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Geochemical study of medieval lead-silver slag - le Minier (Aveyron, France)

Céline Tomczyk, Mehmet Shah, Nicolas Minvielle Larousse

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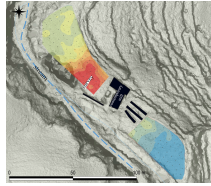
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Looking for a foundry

The Minier valley (Aveyron, commune of Viadud-Tam) is an area of silver and lead production in the south of France in the central Middle Ages (12th-15th century).

Although the mining areas have been identified and some mineralurgical workshops are being excavated, the foundries have not yet been located. However, we know that at least part of the metallurgical processing took place in the valley.



Implementation of a survey

An archaeological survey was carried out in the Rode mill area, where the presence of slag was reported during pedestrian surveys. The presence of a foundry was thus expected, close to an ore mill mentioned in this place in the 13th century. Prior to this, surface geochemical surveys were undertaken and the survey was located in the area with the highest lead concentrations (>5000 ppm).

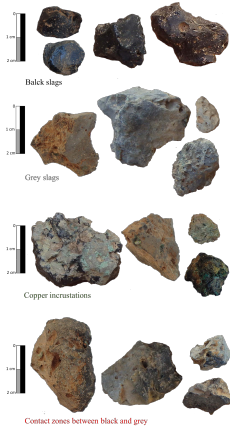
survey and map by Mehmet Shah



Numerous slags but in secondary positions

The survey revealed the presence of about 5,000 slags with a total weight of 25 kg as well as 5 leaded metal balls. One slag rich in charcoal residue was radiocarbon dated to the 14th century. Nevertheless, while the quantity of waste is substantial, we were unable to identify a foundry within the survey area, and the slag collected was all in a secondary position, dumped in small pits.

Two main types of slag



The color of the slag on the weathered surface provides us with 2 categories: black and grey. These two categories are distinguished by many factors.

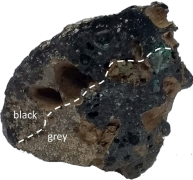
Black:

- Very glassy and brittle
- Average size 1,5cm
- Traces of edges and castings

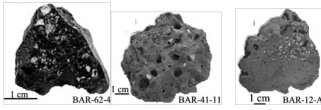
Grey:

- More porous and poorly glassy
- Average size 3cm
- Traces of edges

Copper incrustations are observed in both facies as well as small white nodules of lead oxides.



These facies are close to material uncovered in other medieval areas including nearby Mont Lozère (Mahé-Le Carlier *et al.*, 2010), as well as further afield in Tuscany (Chiarantini *et al.*, 2021) and Jihlava (Kapusta *et al.*, 2022).

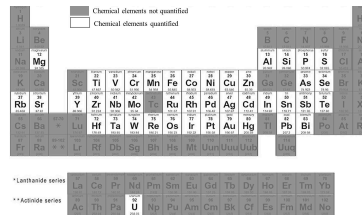


Main types of medieval slag from Mont Lozère (picture from Mahé-Le Carlier *et al.*, 2010)

Chemical differences?

The large quantity of slag uncovered makes it necessary to select only some of it for sampling in order to carry out detailed analyses. It is necessary to determine:

- Whether the identified types have different chemical compositions
- Whether there are groups of different chemical compositions within the same facies



Portable X-ray fluorescence analysis

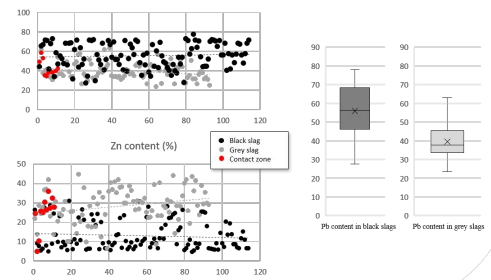
Portable X-ray fluorescence analysis was performed using a Tracer 5i. The alloy calibration of the device was used with an acquisition time of 45s. The speed of execution of this type of analysis allowed us to test more than 200 slags (114 black, 94 grey and 11 contact zones).

However, if the XRF gun allows the quantification of more than 40 chemical elements, it is not able to detect very light elements and notably the oxygen present in the slag. The grades obtained with the portable XRF are therefore only indicative and exploratory and the metal grades are largely overestimated.

Grey slags are richer in zinc and poorer in lead, iron and silicon than black slags.

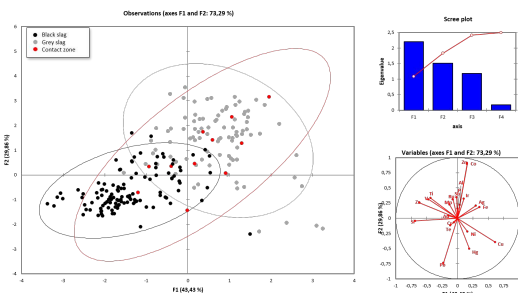
However, a simple binary diagram shows that grey and black slags do not separate clearly according to their composition. Moreover, half of the grey slags have lead contents comparable to the 25% of black slags with the lowest lead contents.

A multivariate statistical treatment does not allow to separate the slags in two distinct classes corresponding to the two types of slags.



Multivariate statistics

The lack of clear chemical distinction between grey and black slag highlighted by the binary graphs is observed when taking into account all the quantified chemical elements.

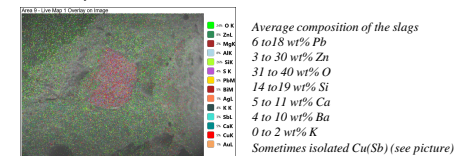


Therefore, grey and black slag form a continuous series. It is then possible to affirm that these slags come from the same metallurgical process and not from two distinct processes. The case of the slags corresponding to the grey and black contact (containing both facies on the same sample) is particularly striking, as they do not fall within the median values of two distinct groups, but are distributed within this continuous series.

An DA (Discriminant Factorial Analysis) makes it possible to assess the quality of the discrimination between black slag and grey slag and to determine whether these two groups are clearly differentiated by taking into account all the quantified elements. However, if the DA shows that indeed grey and black slags are differentiated by their Si, Pb and Zn content, it also demonstrates that the two categories of slags do not discriminate (their barycentres overlap).

Confirmation by SEM analysis

EDS (SEM) analysis of the selected samples showed that the slags contain 30 to 40% oxygen. Lead and zinc contents were therefore, as expected, greatly exaggerated by portable XRF. However, the major trends observed by pXRF were confirmed by SEM.

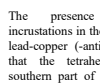


Hypotheses

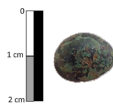
An imperfect sorting of ores?



The geochemical study of the veins showed the presence of silver-bearing galenas finely linked to sphalerites. The presence of zinc in the slag could be linked to a poor separation of the ores.



The presence of copper-antimony incrustations in the slag and the discovery of lead-copper (antimony) beads also testify that the tetrahedrites abundant in the southern part of the valley would also be melted with the galena.



A possible couppellation of the production

Pure lead metal beads were also discovered as well as a lead bullion bead, emphasizing that the process provides material that can then undergo a couppellation process.



However, the high levels of silver measured in the slag (although still below 2,000 ppm) suggest that some silver is lost during this metallurgical process.

Conclusion

If, at first sight, the macroscopic observations led us to separate the slags into two main categories (black glassy and grey slightly porous), the realization of analyses with the portable XRF on 220 slags randomly selected in these two categories allowed us to demonstrate that they constituted a continuous series and that they thus resulted from a single metallurgical process.

Thus, the use of pXRF allowed us within two days to select samples corresponding to the whole chemical variability of the slags, without relying on a single morphological criterion. EDS (SEM) analyses were then used to confirm the trends observed by pXRF. Although further studies and more precise analyses need to be carried out on this material, it is already possible to draw some initial conclusions about the smelted ores employed.

References quoted

Chiarantini, L., Beovanni, M., Buschi, G., Dattoli, L., Volpi, V., Manca, R., 2021. Medieval Pb (Cu-Ag) Smelting in the Colline Metallifere District (Tuscany, Italy): Slag Heterogeneity as a Tracer of Ore Provenance and Technological Process. Minerals 11, 97.
Kapusta, J., Dolnick, Z., Sracok, O., Maty, K., 2022. Origin of Historical Ba-Rich Slags Related to Pb-Ag Production from Jihlava Ore District (Czech Republic). Minerals 12, 985.
Mahé-Le Carlier, C., Piquin, A., Fleck, P., 2010. Apport de la géochimie et de la pétrologie à la connaissance de la métallurgie primaire du plomb-argentifère au Moyen Âge. ArcheoSciences. Revue d'archéologie 159-176.