al and some traces of Mg, Ca and K, Zn and Pb which confirm the mineralogical composition of these slags obtained by x-ray diffraction. They were originated probably from the transformation of a gossan ore deposit.

4. Conclusion

The ancient city of Volubilis had known its apogee during the Roman period. Morocco is close to Europe...
and in this period, Romans import some of their needs in iron and metals from Iberian Peninsula (El Ajaoui 2008). Indeed, the proximity of this site to ancient mines like Jabal Awam in middle Atlas mountains makes this city an attractive mining centre during this period. The slags and the metal objects discovered testify this presence.

The Mineralogical analysis of Volubilis slags shows similar compositions with the presence of iron oxihydroxides matrix, calcite, pyroxene, (forsterite?) and quartz remnants. These minerals were found in low furnace slags (Mahé-Le Carlier et Ploquin 1999). The occurrence of the most iron minerals such as magnetite, hematite, goethite and wustite indicate an iron production (Kramar et al. 2015). The calcite and quartz may have different sources; they can be originated from ore deposit or be introduced as influx. The bulk chemical compositions of slags are similar and related to a refining of a homogeneous ore. The very low contents of metals plead for well mastered pyrometallurgical methods. The metal composition of the treated ore is close to a polymetallic ore deposit probably similar to that of Jabal Awam (Pb and Ag).

For comparison, the Awam mine slag’s have the same x-ray diffraction patterns, the sample A7 exhibits a high iron content compared to the sample A6. The presence of quartz and muscovite are related to a granite mineralogical heritage. All these data indicate that probably, that slags came from the transformation of gossan type ore deposit from Awam mining area.

From this study we can conclude that in Morocco, Volubilis city was considered as one of the most important metallurgical centre in roman period. The bronze items (Piccot-Boube 1960) and slags found suppose the presence of metal workshops despite the fact that until now most of geophysical surveys did not confirm the presence of buried furnaces structures. So, the extracted ores from the neighbouring mines in middle Atlas and Anti-Atlas or imported from Iberian Peninsula were probably refined in-situ (mining areas) or transported in Volubilis for treatment and coinage processes.

Though, this study has shed light on the relevancy of Volubilis archaeometallurgical activities, a high resolution geophysical exploration could perhaps bring additional insight to this pertinence.

Disclosure statement
No potential conflict of interest was reported by the authors.

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