# PHOSPHORUS AND COPPER ANALYSIS IN A RESCUE EXCAVATION (JAEN, SPAIN)

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Received: 5-3-2002
Accepted: 16-4-2002

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## ABSTRACT

This paper presents the procedure for chemical analysis in a rescue excavation. The site under study is the Chalcolithic settlement of Marroquies Bajos in Jaen, Spain. Phosphorus and copper (Cu) were the most suitable analyses to obtain supplementary information of this site in view of its archaeological structures and of the archaeological data available. The paper also improves on the procedure for Cu analysis.

## INTRODUCTION: some methodological remarks

The variety of activities held in archaeological structures during their active period leaves behind archaeological materials. Some of these are visible, others are not. The latter settle on the soil and the floors of archaeological sites, and can be identified by their chemical traces, the so-called chemical markers.

A principle of archaeological research with chemical analysis is that it proves most revealing when it takes into account the data yielded by research on other archaeological materials. Similarly, chemical markers are relevant not only when

they occur abundantly, but also when they are scarce. Any figure obtained may be significant not only in itself, but in relation to the other archaeological materials, and to the structure from which it is obtained. From this point of view, the soil hosts a huge amount of data in the form of chemical markers. The raw material of which floors and occupation levels are composed are to be viewed no longer as the physical environment from which materials are retrieved, but as relevant archaeological material too. Correct archaeological practice should be capable of retrieving and interpreting these data.

Another principle is that the analysis of chemical markers can not be done always in the same way. A number of highly influential factors may determine both the sampling and the interpretation of the results. Some of these factors include the type of excavation, the type of abandonment of the settlement, and the markers selected for analysis in each particular excavation (Sanchez and Canabate 1998).

For obvious reasons, extensive and microspatial excavations are the kind from which most can be expected in the field of the combined analysis of chemical and archaeological data. Other excavations, like rescue ones of the type considered here, may also give interesting results. Regarding the type of abandonment, planned abandonments of sites, in which few archaeological materials are left behind, are the context in which chemical analysis of floors and activity levels may prove most useful for the interpretation of the activities hosted by the site prior to abandonment. The decision of which markers are to be analysed must be based on three closely interrelated factors: the information given by each marker, the technical resources available, and the alteration processes that may have affect-ed the markers. Needless to say, it may be pointless to search for a potentially very specific, highly discriminating marker, if it can not be examined appropriately, or if it may have been altered substantially (Sanchez and Canabate 1998; Sanchez et al. 2001)

In principle, it is advisable to use wide-scope markers, liable to wide systematic analysis without very sophisticated facili-ties, and highly resistant to alteration. However, more complex analyses for spe-cific purposes can be made on subsets of samples, if the results or if each particular study needs.

## AIMS

Based on these assumptions, this paper first shows how use of chemical markers may provide additional information to purely archaeological data. The activity or activities held by archaeological structures can thus be identified and classified. In particular, the archaeological structures under study are part of an excavation in a fast growing urban area that precluded further exhaustive research, as a result of the pressure by building companies. Shortage of archaeological materials in the site indicates pre-planned abandon-ment, which makes chemical analysis par-ticularly important.

Correct analysis of chemical markers requires a certain methodology. This is the second point at issue in this paper. Reliable chemical markers like phospho-rus (P) and copper (Cu), together with rel-atively fast and accessible analysis tech-niques (UV-VIS spectrophotometry and atomic absorption spectrophotometry), can reveal important information on the most common activities held in a study area. The methodology for P analysis pre-sented here is the improved version described elsewhere (Sanchez et al. 1996).

Our experience with P analysis has also made it possible to propose a methodolo-gy for Cu analysis simpler, faster and more accurate (or at least as accurate) than the usual one.

Two structures from the total sampled were selected to illustrate the correct pro-cedure. These structures (62 and 69) were used for analysis of contents of P and Cu, and then for comparison of the results obtained not only in relation to each other, but in relation to the rest of the structures sampled too. Concerning the data obtained, and bearing in mind the nature of some archaeological remains excavated, it was deemed relevant to assess how important metallurgical work was in these structures, that is, to identify whether it was an exclusive activity or whether the space was used for other activities too.

## THE MARKERS: P and Cu

Use of P in archaeological research grew over the XXth century from a methodological point of view, as well as, in the field of its applications. It appears as a complementary (sometimes the only) tool in a large number of research projects, where it is intended as a source of infor-mation on two major areas: the activities held in archaeological sites (Manzanilla and Barba 1990; Middleton and Price 1996; Sanchez and Capabate 1999; Wells et al. 2000), and for research, identifica-tion and delimitation of a site prior to excavation (Eidt 1984; Lippi 1988; Buck et al. 1993; Weston 1995).

Systematic application of Cu in a site as a single marker capable of revealing information is rarer. Cu analysis is nor-mally used for archaeological studies together with other chemical elements appropriate for identification of groups of markers that, being unusually high, may be related to: recognisable features from a site (Linderhold and Lundberg 1994), varying degrees of human activities (Bintliff et al. 1992; Entwistle et al. 1998, 2000), or identification of settlements without physical traces at a surface level (Aston et al. 1998). Cu analysis has not always proved reliable: whereas in some cases it is clearly linked to human occupa-tion or to other more specific activities (Aston et al. 1998, Bintliff et al. 1992), in others it was too scarce to be used as an activity indicator (Entwistle et al. 1998, 2000).

## THE ARCHAEOLOGICAL SITE

Urban growth in Jaen since 1992 (Fig. 1) has extended mostly northwards, in par-ticular towards the area known as Marroquies Bajos. Extensive building brought to light a large archaeological set-tlement in the then outskirts of the city, and forced rescue excavations in the area.

The time span of the archaeological settlement starts in the Chalcolithic, goes through all the prehistorical, protohistori-cal, Roman, and Middle Ages, and reach-es present-day. In the Chalcolithic, the settlement spread over about 113 ha., and was surrounded at its highest by five con-centric ditches housing a large number of circular huts. Some of these were excavat-ed in the bedrock substrate and served a variety of functions (Hornos et al. 1998). The rescue excavation and, therefore, the structures sampled, are a part of this set-tlement. The surface of the excavation covers 1673.25 m², and is referred to as plot A6, the southernmost area of Block A of the Intervention Unit 23 (IU 23) (Fig. 2).

The excavation of this area in 1999 revealed 70 structures of the Chalcolithic. These were classified as:

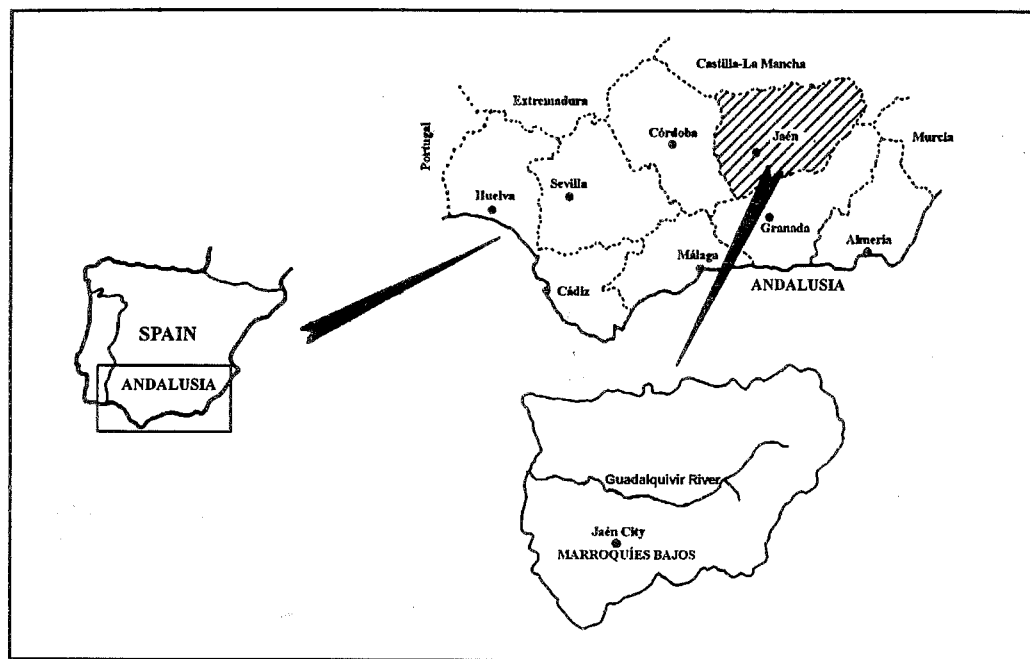- Circular structures with bell-shaped

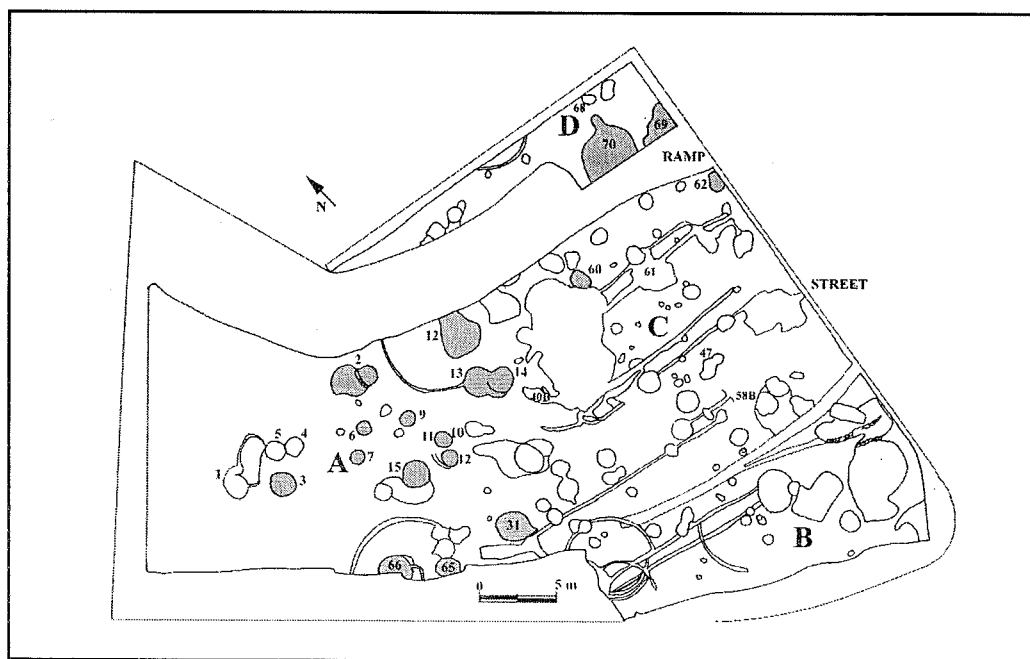Figure 1. Location of the Archaeological Area of Marroquies Bajos.



Figure 2. Ground plan of the excavation site. The structures sampled are shown in grey.

cross-cut built in the bedrock sustrate,

- Circular huts encircled by a furrow,
- Parallel furrows excavated in the bedrock substrate.

The sequence also has structures with wheel-made pottery and contemporary materials and structures (Puerta *et al.* 1999). As a result of the different occupation phases and of the bulldozing of the area, the Chalcolithic phase appeared considerably altered. It was therefore decided that the structures of the first type were the most appropriate for chemical analysis, as they still retained a large part of the stratigraphical sequence and were least affected.

## FIELD AND LAB METHODOLOGY

### Sampling

By the time these structures were known to us, some had already been excavated completely, whereas 18 of them had been uncovered only by half. This provided a stratigraphical section to sample. Although all 18 were sampled, only two of them, structures 62 and 69, were selected as the most appropriate to illustrate the method of analysis.

Samples of approximately 100 g. were taken in each stratigraphical profile. These columns are usually intended to sample all the significant sedimentary units; when they are thick, each unit is sampled at intervals of approximately 10 cms. The total number of samples was 221, and each of them was analysed twice. The average value of both measurements is shown in Table 1.

Four samples taken from the bedrock of several parts of the settlement were analysed too. Their results revealed the base levels of the markers analysed for this

settlement: 0.46 mg Cu/100g, and 61.25 mg P/100g.

### Phosphorus analysis

The analysis of the content of phosphorus in a soil sample follows this procedure: the sample must first be passed through a 0.25 mm sieve; 0.1 g of the sieved soil are then placed in a crucible which is kept for twelve hours in a muffle furnace at 450°C (Bethell and Mate 1988).

Once the sample has been cooled in a desiccator, it is dissolved in 5 ml of 2M hydrochloric acid (HCl). The sample is extracted for 15 minutes in an ultrasonic bath (Sanchez *et al.* 1996). After the extraction, it is centrifuged at 3,500 rpm. Finally, an aliquot of 0.1 ml is pipetted from the supernatant liquid into a 50 ml volumetric flask.

The colorimetric determination of the P extracted is made by adding 10 ml of a standard Murphy-Riley solution (Murphy and Riley 1962) to the volumetric flasks containing the 0.1 ml aliquot, and then filled to volume with distilled water. Phosphorus forms a blue-coloured complex with the molybdenum in the Murphy—Riley solution. After 20 minutes, this complex becomes stable and can be measured on a UV spectrophotometer (Perkin Elmer Lambda 19) at 882.5 nm in a quartz cuvette of a path length of 1 cm.

The intensity of the resulting colour is directly proportional to the amount of phosphorus contained in the sample; this amount can be determined through a previous calibration line. In this line, every one of the known concentrations of phosphorus is related to their absorbance measurement. This relationship is obtained from the addition of the standard Murphy—Riley solution to known concentrations of phosphorus, bearing in

mind that the Lambert—Beer Law holds for phosphorus concentrations in the range 0.1 to 0.8 ppm.

## Copper analysis

The soil sample is passed through a 0.25 mm sieve and ground in an agata mortar. 0.1 gr of the sample are then weighed in a muffle furnace at 500°C for 12 hours. After this, and once the sample has cooled, 8 ml of a solution of concentrate nitric and perchloric acids (5/3, v/v) are added (Sommer and Nelson 1972). The sample is next extracted for 15 minutes in an ultrasonic bath. After the extraction, the sample is centrifuged at 4000 rpm. Patterns with known concentrations of Cu (between 0.1 and 10 ppm, which is ideal lineal range for the Law Lambert-Beer) were prepared in identical conditions. Measurements were taken in a CBC Atomic Absorption Spectrophotometer as follows: l=324.7 nm, I=3mA, air-acetylene flame and 0.5 nm slit width (Rousselet 1968).

The revised analysis method of Cu focuses on the sample extraction: instead of extracting by digestion, as some authors describe (Thompson and Wood 1982), we did by ignition and ultrasonic extraction. This is similar to the process used for P, avoids a complex procedure for the archaeologist, and the concentrations of Cu obtained using our system are similar or higher than those obtained by digestion. Although in the comparative experiment lower values were obtained in one sample (no. 8) using ignition and extraction with ultrasounds, the difference is so small that it is archeologically insignificant (Table 1).

## Results

The results obtained are interesting especially in respect of structures 62 and 69. Lack of clear occupational levels in these structures as a result of planned abandonment, might indicate that the stratigraphical sequence consists only in fills. However, the concentrations of P and Cu found and the archaeological materials excavated show that both structures were used for specific activities. In fact, there were hints that these structures may have been used for metallurgical purposes: remains of crucibles, slag and Cu greenish-stained soil were found in them. The analysis of the whole sequence revealed that metallurgical work did not cover the occupation sequence of both structures evenly, and that it very likely co-existed with some other activity.

Structure no. 62 is bell-shaped, with a maximum diameter of 1.90 m, and lies in

TABLE 1: Digestion versus ignition/ultrasonic extraction. The results (mg Cu/100 g per sample) show the arithmetical mean obtained after analysing twice six samples of structure 62. Samples selected at random, plus one sample of slag.

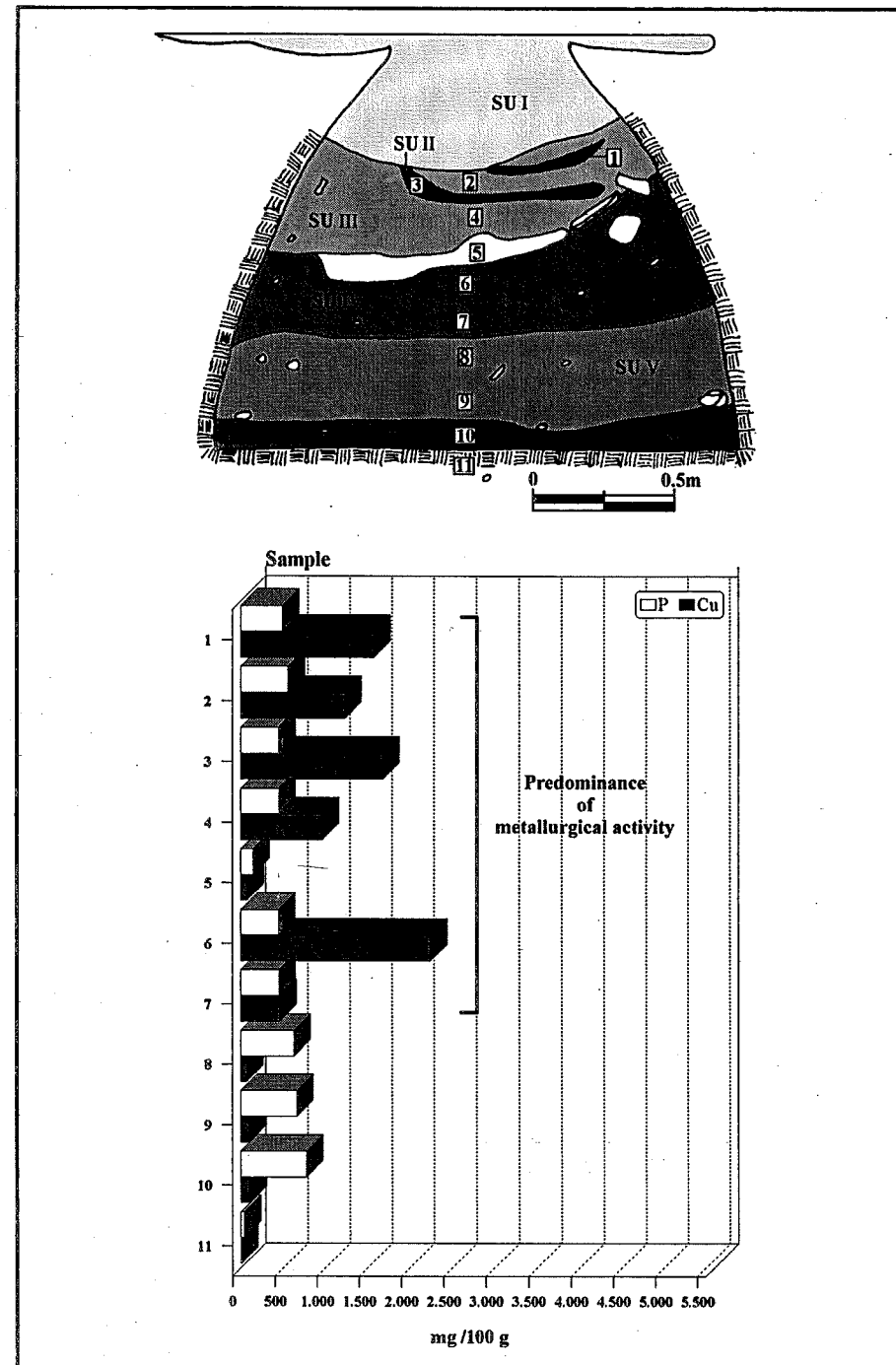| Sample | Digestion:HNO3-HClO4 (5/3, v/v) | Ignition/Ultrasonic extraction | Difference |
|--------|-------------------------------|-------------------------------|------------|
| 1 | 1165.80 | 1580.50 | +414.7 |
| 2 | 937.92 | 1233.40 | +295.48 |
| 4 | 858.65 | 963.73 | +105.08 |
| 8 | 84.96 | 73.65 | -11.31 |
| 9 | 86.23 | 103,53 | +17.3 |
| Cu slag | 15210 | 20305.7 | +5095.7 |



Figure 3. Structure 62: Stratigraphical profile, sampling and results.
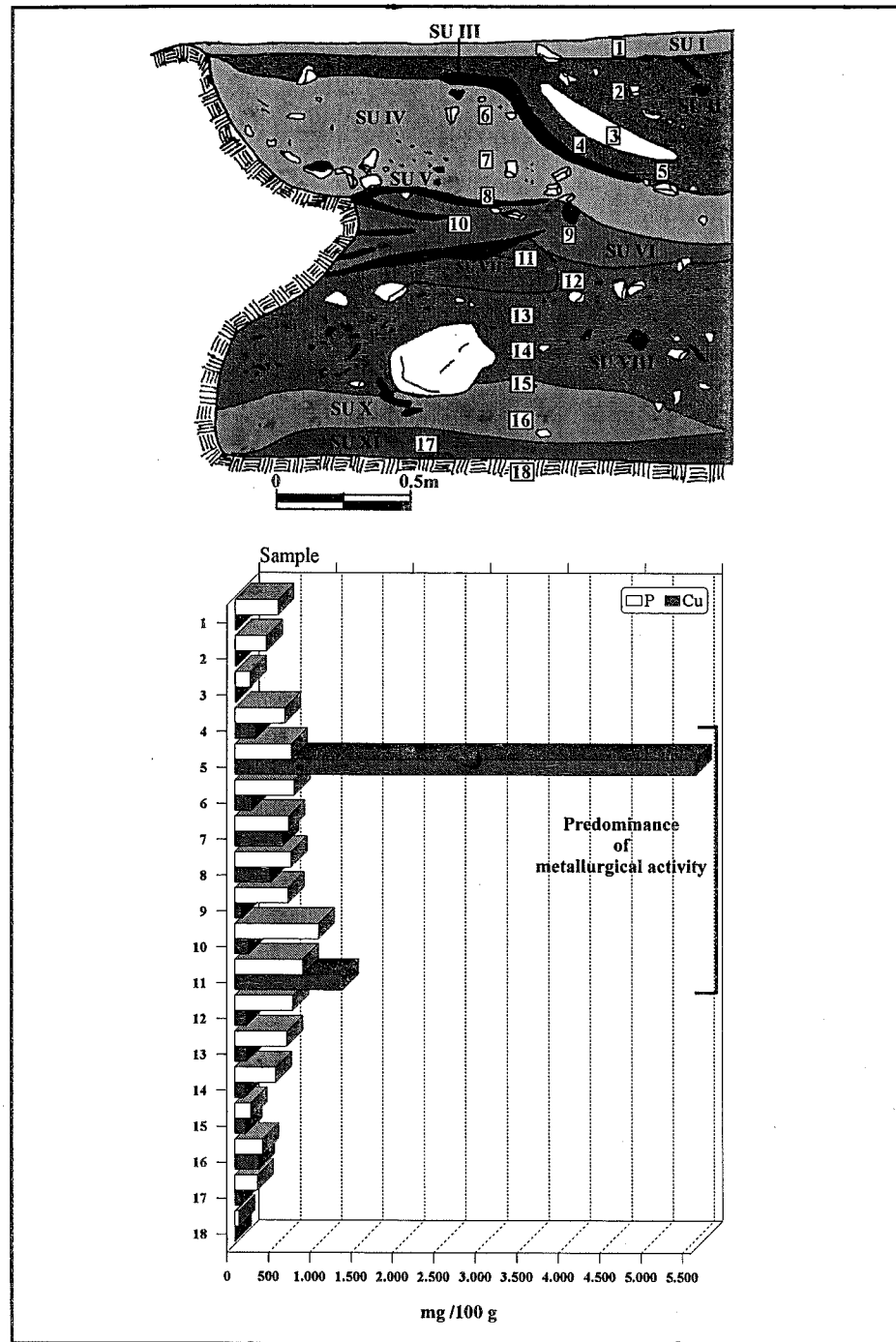
Figure 4. Structure 69: Stratigraphical profile, sampling and results.

the northern part of the study area. The uncovered section of this structure lies under the pavement of the street that sets a limit to one side of the study area. Samples of the whole sequence were taken. Sedimentary unit I was not sampled, though, as it was clearly affected by the above mentioned street.

Examination of the values of this structure show that samples 8 to 10 are low in Cu but high in P (reaching 780 mg P/100 g in sample 10). It is from sample no. 7 until the end of the sequence that the highest value of Cu can be found, peaking 2,252 mg in sample no. 6. Phosphorus reaches 558.75 mg (sample 2) at its most, but is lower than in previous samples.

Two points of activity can therefore be distinguished here. The first (samples 8-10) is marked by a moderate presence of Cu on the one hand, and a marked presence of P plus bone remains (still to be analysed at the time of writing this paper) on the other. These values indicate that the metallurgical activity was not dominant. In fact, the prevailing activity must have coexisted with some domestic activity of consumption and waste in the same space. Conversely, the second point of activity (samples 1-7) must have been used mainly metallurgical purposes, even if other domestic activities must have coexisted, as shown by the occurrence of P. The second point is altered only by a land accretion similar to the loams that form the bedrock substrate on which the structures were built. This might represent an accidental fall of the walls of the structure. Metallurgical activity may have been resumed on this material (sample 5). This would explain the values of P and Cu of this sample (76,41 mg Cu and 145 mg P). Otherwise, these values would be unlikely to occur in the bedrock, as attested by the control samples (Fig. 3).

The shape of structure 69 differs from the former, even if its excavated part must be a third of the whole structure (the rest being covered by a street and by a ramp leading to the study area). The results obtained coincide with those of structure no. 62, that is, Cu occurs all through the sequence, but it peaks at a given point.

The first samples show low values of P and higher values of Cu (samples 15, 16 and 17), but the former increase in samples 12, 13 and 14, Cu remaining present but not being as important as in later stages. Other activities, probably of a domestic type, must have taken place in this structure, either occasionally, or permanently together with metallurgical activities. Occurrence of pottery and bone remains (the latter yet to be identified) through all the sequence support this hypothesis.

The peak of metallurgical activity appears from samples 4 to 11, peaking in sample no. 5 with 5,568.6 mg Cu/100g. This is also the stage to which a crucible and rests of Cu ore found in the site belong. Important as this activity may have been, it was not the only one according to the values of P found. The P values may be due to the occurrence of ash caused by burning (samples 5, 8 and 11), but other concentrations, like those of samples 6, 7 or even 10 (1011.25 mg P/100g), suggest other activities than work with Cu.

The last phase in the sequence is that of samples 1, 2 and 3, in which the levels of P and Cu are low, except for P in sample no. 1 (515 mg P/100g), again a hint of an activity unrelated to metallurgical work. Unadvised interpretations of this value should be avoided, especially considering the closeness of this sample to the surface level, as well as later occupations of the site (Fig. 4).

Apparently, these two structures are not the only ones to have been connected with metallurgical activity in this area. Remains of slag and Cu ore were also found in others (structures 40B, 58B, 61 and 68). These had been excavated prior to our sampling and were, therefore, left out of our study. However, it seems more than likely that an area of this site was used for metallurgical work, even if such a use was probably not an exclusive one in view of the data obtained from structures 62 and 69.

Contrary to the results of structures 62 and 69, the values of Cu elsewhere in the study area are clear: none of the remaining 16 structures sampled yield values higher than 8.25 mg Cu/100 g. Metallurgical work should then be ruled out as a possible activity in them. The activities must have been of a domestic type, like storage, waste or other productive processes.

## CONLUCIONS

Chemical markers can be used advantageously as a tool for a better knowledge of the activities held in a settlement. The advantages become evident under special circumstances, for example, when the settlement has been excavated under the time pressure of a rescue excavation, or when the settlement shows planned abandonment. It is essential that the methodology be not only adequate but also adapted to the conditions occurring in each case, otherwise a balance between the number of samples to be analysed, the accuracy of the results, and their interpretation may become hard to achieve.

The analysis of Cu and P in plot A6 of the Archaeological Area of Marroquies Bajos is used here as an example of the use of chemical analysis in a settlement strongly influenced by the factors mentioned above. It was also possible to assess the importance of metallurgical activities in two structures, as well as to rule it out in 16 more. The archaeological data obtained from a number of structures not sampled yet may indicate the existence of an area where metallurgical activity may have been present.

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