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## Iberian variscite: ICP-MS-LA and PIXE analysis of recent prehistory beads and pendants from Spain and Portugal

Salvador Domínguez-Bella, Guirec Querré, Thomas Calligaro, Javier Martínez López

**Abstract.** At the European recent Prehistory variscite was a precious gemmological material that appears in scarce megalithic burials of the Atlantic facade, especially at the Iberian peninsula and West France.

Here we describe the main results of the mineralogical and geochemical analysis of a great and diverse group of archaeological and geological variscite and turquoise samples from the Iberian peninsula, especially from the Atlantic facade and the SW of Spain. Samples were analysed last years by the use of different analytical techniques as XRD, WDXRF, ICP-MS-LA and PIXE and stereomicroscopy.

The geochemical results, obtained especially by PIXE and ICP-MS-LA techniques, on these archaeological samples were discussed in relation to their possible provenance areas, related with the three main geological areas with variscite and turquoise outcrops in the Iberian peninsula: Palazuelo de las Cuevas-San Vicente area, that included other sites as El Bostal and Bragança district in Portugal; Pico Centeno mines, Encinasola area, in Huelva province, SW Spain; Gavá mines in Catalonia, NE Spain, and other possible sources in Europe as Pannecé, France.

Geochemical data were subjected to statistical analysis selecting different chemical variables in variscites and turquoises. A relatively good discrimination has been obtained through an interactive geochemical model using specially the Fe-Cr-V relationship, represented by a triangular diagram and the elementary relationships between other chemical elements.

These results show the existence, in Neolithic and Chalcolithic times, of great exchange networks of exotic or prestige lithic products that extended in Western Europe, hundreds and thousands of kilometres away from their source areas.

*Keywords:* Archaeomineralogy, variscite, turquoise, PIXE-PIGE, ICP-MS-LA, Recent Prehistory, Iberian Peninsula.

**Résumé.** Durant la Préhistoire récente européenne, la variscite est une gemme précieuse qui apparaît dans des sépultures mégalithiques de la façade atlantique, en particulier dans la péninsule Ibérique et l'ouest de la France.

Nous décrivons ici les principaux résultats de l'analyse minéralogique et géochimique d'un important ensemble de variscites et turquoises d'origines variées, à la fois des échantillons archéologiques et géologiques de la péninsule Ibérique, tout particulièrement de la façade atlantique et du sud-ouest de l'Espagne. Les échantillons ont été analysés au cours de ces dernières années à l'aide de différentes techniques d'analyse : XRD, WD-XRF, LA-ICP-MS, PIXE et stéréomicroscopie en particulier.

Les résultats géochimiques, obtenus en particulier par méthodes PIXE et LA-ICP-MS, sur ces échantillons archéologiques sont interprétés en terme de zones de provenance possibles, en rapport avec les trois principaux domaines géologiques où affleurent la variscite et la turquoise dans la péninsule Ibérique : Palazuelo de las Cuevas – San Vicente, y compris d'autres sites comme El Bostal et le district de Bragança au nord de Portugal ; les mines de Pico Centeno, dans la commune d'Encinasola, province de Huelva, dans le sud-ouest de l'Espagne ; les mines de Gavá en Catalogne, dans le nord-est de l'Espagne et d'autres sources possibles en Europe.

Les données géochimiques ont été soumises à une analyse statistique sélectionnant différentes variables chimiques des variscites. Une relativement bonne discrimination a été obtenue grâce à un modèle interactif géochimique utilisant en particulier les rapports Fe-Cr-V, ainsi que les relations entre d'autres éléments traces.

Ces résultats montrent l'existence durant les temps néolithiques et chalcolithiques de grands réseaux d'échange de biens de prestiges en matières minérales exotiques qui s'étendaient en Europe occidentale sur des centaines et des milliers de kilomètres de leurs régions d'origine.

*Mots clés* : Archéominéralogie, variscite, turquoise, PIXE-PIGE, LA-ICP-MS, Préhistoire récente, péninsule Ibérique.

## Introduction

The program CALLAIS, name given by Pliny the Elder to a green-blue group of minerals or stones near the turquoise, has been an interdisciplinary program within both the Humanities and Sciences of the Earth. Our work is the result from the convergence of two programs, one Spanish, and the other French, which had been operating independently up to 2010, beginning together from that moment, into the CHARISMA European framework.

The program focuses on gorgeous jewellery variscite, a green aluminium phosphate hydrate. This precious gemmological material appears with other greenish minerals such as turquoise, in scarce megalithic burials of the Atlantic facade, especially concentrated in Neolithic graves at the Iberian Peninsula and south and west France (Armorican peninsula).

These objects are mainly found in tombs dating from the 5th millennium to the 3rd millennium BC. (Damour, 1864). They were considered by these groups as prestige goods used as jewels or symbolic objects (Cassen, 1998). Their study through the archaeomineralogy and other disciplines is of special interest for archaeologists (Muñoz-Amilibia, 1971; Huet, Gonçalves, 1980; Fernández Vega, Pérez Cañamares, 1988; Calligaro, 2005; Domínguez-Bella, 2012).

In this context, the objective of the program is to determine the nature, origin and movement of jewellery elements made in variscite and turquoise during prehistory.

In most cases, different materials as jadeitites, sillimanite-fibrolite, quartz, talc, muscovite, chlorite, fluorite, amber or cinnabar appear as prestige goods present into the megaliths (Salvado Canêlhas, 1973; Vázquez-Varela, 1975; Huet, Gonçalves, Reis, 1982; Domínguez-Bella, Morata, 1995; Cassen, 1998; Cassen *et al.*, 2012; Domínguez-Bella *et al.*, 2015).

In this international collaboration, a great series of geological samples from the main variscite deposits of Iberian Peninsula and France have also been analysed and we have shown by comparison, the Iberian origin of Armorican beads in France (see Querré *et al.*, in this book) and the different ways for the trade of these materials in the Iberian Peninsula and France (Querré *et al.*, 2014).

In the last five years we complete this comprehensive study of the Atlantic coast from Europe (France, Spain, Portugal) about these phosphates, their use and distribution in the Prehistory.

Whereas in the rest of Europe the outcrops of variscite and turquoise are very scarce (Forestier *et al.*, 1973), in the Iberian Peninsula the geological contexts are relatively abundant, generally associated to Silurian age formations and metamorphic rocks of the aluminous shales group that usually occurs with lydites and chert associated with phosphatic minerals (Moro *et al.*, 1992, 1995) (fig. 1). Variscite, metavariscite, strengite, turquoise, wavellite, crandallite, quartz are usually present inside these mineral paragenesis (Arribas *et al.*, 1971; Moro, *et al.*, 1995) (fig. 2).

Some of these sites with aluminous-phosphatic rocks are concentrated specially in three specific geographic areas: the Alcañices synform, where these rocks are present in a wide geographical area which includes the province of Zamora, in Northwest Spain (Moro *et al.*, 1995; 1997) and a part of Trás-os-Montes/Bragança region, in northern Portugal (Meirelles *et al.*, 1987). This zone presents a large number of small outcrops of slate rocks rich in phosphates, as occurs in the region of Aliste: Palazuelo de las Cuevas, Bercianos de Aliste, San Vicente de la Cabeza, El Bostal, or in places like Ermita de Jou and Ervedosa, Vinhais, at the Portuguese zone (fig. 1).

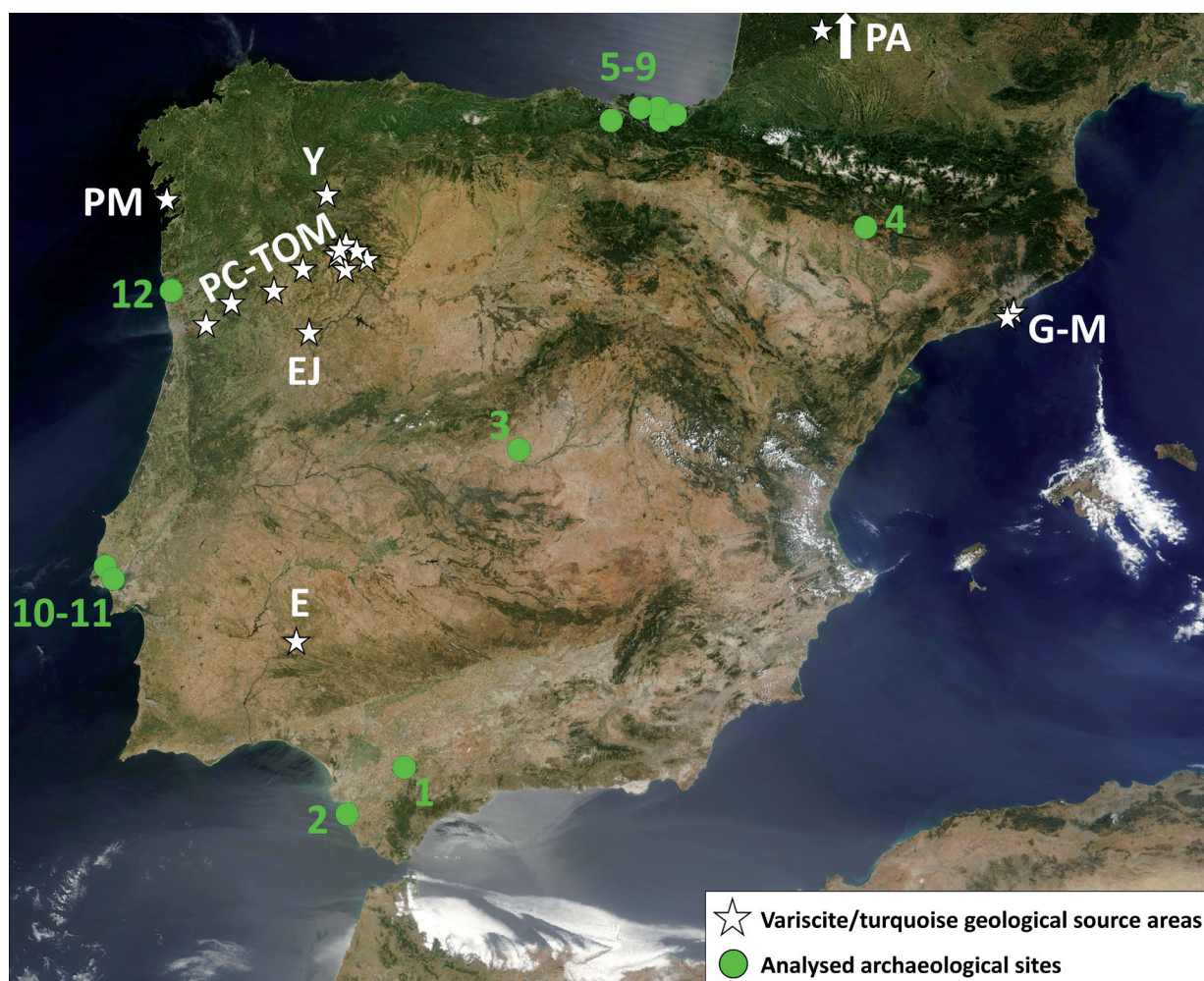


Fig. 1: Localization of the main geological outcrops of aluminium phosphates in the Iberian Peninsula and the studied archaeological sites for variscite sample provenance.

Other area with similar characteristics, but with less mineralogical variety is Pico Centeno, Encinasola, located in the SW of Spain, in the province of Huelva (Moro *et al.*, 1992, 1995). The third area is Gavá-Montcada zone, situated in Barcelona province, at the East of the Iberian Peninsula, with important outcrops of phosphate minerals, also associated to Silurian age shales and with a great variety of minerals in their paragenesis (Rosell *et al.*, 1993) (fig. 1).

With minor size and importance, we have also sampled Punta Montalvo (usually cited as Punta Corveiro in the literature) (Moro *et al.*, 1995) on the Galician coast, at the NW of Iberian Peninsula. Although we have a large database of major geological deposits in Europe, in recent years, some new small outcrops of variscite have appeared, unknown until the current date as the recently one discovered in Yeres, in the west of the Leon province, NW Spain (Arias Ferrero, Jiménez Martínez, 2014) and others, mainly of turquoise (Comendador Rey, 1998)

Some of these outcrops, which existence has been known since antiquity, have possibly been exploited from the Neolithic by open air mining or underground chamber and pillar mining (Blasco *et al.*, 1992; Domínguez-Bella, 2004; Baldellou *et al.*, 2012; Odriozola *et al.*, 2015).

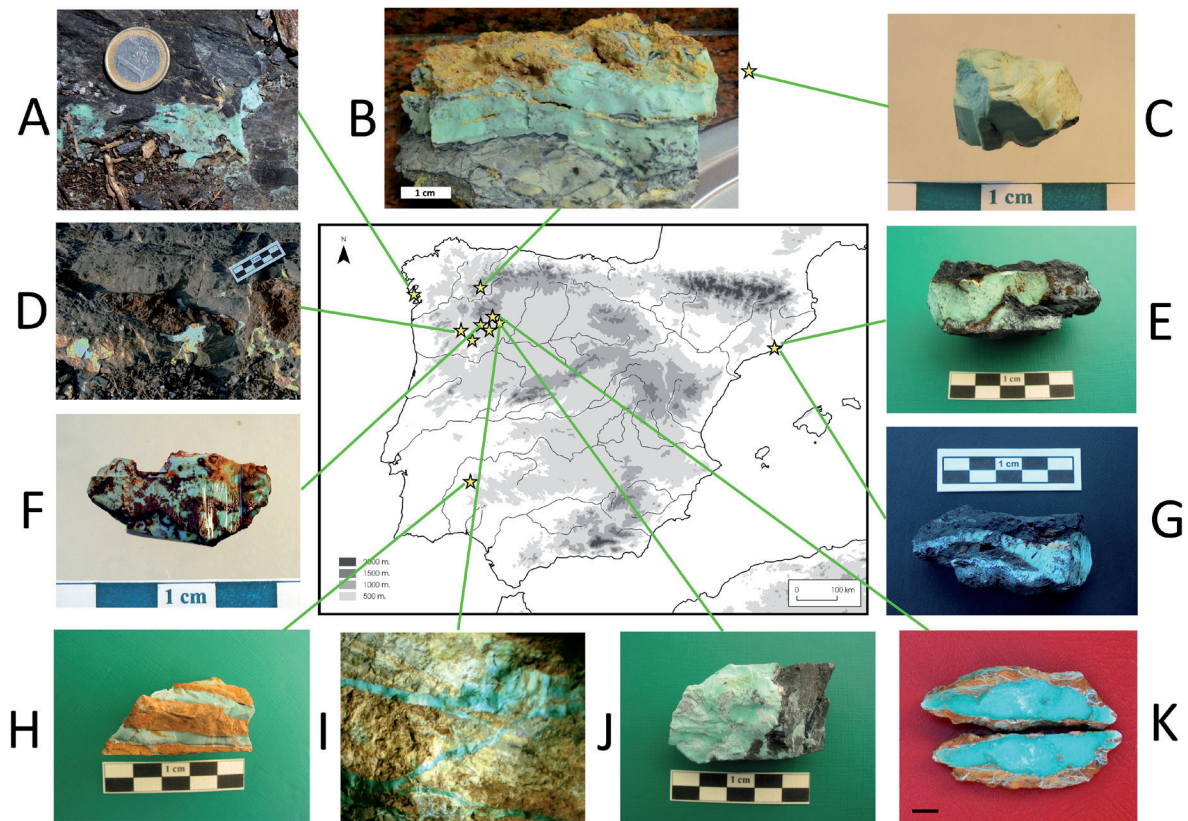


Fig. 2: Variscite-Turquoise geological samples from the main outcrops in the Iberian Peninsula and West France. A: Punta Montalvo (turquoise); B: Yeres (variscite); C: Pannecé, France (variscite); D: Ermita de Jou, Portugal (turquoise); E: Montcada (variscite); F: El Bostal (variscite); G: Gavá (variscite/turquoise); H: Encinasola (variscite); I: Palazuelo de las Cuevas (variscite); J: Bercianos de Aliste (variscite); K: Palazuelo de las Cuevas (turquoise).

## Objectives

The questions that were initially raised were (Domínguez-Bella *et al.*, 2011):

- 1: if there are several sources within a single Iberian archaeological site,
- 2: if the type of beads is related to their geological source, from previous determinations based on the geological context of archaeological sites with beads, to confirm the allochthonous origin of these.
- 3: the evolution of the exploitation of each of the Iberian geological resources in the 2.5 millennia of use,
- 4: the operation of the network and evolution from the 5th to the 3rd millennium due to the loss of relationship with a given region for the benefit of another resulting from either: a conflict in a region blocking communication channels or the depletion of a deposit is another reason to be determined.
5. if the mineralogical nature of the constituent materials of archaeological finds is variscite, because it is frequently confused in museum collections with other minerals or even with archaeological glass.
6. its geological and geographical origin.

This type of research concerning the origin of objects and materials can be accomplished only by reference to a database, database which was established from the systematic analysis of European geological samples obtained by different analytical techniques.

The archaeomineralogical and geochemical analysis of mineral raw materials from the geological outcrops and the archaeological artefacts have been carried out in the last years by the use of different analytical techniques as XRD, WDXRF, LA-ICP-MS, PIXE-PIGE and stereomicroscopy.

In this project they are two basic objectives in relation with the samples from the Iberian Peninsula:

- To characterize new geological samples of variscite representative of all Iberian Peninsula deposits using PIXE, already characterized by other analytical techniques (Blasco *et al.*, 1992; Edo *et al.*, 1998; Domínguez-Bella *et al.*, 2002; Odriozola *et al.*, 2010) and extend the PIXE database on variscite in Europe.
- To characterize different samples of archaeological variscite (and turquoise), of great importance in the Neolithic and Chalcolithic of the Iberian Peninsula, especially the North, Southwest and West Peninsular (Spain and Portugal), from different museums of Spain and Portugal (Bilbao, Villamartín, Huesca, Braga, etc.)

### **Analytical methodology**

This research line, which we have been developed the last two decades in relation with the characterization of necklace beads and pendants of Neolithic-Chalcolithic chronologies, has started with an exhaustive sampling of geological materials from different sites in the Iberian Peninsula and the rest of Europe.

The geological, mineralogical and geochemical characterization for different variscite-turquoise mineral deposits in the Iberian Peninsula has allowed us to analyze the great majority of the geological sources known in Europe for this mineral (fig. 1).

Here we use two different analytical techniques as the Particle-induced X-ray emission or proton-induced X-ray emission (PIXE) and the Particle-induced gamma-ray emission (PIGE) (AGLAE facility, CRMNF, Musée du Louvre, Paris) (CALLAIS Project, 2010-2011), (Querré *et al.*, 2014) and the Laser Ablation Inductively coupled plasma mass spectrometry (LA-ICP-MS) (University of Huelva) (Domínguez-Bella *et al.*, 2003).

In previous works, mineralogy, geochemistry of trace elements and the multifactorial analysis from LA-ICP-MS geochemical data (12 variables), in geological and archaeological Neolithic variscites, are allowing their potentially-source geological areas (Domínguez-Bella *et al.*, 2002).

Materials used as prestige items as variscite and turquoise, with geological source areas quite well known and almost exclusive to the Iberian Peninsula, show large geographical mobility, exceeding a thousand kilometres.

For the study of more of the 280 samples of geological raw materials and green beads from different sites of Recent Prehistory in the Iberian Peninsula and France, we implemented three methods of investigation: macroscopic observation, the binocular microscope and geochemical analysis by PIXE beam extract and LA-ICP-MS.

### **PIXE analysis**

PIXE allows a rapid and accurate chemical analysis covering a broad spectrum. FIXLAB - A PLATFORM AGLAE has been employed for major, minor and trace elements analysis and to obtain the features of the phosphate minerals present in Neolithic-Chalcolithic jewellery (beads and pendants) (tabl. I) and their geologic deposits (fig. 3).

Experimental conditions are: External proton microbeam in PIXE mode. Particle accelerator AGLAE. External beam and detection system. Particle: Proton Energy: 3 MeV; Intensity: 1,5 nA; Size: Ø 0,5 mm approx. Samples: from Spain and Portugal, and other European geological references.

The main advantages of this technique are: the analysis of objects of various sizes and shapes; it is not necessary sampling and preparation; the volume probe is of 30 mm<sup>3</sup>; the selection of details on the sample surface; it is possible the quantification of 26 elements, from Na to U ; a good speed of analysis (3 to 4 min by analysis) (for more details, see Querré *et al.* 2014; this volume).

The main limits are: the surface analysis, especially if this is altered and the influence in the alteration of gems by the high energy radiation.

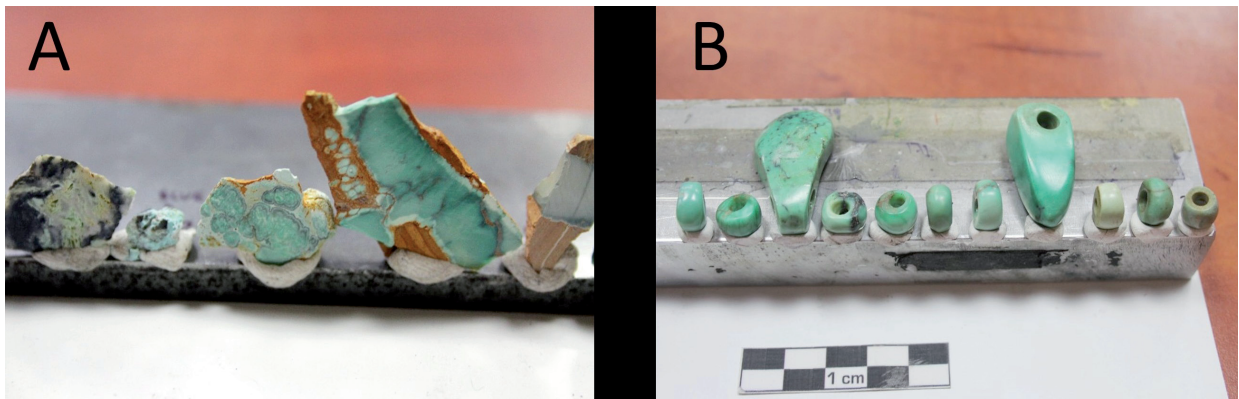


Fig. 3: Analysis by PIXE of variscite: geological (A) and archaeological samples (B) (AGLAE, Louvre, Paris 2012)

### LA-ICP-MS analysis

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LAM-ICP-MS) is an advanced technique for trace elements analysis, specially used in mineral characterization. LA-ICP-MS determinations of major elements and Ti, Cr, V, Ni, Co, Pb, Cu, Zn, U, La, Ce, Nd, Sm, Eu, Dy, Tm, Yb was carried out with a Hewlett-Packard 4500 Series equipment (University of Huelva). Sample surface laser ablation was made with a Laser Ablation System, mod. LSX-100 of Cetac-Technologies. Operating conditions at the laser microprobe are: laser mode Q-switched; flash lamp voltage 700-750 V; laser repetition rate 4-10 Hz; sample pit size of 150-300 microns and scans in "L" shape, of 500 microns length (fig. 4); and an Ar plasma-flux of 14 L/min, Points per mass: 6; Peri Pump: 0.12 r.p.s., with a NIST 612b standard glass as reference.

A statistical approach was used looking for similarities between archaeological variscite samples and those coming from the above quoted Iberian geological localities.



Fig. 4: Variscite archaeological samples after ICP-MS-LA analysis (SCID, Huelva University, 2002)  
A statistical approach was used looking for similarities between archaeological variscite samples and those coming from the above quoted Iberian geological localities.

**Results** Analysed samples come from three archaeological sites in Portugal: Leceia, Pena Verde and Esposende; one in the central area of Iberian Peninsula, Valle de las Higueras, Toledo; eight in the South Spain, Alberite I Dolmen, Villamartín, Cadiz and El Tomillo Dolmen, Alcalá del Valle, Cádiz; ten in the North of Spain, in the Basque Country and one in Olvena, Huesca, at the Pyrenean region of Aragón, North East Spain (tabl. I).

### Chemometric model

The variscite program is based on two complementary approaches: one focused on the study of variscite sources, the other on the study of Neolithic callaïs jewellery. The first one on Western European raw material sources is based on their inventory, exhaustive sampling, PIXE analysis of reference samples and data synthesis. It is on the basis of the archaeological, geographical, geological and geochemical criteria of each of the western European callaïs, variscite and/or turquoise deposits that a chemometric model has been established (Querré *et al.*, this volume).

Without detailing the entire process that led to the development of this model, presented in the above-mentioned article, the main elements are as follows. Fourteen deposits or gîtological basins are currently inventoried in Western Europe. Among them and although reference samples of most of them were analyzed.

Five European deposits are likely to have been exploited in the Neolithic, four Iberian and one Armorican. For the Iberian deposits, three of them are those with traces of ancient exploitation: Gavá in the south of Barcelona where the Neolithic mines of Can Tintorer are located, Palazuelo de las Cuevas in the Zamora region of northwest Spain and Encinasola in the Huelva region of southwest Spain where the Pico Centeno mine is located in the municipality of Encinasola. The El Bostal deposit is located in the Zamora region; no evidence of exploitation was found. This is also the case for the Pannecé Armorican deposit in the Loire Atlantique. It has been preserved because of its location within the Neolithic occupations of western France, particularly those of the Carnac-Lochmariaquer region. These are the reference samples of these 5 deposits for which the most analyses were carried out in order to take into account not only the average composition of variscite but also the range of composition of green stones within these deposits (tab. 1). The chemometric model that has been established is based for its analog version on the concentrations of 8 chemical elements: iron, vanadium, chromium, arsenic, calcium, silicon, zirconium and uranium. It is the absolute and relative concentrations that are taken into account, but also the degree of homogeneity of the deposits or, on the contrary, their heterogeneity. It should be noted that it is precisely these chemical elements that are used in the composition of the various minerals of the variscite family and substitute either phosphorus or aluminium for variscite of "ideal" composition.

Iron, vanadium and chromium are the three chemical elements whose variations from one deposit to another are the most discriminating (Figure 5).

Thus, the chemometric model used to determine the origin of variscite ornaments in Western Europe is iterative (Figure 6) and graphical (Figure 7).



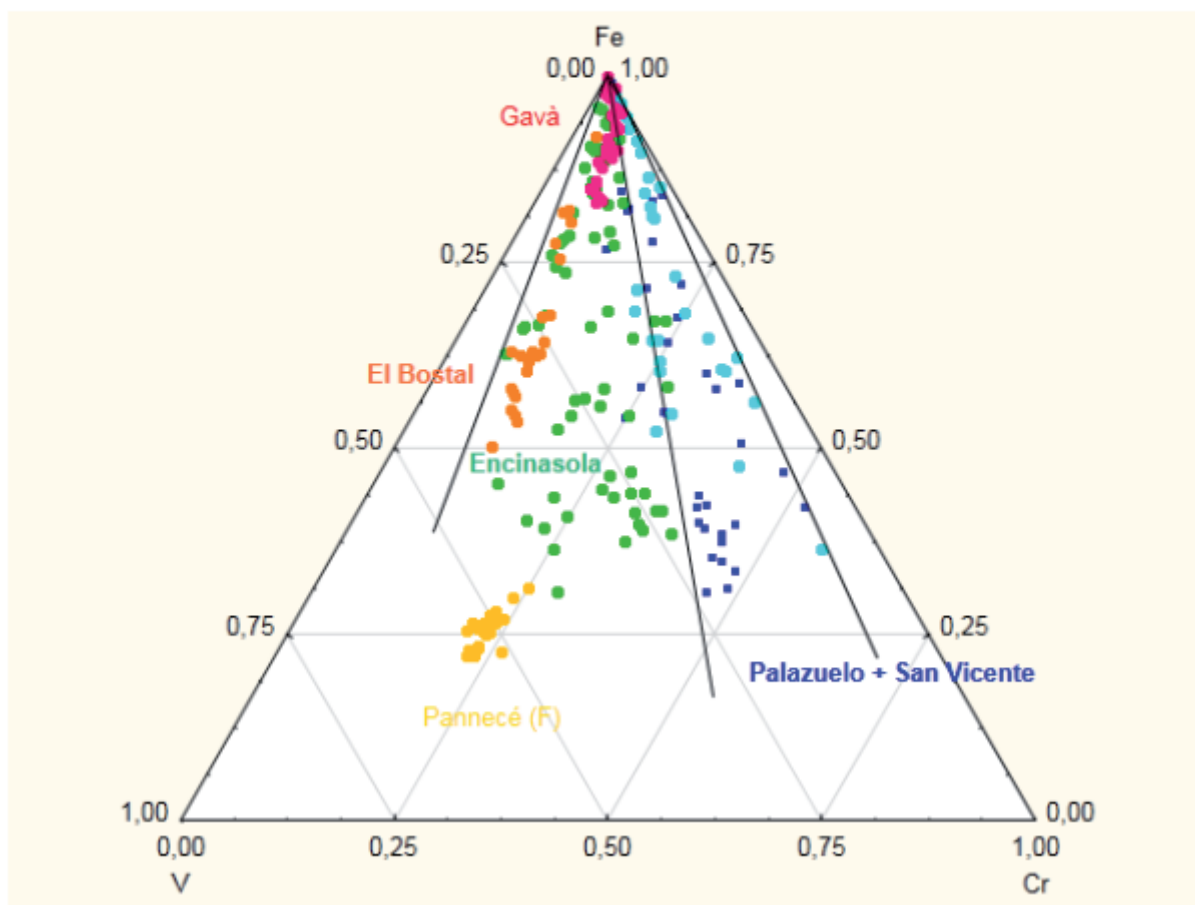


Fig. 5: Ternary Diagram Fe-V-Cr, with the total of geological analysed samples by PIXE. Black points: Gavà-Montcada area; Red points: Encinasola, Pico Centeno mines, Huelva; Green points: El Bostal, Zamora; Blue points: Palazuelo-San Vicente area, Zamora; Orange points: Pannecé, France (after Querré *et al.*, 2012) .

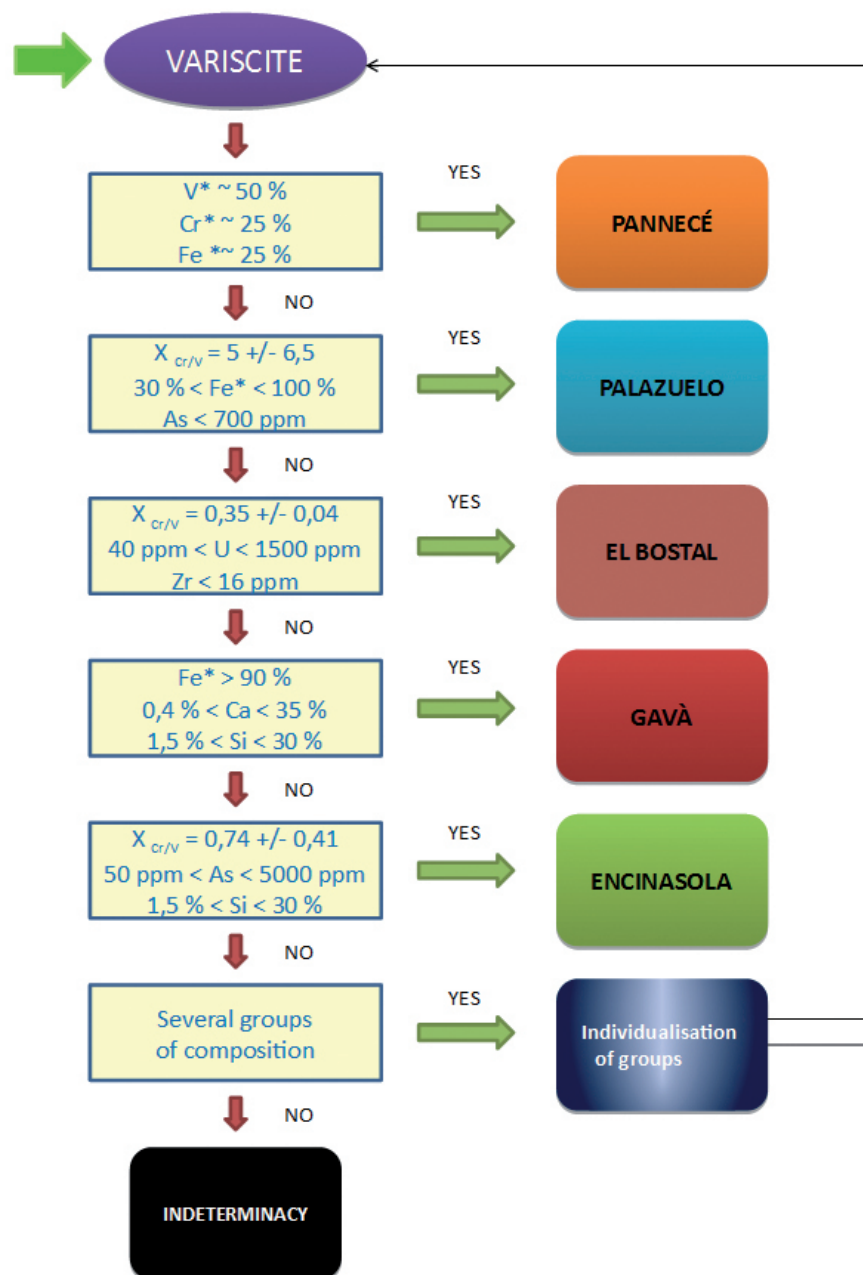


Fig. 6: Chemometric model established is based for its analog version on the concentrations of 8 chemical elements: iron, vanadium, chromium, arsenic, calcium, silicon, zirconium and uranium.

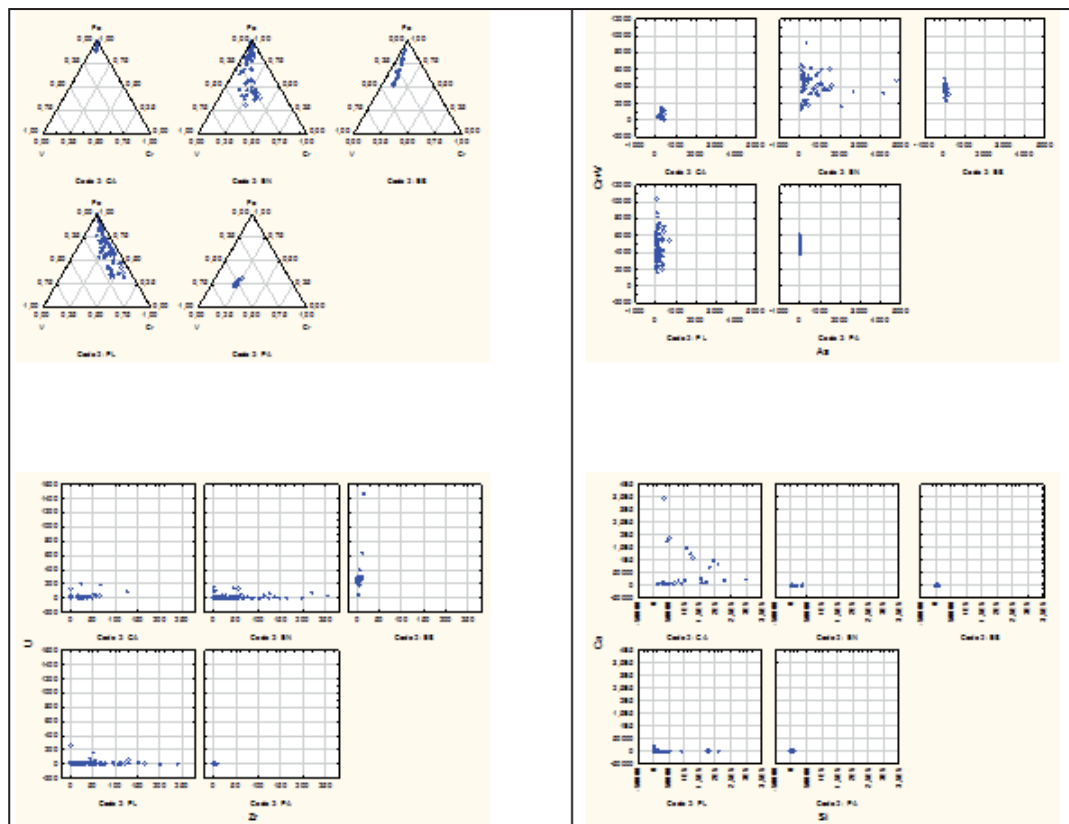


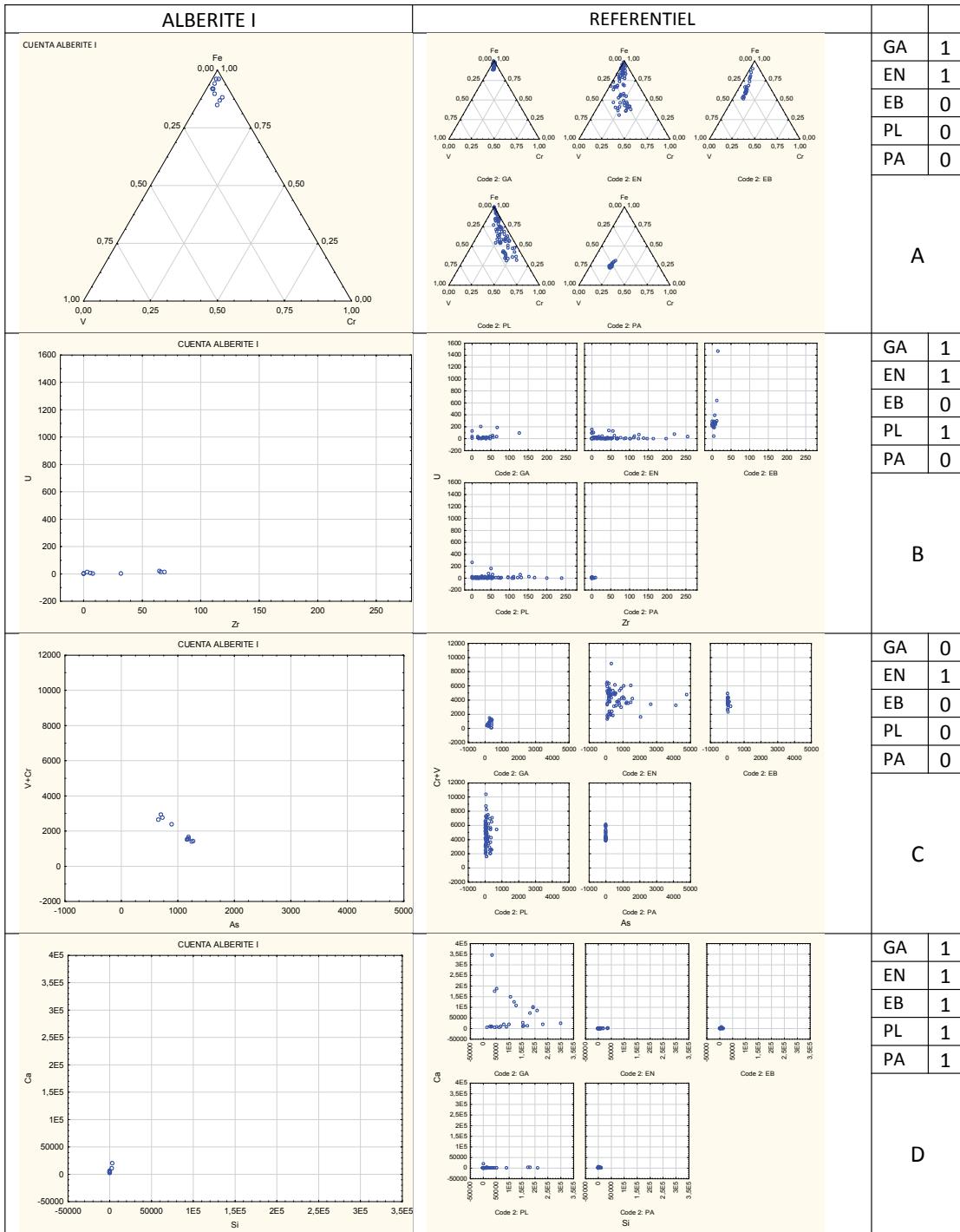
Fig. 7: Chemometric model reference frame. A: Ternary V-Cr-Fe diagrams ; B: Zr-U diagrams ; C: As(V+Cr) diagrams ; D: Si-Ca diagrams for the five geological variscite references.

## Results

Analysed samples come from three archaeological sites in Portugal: Leceia, Pena Verde and Esposende; one in the central area of Iberian Peninsula, Valle de las Higueras, Toledo; seven in the South Spain, Alberite I Dolmen, Villamartín, Cadiz; ten in the North of Spain, in the Basque Country and one in Olvena, Huesca, at the Pyrenean region of Aragón, North East Spain (Table I).

| OBJECT             | ARCHAEOLOGICAL SITE<br>current location<br>and sample reference   | MATERIALS                          | ESTIMATED CHRONOLOGY   |
|--------------------|---|------------------------------------|--|
| 7 Beads            | Alberite I Dolmen, Villamartín, Cadiz. SW Spain.<br>(Beta 80598 & Beta 80602. 4333-3977. 2 sigma Cal. BC. (Hearths) Beta 80600. 4245-3641. 2 sigma Cal. BC. (coal in founding trench)                           | variscite                          | Middle Neolithic<br>(Ramos-Muñoz & Giles (eds.) 1996)                              |
| 1 Bead             | El Tomillo Dolmen, Alcalá del Valle, Cádiz. SW Spain.   | variscite                          | Neolithic-Bronze Age<br>(Martínez and Pereda, 1991)                                |
| 1 Bead<br>(reused) | Campo de Hockey, San Fernando, Cádiz. South Spain<br>4200-3900 BC cal. 2 sigma Cal. BC. (Human Bone)  | variscite                          | Middle Neolithic necropolis.<br>(Vijande et al., 2015)                             |
| 14 Beads           | Valle de las Higueras, Toledo, Central Spain. (VH99 (6 samples)/VH01 (6 samples)/ VH05 (2 samples))<br>Chalcolithic necropolis.   | variscite                          | Neolithic-Chalcolithic<br>(Bueno Ramírez, Barroso Bermejo & Balbín Behrmann, 2005) |
| 35 Beads           | Leceia, Lisbonne region, Portugal.<br>(Excavated by J.L. Cardoso). Chalcolithic fortified settlement. 2600-2700 BC (Cardoso, 2014)  | variscite                          | Chalcolithic   |
| 16 Beads           | Pena Verde, Lisbonne region. Portugal.<br>(PV CASA 1 & PV CASA 2) (Cardoso, 2014)<br>Beta-276399: 3890 ± 40 BP, 2470-2210 (2 σ cal BC)  | Variscite<br>(15)                  | Chalcolithic   |
| 2 Beads            | Bitarados, Esposende, North Portugal<br>(MDDS 2004/0626)<br>S. Lourenzo, Esposende<br>(MDDS 2010/5047)  | variscite<br>variscite             | Neolithic ?<br>Chalcolithic /Bronze Age  |
| 1 Beads            | Añabusti, Busturia, Bizkaia: Dolmen de Urdaibai (in Sollube). Neither absolute dating available nor diagnostic materials. An archaeological site with chronology Chalcolithic-Bronze age exists near the dolmen | variscite<br>(appeared on surface) | Neolithic-Chalcolithic ?   |
| 1 Bead             | Errekatxuetako Atxa:<br>(ERX 4b.1.7.1381)<br>Dolmen de Gorbeia, excavated in 2006.<br>No absolute dating available.   | variscite                          | Main phase of second half of<br>III millennium Cal. BC.<br>Bell-Beaker culture     |
| 1 Bead             | Arenaza I, Galdames: (AI.R3.180)<br>A cave with a good stratigraphy of Chalcolithic and Bronze Age, but also with previous stages of occupation.  | variscite                          | Unknown age  |
| 2 Beads            | Goikolau, Berriatua: (G.Z2.b7.23/11)<br>Cave, excavated in 1981 (by C. Basas) (with a variscite necklace, flint points, etc., in a first phase of inhumation).  | variscite                          | Probably Chalcolithic-Bronze Age.  |
| 5 Beads            | Txotxinkoba, Gizaburuaga:<br>(TXO.B7/B9/B11/B13/A13) Sepulchral cave  | variscite                          | Aeneolithic  |
| 7 Beads            | Cueva del Moro, Olvena. Upper chambers.<br>Sepulchral cave. 4600 BC not CAL.  | variscite                          | Ancient Neolithic  |

Tabl. I: Samples of variscite beads from the Iberian Peninsula analysed in the CALLAIS project.



| ALBERITE I |   |   |   |   |       |            |
|------------|---|---|---|---|-------|------------|
|            | A | B | C | D | Bilan | Provenance |
| GA         | 1 | 1 | 0 | 1 | 0     |            |
| EN         | 1 | 1 | 1 | 1 | 1     | Encinasola |
| EB         | 0 | 0 | 0 | 1 | 0     |            |
| PL         | 0 | 1 | 0 | 1 | 0     |            |
| PA         | 0 | 0 | 0 | 1 | 0     |            |

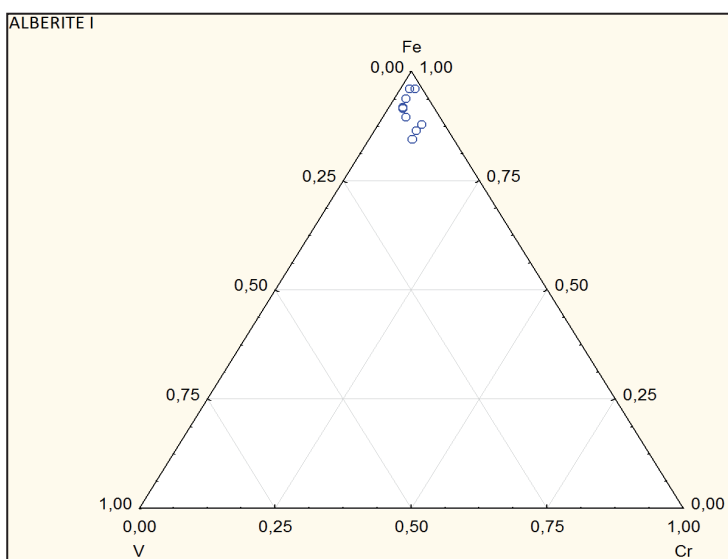
SITE NAME : ALBERITE I  
 Number of objects total : 5  
 Number of analyses : 11

Univocal response : Encinasola

**PIXE analysis. Sites from Spain**

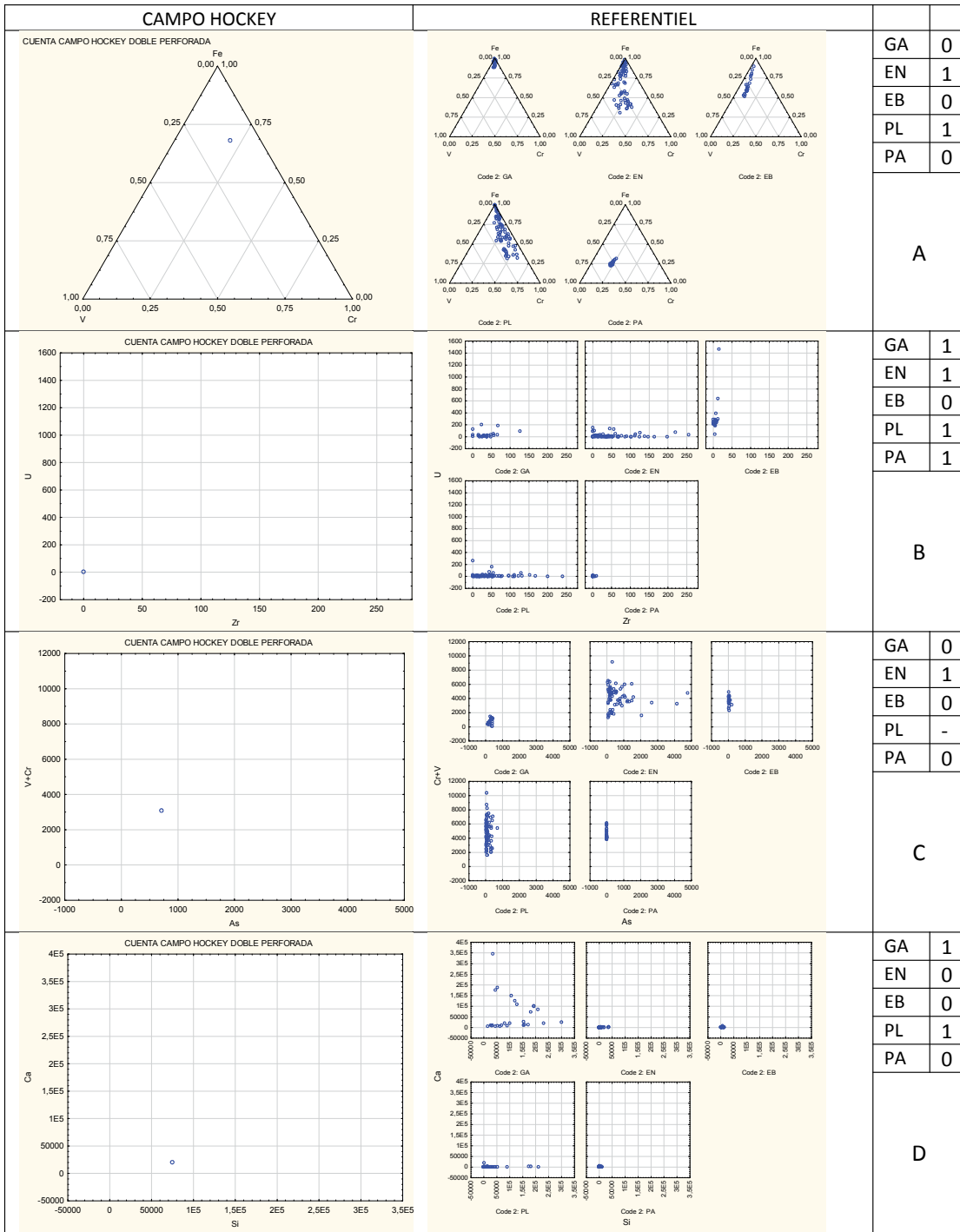
| site       | no | na |            | Na    | Mg   | Al     | Si    | P      | K    | Ca    | Ti   | V    | Cr   | Mn  |
|------------|----|----|------------|-------|------|--------|-------|--------|------|-------|------|------|------|-----|
| Albéríte I | 5  | 11 | min        | 1622  | 0    | 175500 | 0     | 206154 | 421  | 2298  | 655  | 844  | 449  | 0   |
|            |    |    | max        | 12479 | 3305 | 211311 | 40236 | 246240 | 7550 | 23208 | 2096 | 1589 | 1809 | 59  |
|            |    |    | X          | 7346  | 1646 | 202653 | 4180  | 235535 | 1803 | 7852  | 1138 | 1103 | 940  | 8   |
|            |    |    | $\sigma$   | 3870  | 1525 | 11220  | 12014 | 10799  | 2088 | 7140  | 519  | 227  | 544  | 18  |
|            |    |    | $\delta\%$ | 53    | 93   | 6      | 287   | 5      | 116  | 91    | 46   | 21   | 58   | 226 |

|            | Fe    | Co | Ni | Cu  | Zn  | Ga | As   | Rb  | Sr   | Y   | Zr  | Nb  | U   | V* | Cr* | Fe*  | Cr/V  | Cr+V |
|------------|-------|----|----|-----|-----|----|------|-----|------|-----|-----|-----|-----|----|-----|------|-------|------|
| min        | 15863 | 0  | 2  | 31  | 22  | 34 | 361  | 0   | 0    | 0   | 0   | 0   | 0   | 1  | 2   | 85   | 0,43  | 1407 |
| max        | 58006 | 22 | 43 | 340 | 118 | 72 | 1271 | 13  | 1114 | 87  | 69  | 6   | 19  | 8  | 8   | 96   | 1,89  | 2915 |
| X          | 23772 | 9  | 16 | 136 | 52  | 45 | 964  | 3   | 166  | 18  | 26  | 1   | 6   | 5  | 4   | 91   | 0,88  | 2043 |
| $\sigma$   | 12553 | 8  | 14 | 116 | 35  | 10 | 309  | 5   | 319  | 30  | 29  | 2   | 8   | 2  | 4   | 0,56 | 617   |      |
| $\delta\%$ | 53    | 92 | 84 | 86  | 68  | 22 | 32   | 160 | 192  | 164 | 110 | 190 | 127 | 36 | 63  | 4    | 64,26 | 30   |



Alberite I dolmen. Villamartín, Cádiz, Spain. A corridor dolmen with a calibrated age of 4333-3977 and 4245-3641, 2 sigma Cal. BC. (Hearths) Beta 80600. Neolithic. Superb burial goods with a big quartz smoky monocystal, more than a thousand necklace beads of variscite and shell, polished axes and a chisel, a baetylus idol stone, large blades of flint, amber (simetite) beads, a stone palette (dolerite), cinnabar and hematite ochres, etc. (Domínguez-Bella, Morata, 1995, 1996; Ramos Muñoz, Giles, 1996).

Fig. 8: A: Chemical composition table of variscite objects from the site of Alberite I. "no" number of objects analyzed; "na" : number of PIXE analyses; min, max : minimum and maximum values of the variable; X and  $\sigma$  : mean and standard deviation ;  $\delta\%$  : dispersion coefficient in percentage (); V\*, Cr\*, Fe\* are the values normalized to 100% with respect to the sum (V+Cr+Fe). All elemental concentrations are expressed in part per million (ppm). B: Comparison of chemical analyses of variscite objects with the chemometric model reference frame applied to the Alberite I site. C: Medium-Long distance mobility and possible provenance for the variscite samples in Alberite I.



| CAMPO HOCKEY |   |   |   |   |       |   |
|--------------|---|---|---|---|-------|---|
|              | A | B | C | D | Bilan | Provenance                                  |
| GA           | 0 | 1 | 0 | 1 | 0     | Indétermination<br>(Encinasola / Palazuelo) |
| EN           | 1 | 1 | 1 | 0 | 0     |   |
| EB           | 0 | 0 | 0 | 0 | 0     |   |
| PL           | 1 | 1 | - | 1 | 0     |   |
| PA           | 0 | 1 | 0 | 0 | 0     |   |

|  |   |
|--|---|
| SITE NAME : CAMPO HOCKEY<br>Number of objets total :1<br>Number of analyses :1 | Non-unique response : indetermination (Encinasola/ Palazuelo) |
|--|---|

Campo de Hockey, San Fernando, Cádiz. South Spain: Middle Neolithic necropolis. 4200-3900 BC cal. (Vijande, E. et al., 2015) A reused variscite bead.

| site            | no | na | Na   | Mg   | Al     | Si    | P      | K    | Ca    | Ti  | V    | Cr   | Mn |
|-----------------|----|----|------|------|--------|-------|--------|------|-------|-----|------|------|----|
| Campo de Hockey | 1  | 1  | 7480 | 1839 | 191880 | 75214 | 172980 | 2932 | 20122 | 941 | 1086 | 1997 | 26 |

| Fe   | Co | Ni | Cu | Zn | Ga | As  | Rb | Sr  | Y | Zr | Nb | U | V* | Cr* | Fe* | Cr/V | Cr+V |
|------|----|----|----|----|----|-----|----|-----|---|----|----|---|----|-----|-----|------|------|
| 6533 | 9  | 82 | 80 | 43 | 73 | 713 | 9  | 159 | 0 | 0  | 0  | 0 | 11 | 21  | 68  | 1,84 | 3083 |

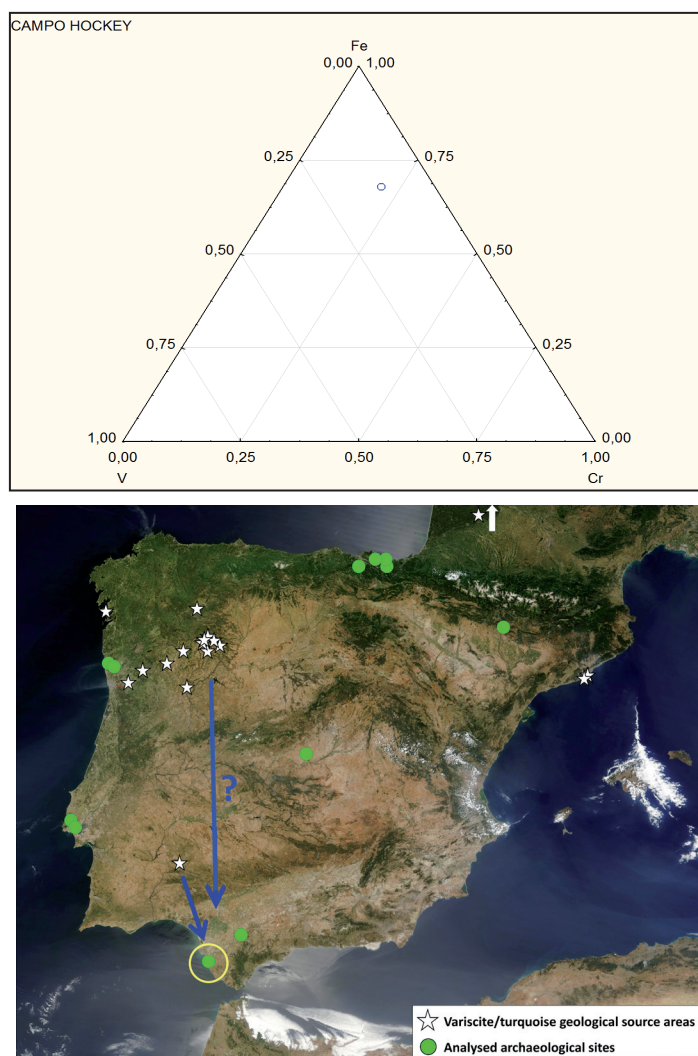
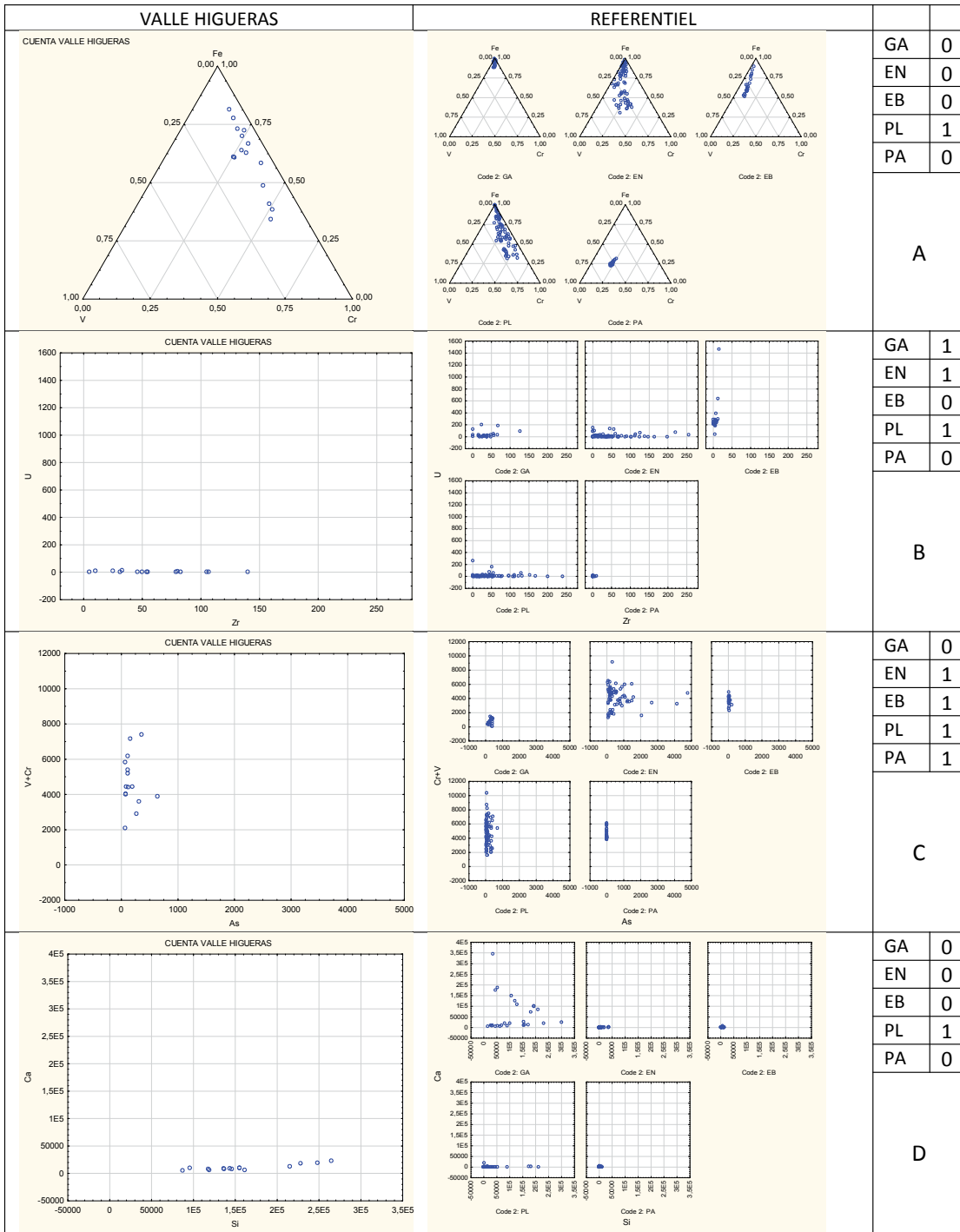


Fig. 9: - A: Chemical composition table of variscite objects from the site of Campo de Hockey, San Fernando, Cádiz. B: Comparison of chemical analyses of variscite objects with the chemometric model reference frame applied to the site. C: Medium-Long distance mobility and possible provenance for the variscite samples in this site.





| VALLE HIGUERAS |   |   |   |   |       |            |
|----------------|---|---|---|---|-------|------------|
|                | A | B | C | D | Bilan | Provenance |
| GA             | 0 | 1 | 0 | 0 | 0     |            |
| EN             | 0 | 1 | 1 | 0 | 0     |            |
| EB             | 0 | 0 | 1 | 0 | 0     |            |
| PL             | 1 | 1 | 1 | 1 | 1     | Palazuelo  |
| PA             | 0 | 0 | 1 | 0 | 0     |            |

SITE NAME: VALLE HIGUERAS  
 Number of objects total :14  
 Number of analyses :15

Univoque response : Palazuelo

Valle de las Higueras, Toledo, Central Spain: Chalcolithic necropolis.

| site     | no | na |            | Na    | Mg   | Al     | Si     | P      | K     | Ca    | Ti   | V    | Cr   | Mn |
|----------|----|----|------------|-------|------|--------|--------|--------|-------|-------|------|------|------|----|
| Higueras | 14 | 15 | min        | 2778  | 595  | 98784  | 87455  | 70588  | 1958  | 5029  | 460  | 230  | 1852 | 0  |
|          |    |    | max        | 11272 | 8598 | 173262 | 264571 | 192182 | 13064 | 22301 | 2294 | 1664 | 5731 | 47 |
|          |    |    | X          | 6314  | 3373 | 140180 | 160671 | 144294 | 6009  | 10591 | 1286 | 1027 | 3700 | 18 |
|          |    |    | $\sigma$   | 2885  | 2532 | 20704  | 54011  | 36549  | 3407  | 5183  | 612  | 429  | 1175 | 14 |
|          |    |    | $\delta\%$ | 46    | 75   | 15     | 34     | 25     | 57    | 49    | 48   | 42   | 32   | 76 |

|            | Fe    | Co | Ni | Cu  | Zn  | Ga  | As  | Rb | Sr  | Y   | Zr  | Nb | U   | V* | Cr* | Fe* | Cr/V  | Cr+V |
|------------|-------|----|----|-----|-----|-----|-----|----|-----|-----|-----|----|-----|----|-----|-----|-------|------|
| min        | 2919  | 0  | 0  | 67  | 5   | 12  | 71  | 0  | 50  | 0   | 5   | 0  | 0   | 4  | 14  | 34  | 1,86  | 2082 |
| max        | 23468 | 22 | 5  | 276 | 101 | 315 | 643 | 10 | 264 | 17  | 140 | 0  | 13  | 14 | 53  | 81  | 8,05  | 7381 |
| X          | 8811  | 9  | 2  | 164 | 40  | 144 | 187 | 4  | 151 | 3   | 60  | 0  | 3   | 8  | 31  | 61  | 4,12  | 4727 |
| $\sigma$   | 6186  | 6  | 2  | 83  | 30  | 89  | 156 | 3  | 74  | 5   | 38  | 0  | 5   | 3  | 12  | 14  | 1,61  | 1474 |
| $\delta\%$ | 70    | 72 | 82 | 51  | 73  | 62  | 84  | 74 | 49  | 156 | 64  |    | 168 | 41 | 40  | 24  | 39,13 | 31   |

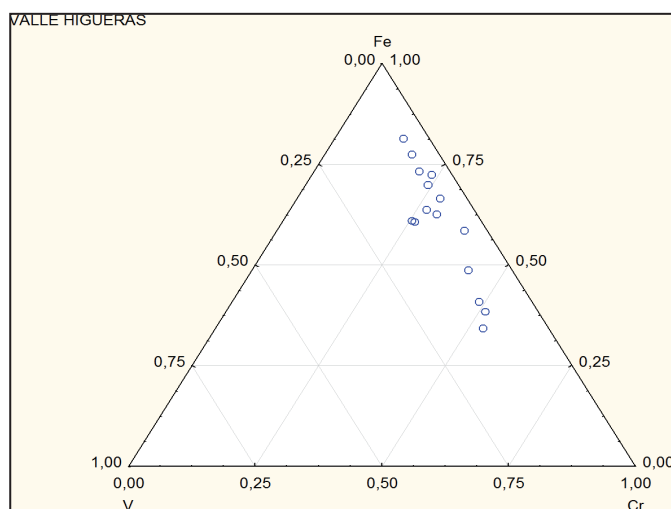
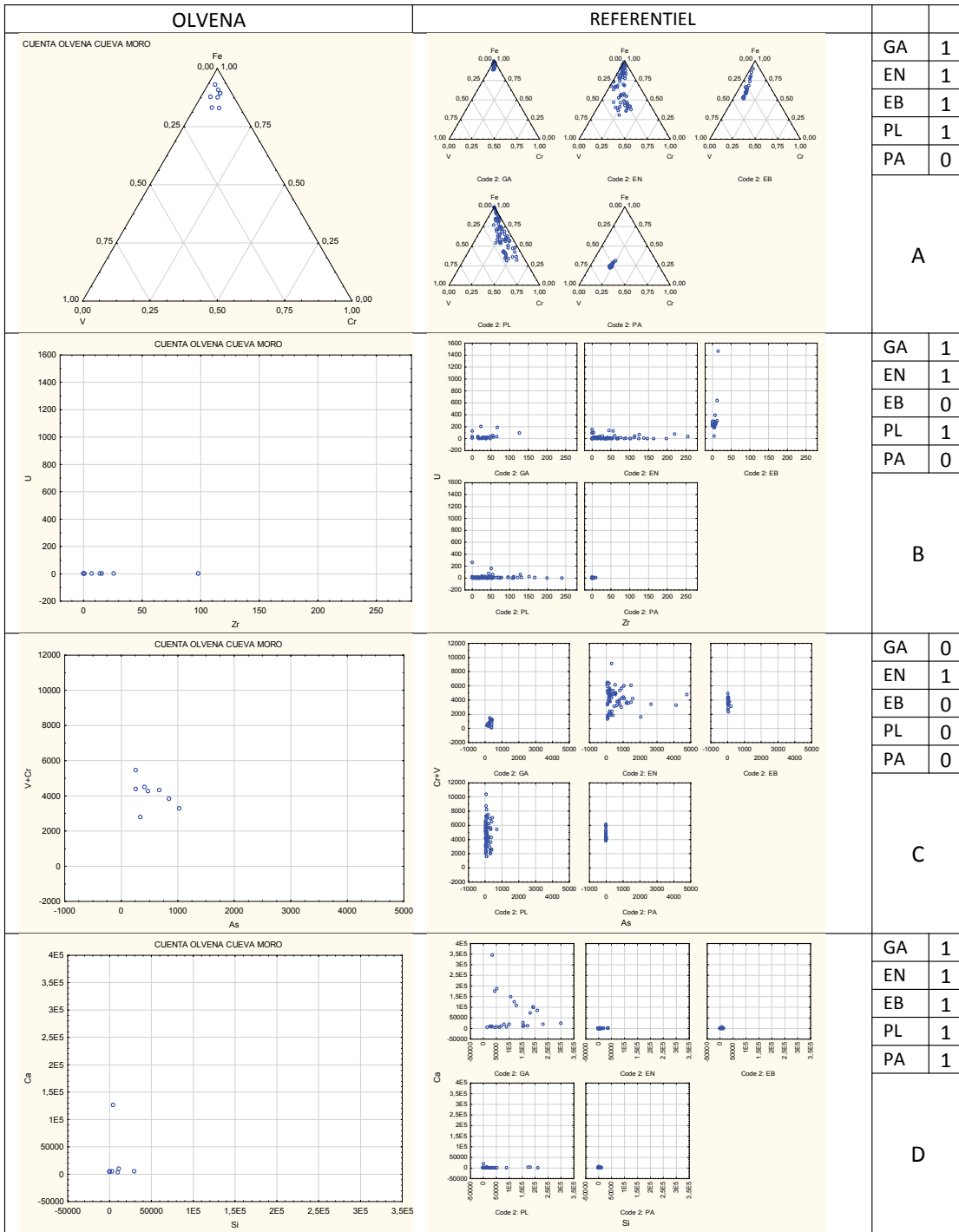


Fig. 10: - A: Chemical composition table of variscite objects from the site of Valle de las Higueras, Toledo, Central Spain. B: Comparison of chemical analyses of variscite objects with the chemometric model reference frame applied to the site. C: Medium-Long distance mobility and possible provenance for the variscite samples in this site.



| OLVENA |   |   |   |   |       |            |
|--------|---|---|---|---|-------|------------|
|        | A | B | C | D | Bilan | Provenance |
| GA     | 1 | 1 | 0 | 1 | 0     | Gavá       |
| EN     | 1 | 1 | 1 | 1 | 1     | Encinasola |
| EB     | 1 | 0 | 0 | 1 | 0     |            |
| PL     | 1 | 1 | 0 | 1 | 0     |            |
| PA     | 0 | 0 | 0 | 1 | 0     |            |

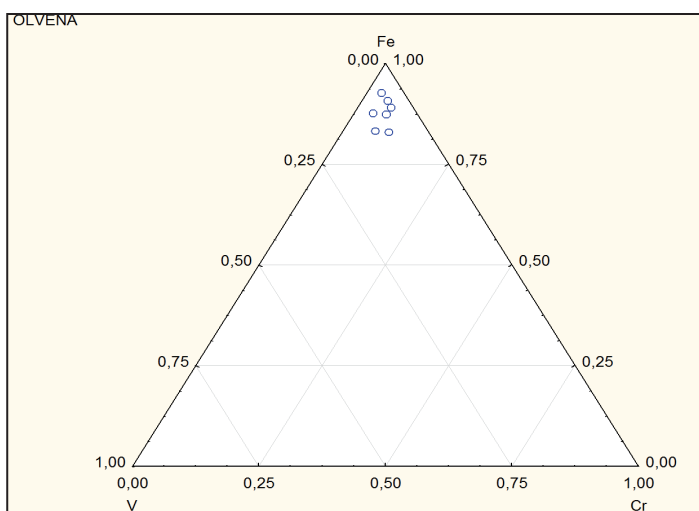
SITE NAME : OLVENA  
 Number of objects total :7  
 Number of analyses :8

Univocal Response : Gavá / Encinasola

Cueva del Moro. Olvena. Northeast Spain: Neolithic cave. Ancient Neolithic. (Baldellou *et al.*, 2012)

| site   | no | na |            | Na    | Mg    | Al     | Si    | P      | K     | Ca     | Ti   | V    | Cr   | Mn  |
|--------|----|----|------------|-------|-------|--------|-------|--------|-------|--------|------|------|------|-----|
| Olvena | 7  | 8  | min        | 1620  | 0     | 143035 | 0     | 206250 | 730   | 3095   | 356  | 1094 | 1135 | 0   |
|        |    |    | max        | 11914 | 16553 | 202980 | 29678 | 245062 | 11769 | 125808 | 3540 | 2698 | 2918 | 56  |
|        |    |    | X          | 4172  | 2373  | 187147 | 7443  | 231815 | 3405  | 20300  | 1089 | 2106 | 2000 | 11  |
|        |    |    | $\sigma$   | 3644  | 5734  | 21142  | 10058 | 14354  | 3853  | 42674  | 1155 | 538  | 655  | 19  |
|        |    |    | $\delta\%$ | 87    | 242   | 11     | 135   | 6      | 113   | 210    | 106  | 26   | 33   | 177 |

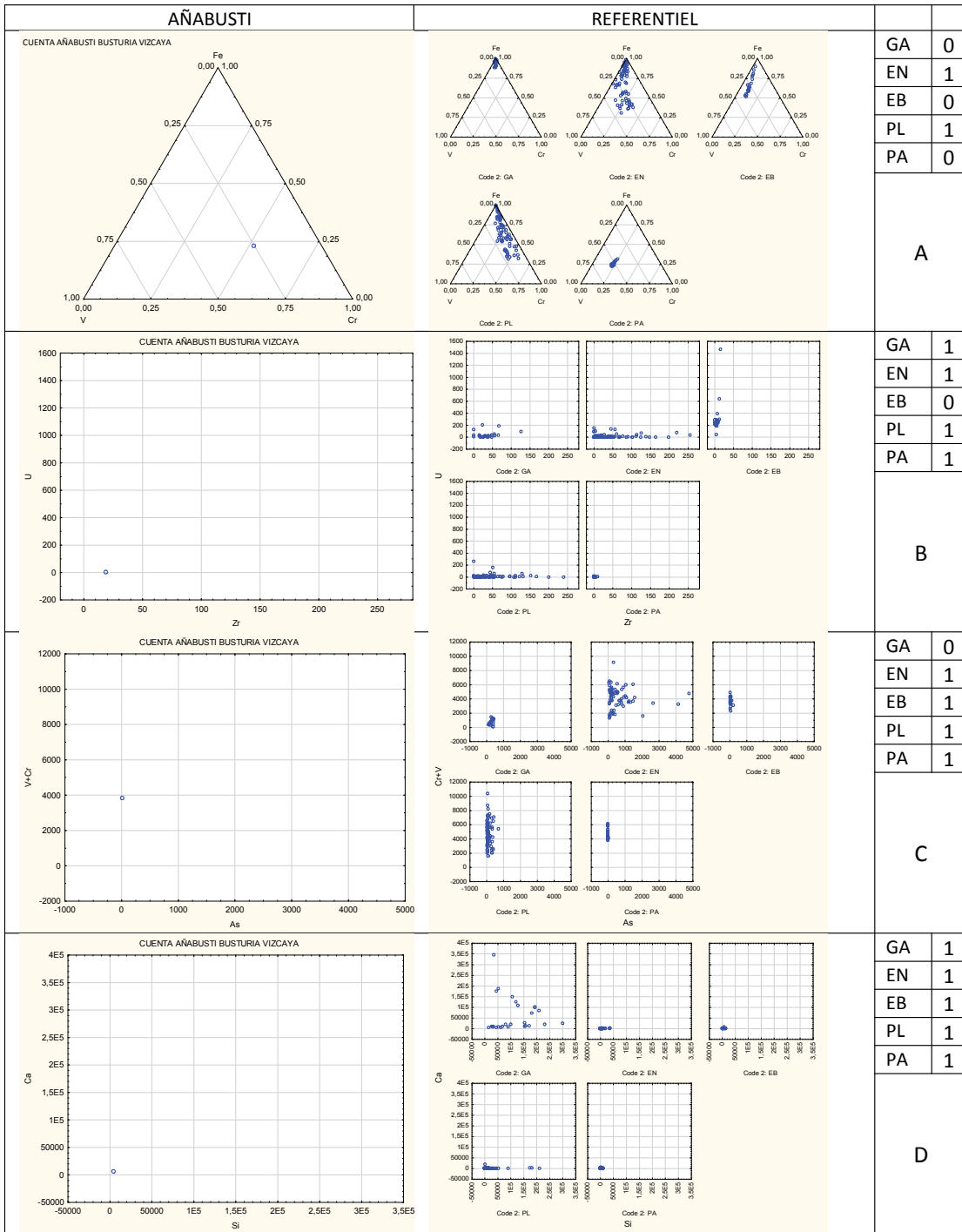
|            | Fe    | Co  | Ni  | Cu  | Zn | Ga  | As   | Rb  | Sr  | Y  | Zr  | Nb | U   | V* | Cr* | Fe* | Cr/V  | Cr+V |
|------------|-------|-----|-----|-----|----|-----|------|-----|-----|----|-----|----|-----|----|-----|-----|-------|------|
| min        | 21138 | 0   | 0   | 71  | 6  | 180 | 256  | 0   | 7   | 0  | 0   | 0  | 0   | 4  | 3   | 83  | 0,42  | 2794 |
| max        | 53704 | 41  | 47  | 297 | 66 | 901 | 1033 | 33  | 260 | 12 | 98  | 0  | 3   | 10 | 9   | 93  | 1,58  | 5461 |
| X          | 32064 | 15  | 10  | 180 | 28 | 414 | 539  | 9   | 120 | 5  | 20  | 0  | 0   | 6  | 6   | 88  | 1,02  | 4106 |
| $\sigma$   | 11523 | 17  | 16  | 94  | 22 | 263 | 287  | 12  | 76  | 4  | 33  | 0  | 1   | 2  | 2   | 3   | 0,43  | 813  |
| $\delta\%$ | 36    | 114 | 165 | 53  | 79 | 64  | 53   | 133 | 63  | 99 | 162 |    | 283 | 39 | 34  | 4   | 41,93 | 20   |



For Olvena, it seems that the origin is Encinasola or Gavá (Figure 11 B), but this apparent not expected result can be due to the burning of these archaeological samples and a possible geochemical change in many parameters of their composition. We agree with other previous authors in a Gavá origin for these materials (Figure 11 C).



Fig. 11: - A: Chemical composition table of variscite objects from the Cueva del Moro, Olvena, Huesca, NE Spain. B: Comparison of chemical analyses of variscite objects with the chemometric model reference frame applied to the site. C: Medium-Long distance mobility and possible provenance for the variscite samples in this site.



| AÑABUSTI |   |   |   |   |       |   |
|----------|---|---|---|---|-------|---|
|          | A | B | C | D | Bilan | Provenance                                  |
| GA       | 0 | 1 | 0 | 1 | 0     | Indétermination<br>Palazuelo/<br>Encinasola |
| EN       | 1 | 1 | 1 | 1 | 1     |   |
| EB       | 0 | 0 | 1 | 1 | 0     |   |
| PL       | 1 | 1 | 1 | 1 | 1     |   |
| PA       | 0 | 1 | 1 | 1 | 0     |   |

SITE NAME : AÑABUSTI  
 Number of objets total :1  
 Number of analyses :1

Non-Univoque response : indetermination Encinasola or Palazuelo

Añabusti: Dolmen de Urdaibai (in Sollube), nowadays practically destroyed (variscite appeared in surface). Neither absolute dating available nor diagnostic materials. Near the dolmen exist an archaeological site with Chalcolithic-Bronze age chronology. We have analysed 1 bead, very altered in surface.

| site     | no | na | Na    | Mg  | Al     | Si   | P      | K     | Ca   | Ti  | V    | Cr   | Mn | Fe   |
|----------|----|----|-------|-----|--------|------|--------|-------|------|-----|------|------|----|------|
| Añabusti | 1  | 1  | 29506 | 504 | 180862 | 4842 | 243491 | 22353 | 5778 | 144 | 1252 | 2578 | 12 | 1147 |

| Co | Ni | Cu  | Zn  | Ga | As | Rb | Sr | Y | Zr | Nb | U | V* | Cr* | Fe* | Cr/V | Cr+V |
|----|----|-----|-----|----|----|----|----|---|----|----|---|----|-----|-----|------|------|
| 8  | 12 | 141 | 108 | 28 | 15 | 9  | 4  | 0 | 19 | 0  | 0 | 25 | 52  | 23  | 2,06 | 3830 |

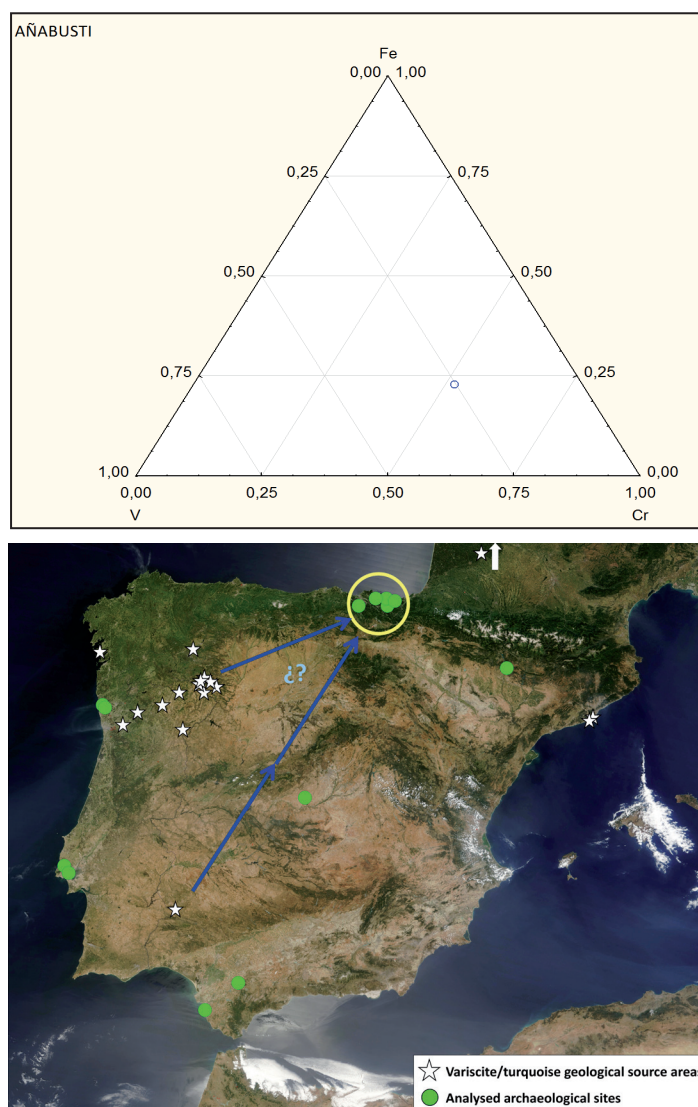
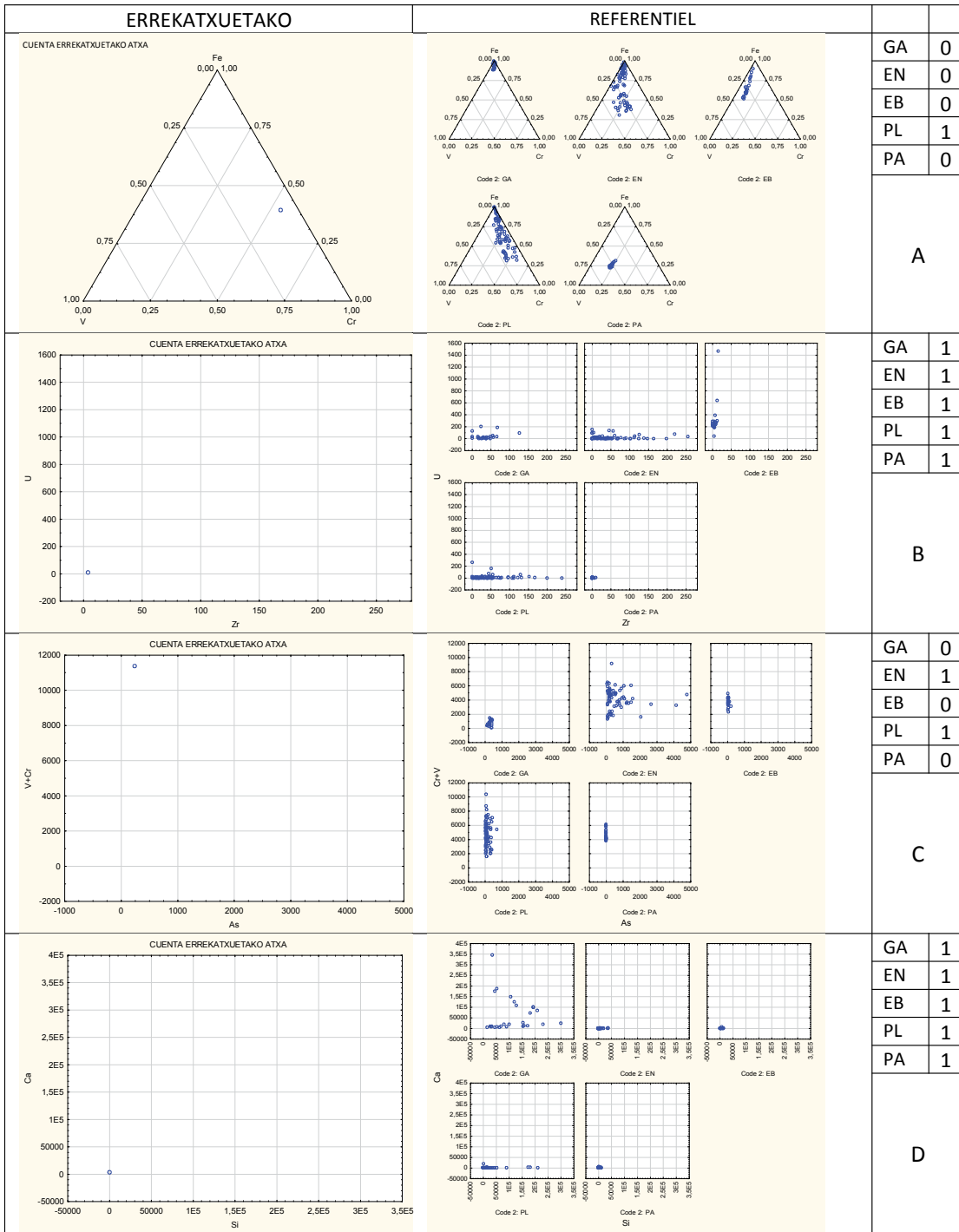


Fig. 12: - A: Chemical composition table of variscite objects from the Dolmen de Urdaibai, Añabusti, Sollube, North Spain. B: Comparison of chemical analyses of variscite objects with the chemometric model reference frame applied to the site. C: Medium-Long distance mobility and possible provenance for the variscite samples in this site.



| ERREKATXUETAKO |   |   |   |   |       |            |
|----------------|---|---|---|---|-------|------------|
|                | A | B | C | D | Bilan | Provenance |
| GA             | 0 | 1 | 0 | 1 | 0     |            |
| EN             | 0 | 1 | 1 | 1 | 0     |            |
| EB             | 0 | 1 | 0 | 1 | 0     |            |
| PL             | 1 | 1 | 1 | 1 | 1     | Palazuelo  |
| PA             | 0 | 1 | 0 | 1 | 0     |            |

SITE NAME : ERREKATXUETAKO  
 Number of objets total : 1  
 Number of analyses : 1

Univocal response : Palazuelo

Errekatxuetako Atxa: Dolmen de Gorbeia, excavated in 2006. No absolute dating available. Main phase of second half of III millennium Cal. BC. Very homogeneous materials, with typical Bell-Beaker culture elements, without ceramic.

| site           | no | na | Na   | Mg | Al     | Si | P      | K    | Ca   | Ti   | V    | Cr    | Mn | Fe   |
|----------------|----|----|------|----|--------|----|--------|------|------|------|------|-------|----|------|
| Errekatxuetako | 1  | 1  | 4900 | 0  | 206834 | 0  | 245427 | 1676 | 3270 | 1310 | 1253 | 10118 | 46 | 7371 |

| Co | Ni | Cu | Zn | Ga  | As  | Rb | Sr | Y | Zr | Nb | U  | V* | Cr* | Fe* | Cr/V | Cr+V  |
|----|----|----|----|-----|-----|----|----|---|----|----|----|----|-----|-----|------|-------|
| 28 | 3  | 87 | 36 | 191 | 240 | 5  | 3  | 0 | 4  | 0  | 10 | 7  | 54  | 39  | 8,08 | 11371 |

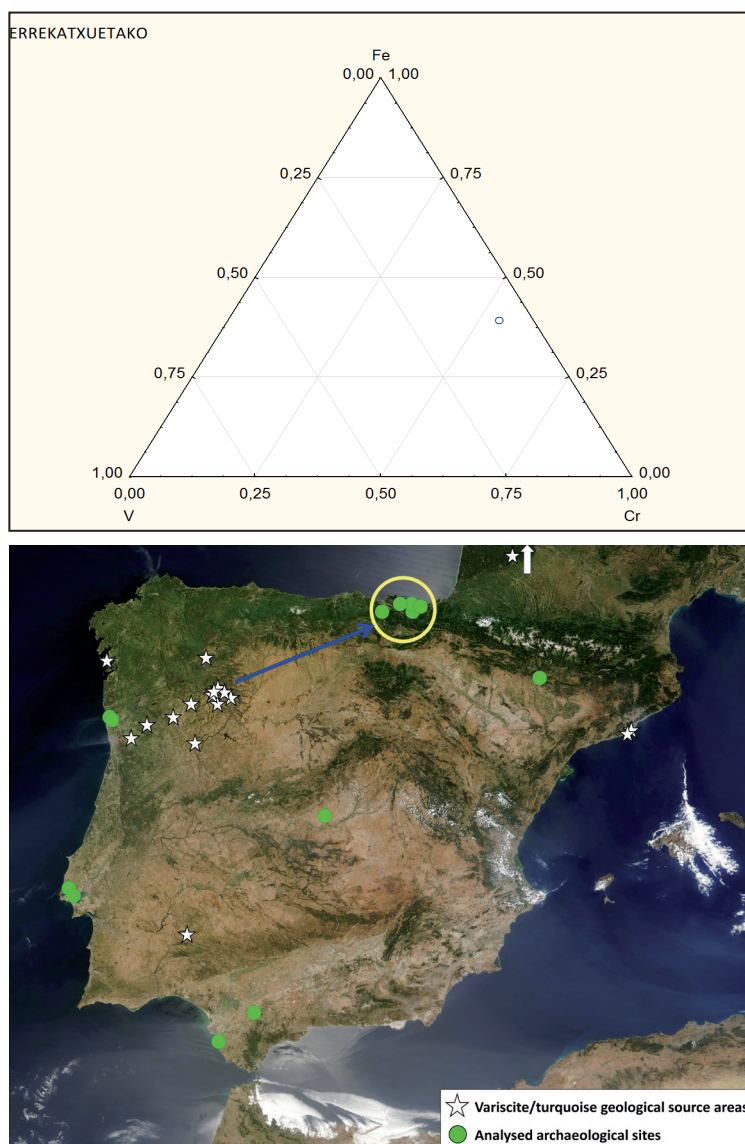
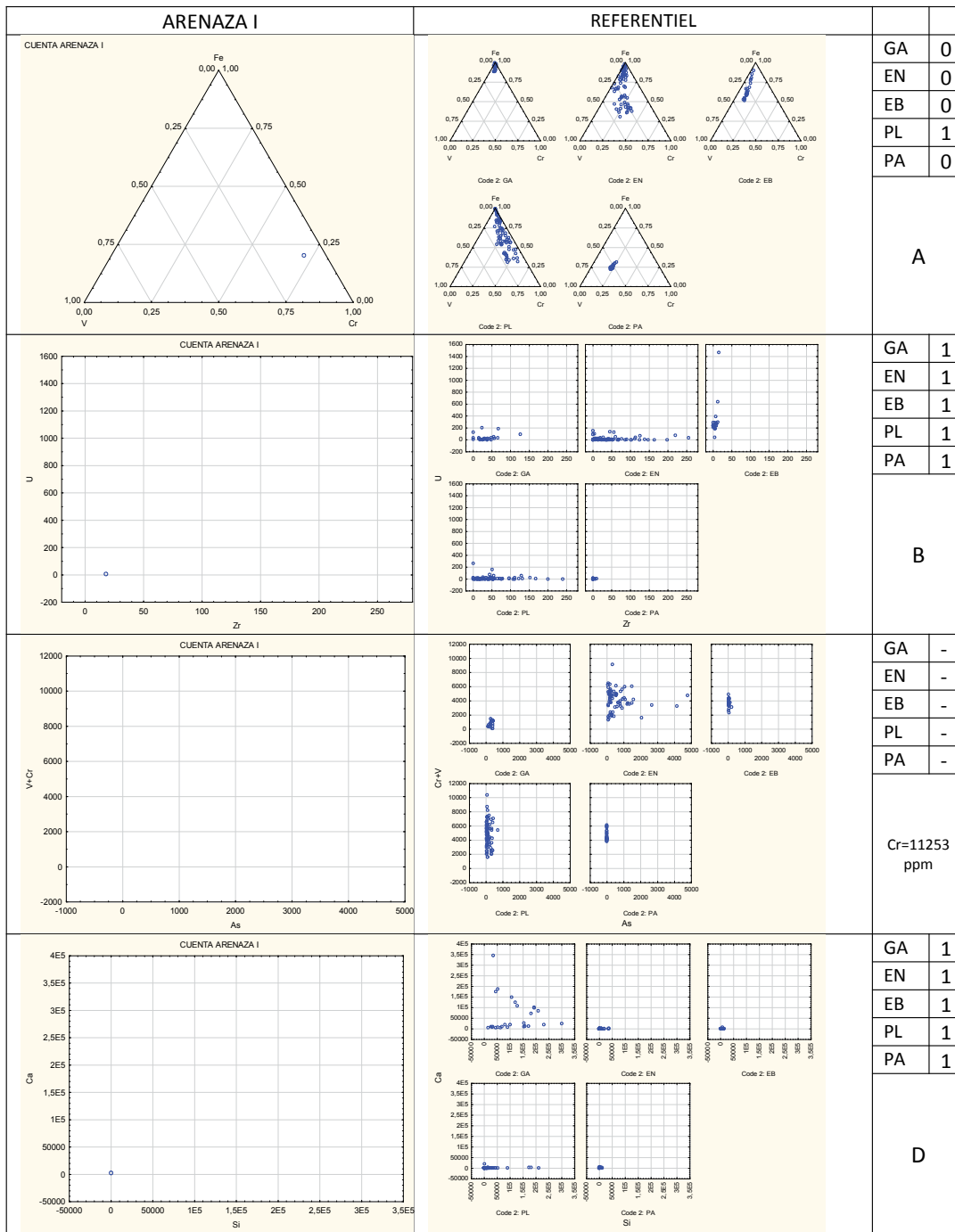


Fig. 13: - A: Chemical composition table of variscite objects from the Dolmen de Gorbeia, Errekatxuetako Atxa, North Spain. B: Comparison of chemical analyses of variscite objects with the chemometric model reference frame applied to the site. C: Medium-Long distance mobility and possible provenance for the variscite samples in this site.





| ARENAZA I |   |   |   |   |       |                               |
|-----------|---|---|---|---|-------|-------------------------------|
|           | A | B | C | D | Bilan | Provenance                    |
| GA        | 0 | 1 | - | 1 | 0     |                               |
| EN        | 0 | 1 | - | 1 | 0     |                               |
| EB        | 0 | 1 | - | 1 | 0     |                               |
| PL        | 1 | 1 | - | 1 | 1 ?   | Palazuelo<br>(Anomalie en Cr) |
| PA        | 0 | 1 | - | 1 | 0     |                               |

|   |  |
|---|--|
| NOM DU SITE : ARENAZA I<br>Nombre d'objets total :1<br>Nombre d'analyses :1 | Réponse non univoque : indétermination - Palazuelo ?<br>Forte anomalie en chrome Cr=11253ppm |
|---|--|

Arenaza: A cave with a good stratigraphy of Chalcolithic and Bronze Age, but also with previous stages of occupation. Unknown age.

| site     | no | na | Na   | Mg | Al     | Si | P      | K    | Ca   | Ti  | V    | Cr    | Mn | Fe   |
|----------|----|----|------|----|--------|----|--------|------|------|-----|------|-------|----|------|
| Arenazal | 1  | 1  | 1898 | 0  | 212063 | 0  | 247163 | 1130 | 2284 | 683 | 1274 | 11253 | 86 | 3182 |

| Co | Ni | Cu | Zn | Ga | As | Rb | Sr | Y | Zr | Nb | U | V* | Cr* | Fe* | Cr/V | Cr+V  |
|----|----|----|----|----|----|----|----|---|----|----|---|----|-----|-----|------|-------|
| 14 | 0  | 69 | 42 | 78 | 59 | 1  | 16 | 0 | 18 | 0  | 7 | 8  | 72  | 20  | 8,83 | 12527 |

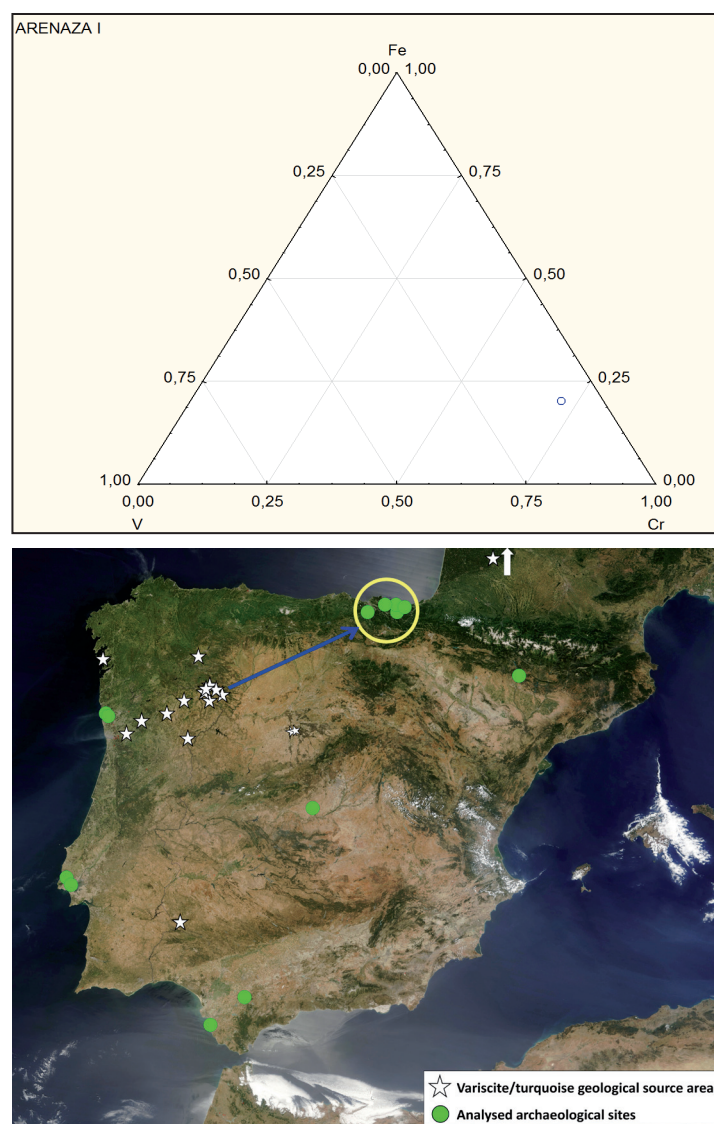
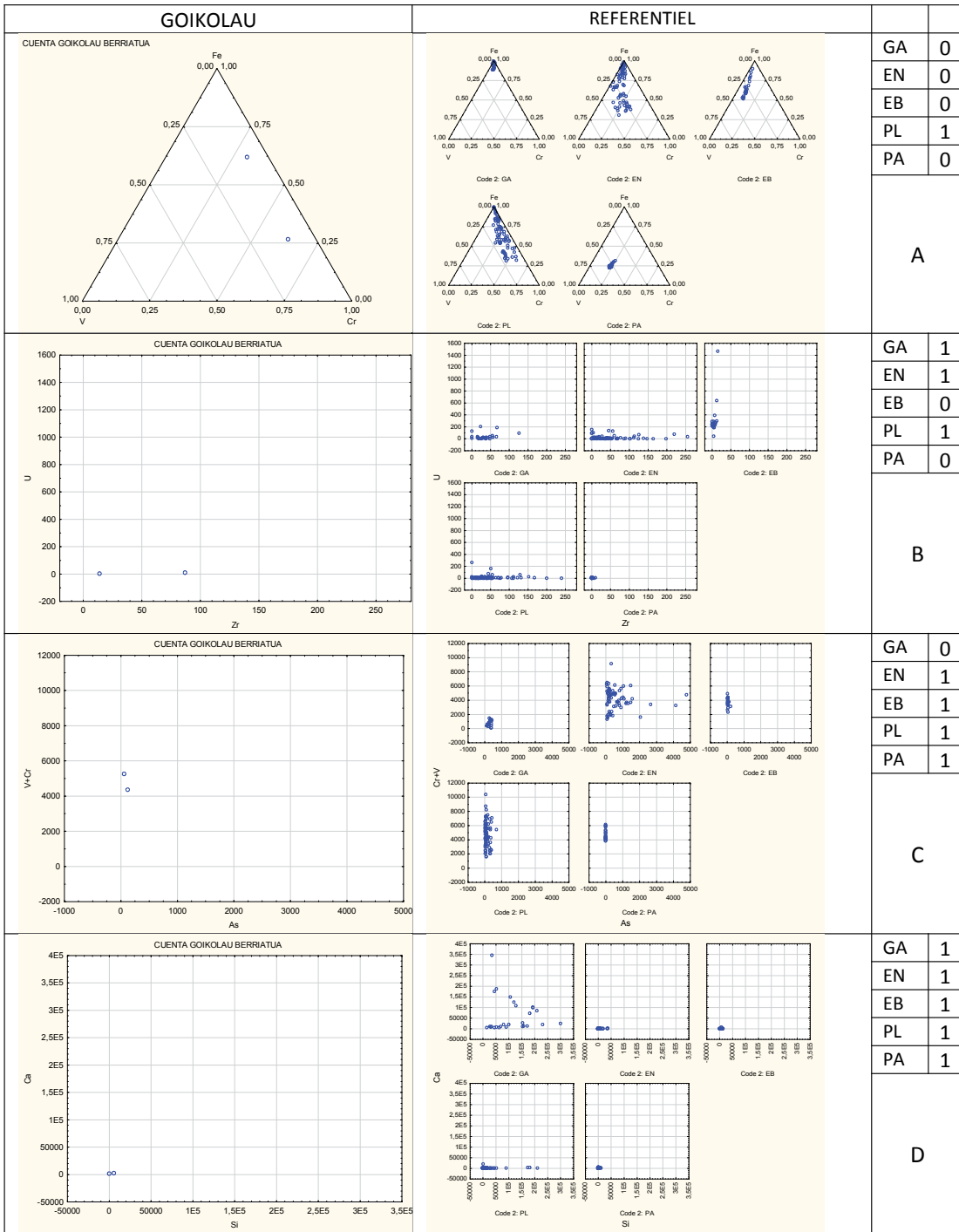


Fig. 14: - A: Chemical composition table of variscite objects from Arenaza cave, North Spain. B: Comparison of chemical analyses of variscite objects with the chemometric model reference frame applied to the site. C: Medium-Long distance mobility and possible provenance for the variscite samples in this site.



| GOIKOLAU |   |   |   |   |       |            |
|----------|---|---|---|---|-------|------------|
|          | A | B | C | D | Bilan | Provenance |
| GA       | 0 | 1 | 0 | 1 | 0     |            |
| EN       | 0 | 1 | 1 | 1 | 0     |            |
| EB       | 0 | 0 | 1 | 1 | 0     |            |
| PL       | 1 | 1 | 1 | 1 | 1     | Palazuelo  |
| PA       | 0 | 0 | 1 | 1 | 0     |            |

SITE NAME: GOIKOLAU  
 Number of objects total :2  
 Number of analyses :2

Univocal response: Palazuelo

Goikolau: Cave with an impressive burial structure. Excavated in 1981 (by C. Basas) (with a variscite necklace, flint points, etc., in a first phase of inhumation). Probably Chalcolithic-Bronze Age.

| site     | no | na | Mg | Al     | Si   | P      | K    | Ca   | Ti  | V   | Cr   | Mn | Fe   |
|----------|----|----|----|--------|------|--------|------|------|-----|-----|------|----|------|
| Goikolau | 2  | 2  | 0  | 213820 | 0    | 251415 | 1108 | 1343 | 431 | 740 | 4505 | 26 | 1887 |
|          |    |    | 0  | 208244 | 5727 | 241953 | 3070 | 2291 | 856 | 896 | 3454 | 7  | 7069 |

| Co | Ni | Cu | Zn | Ga | As  | Rb | Sr | Y | Zr | Nb | U | V* | Cr* | Fe* | Cr/V | Cr+V |
|----|----|----|----|----|-----|----|----|---|----|----|---|----|-----|-----|------|------|
| 3  | 4  | 57 | 15 | 43 | 59  | 4  | 3  | 0 | 14 | 0  | 0 | 10 | 63  | 26  | 6,09 | 5245 |
| 12 | 2  | 65 | 32 | 90 | 123 | 2  | 7  | 0 | 87 | 0  | 8 | 8  | 30  | 62  | 3,85 | 4350 |

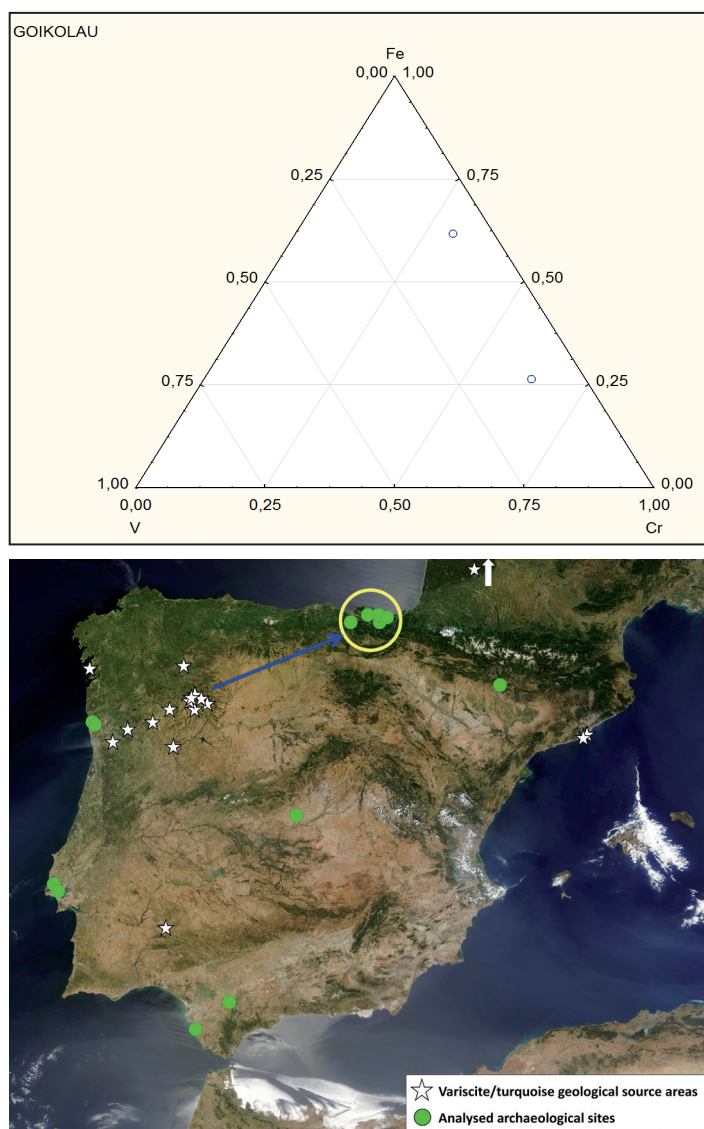
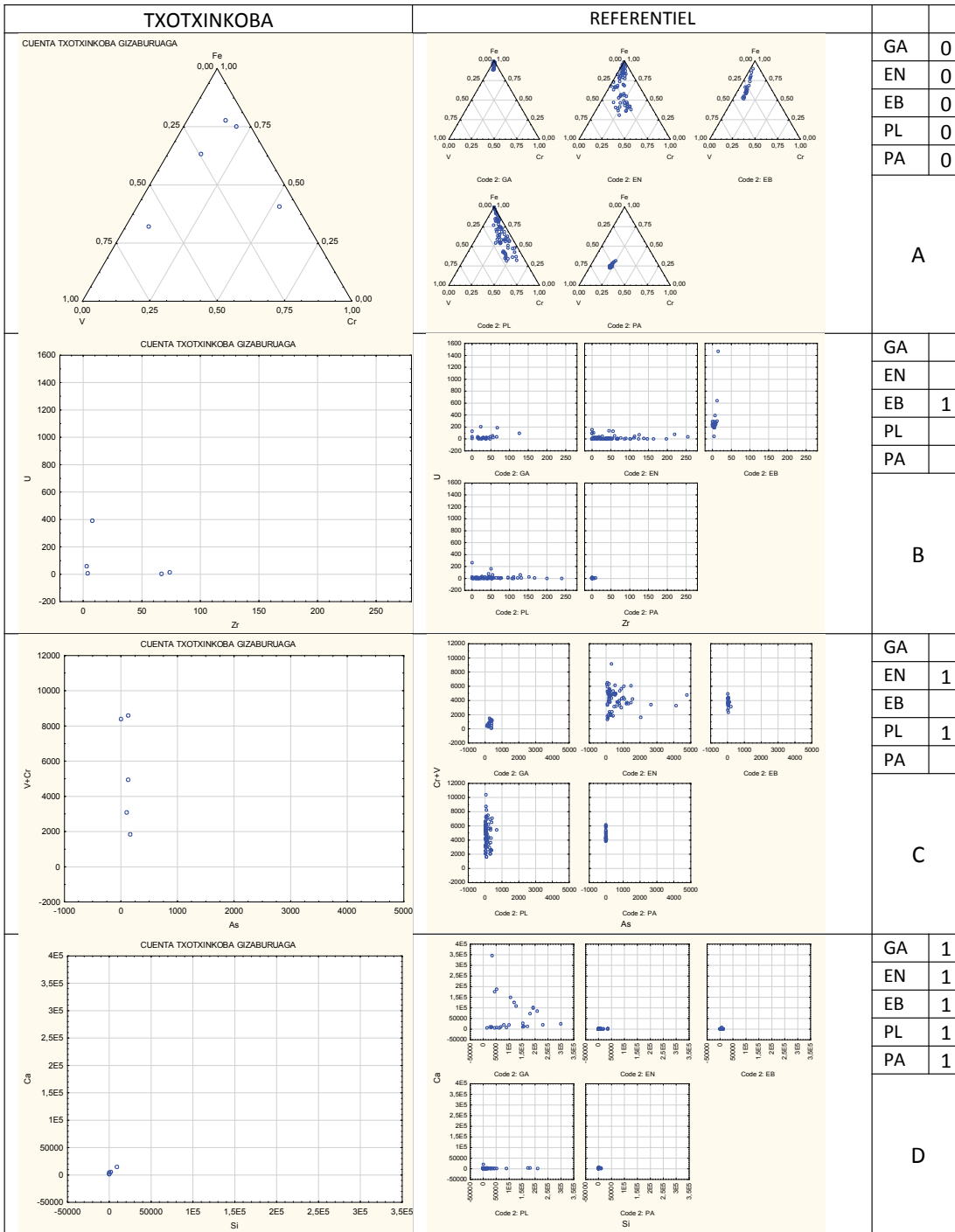


Fig. 15: - A: Chemical composition table of variscite objects from Goikolau Cave, North Spain. B: Comparison of chemical analyses of variscite objects with the chemometric model reference frame applied to the site. C: Medium-Long distance mobility and possible provenance for the variscite samples in this site.



| TXOTXINKOBA |   |   |   |   |       |  |
|-------------|---|---|---|---|-------|--|
|             | A | B | C | D | Bilan | Provenance   |
| GA          | 0 | 0 | 0 | 1 | 0     | Indétermination<br>(Palazuelo,<br>Encinasola,<br>Gavá) |
| EN          | 0 | 0 | 1 | 1 | 0     |  |
| EB          | 1 | 0 | 0 | 1 | 0     |  |
| PL          | 1 | 0 | 1 | 1 | 0     |  |
| PA          | 0 | 0 | 0 | 1 | 0     |  |

SITE NAME: TXOTXINKOBA  
 Number of objects total: 4  
 Number of analyses : 4

Univocal response: Palazuelo, Encinasola, Gavá  
 Non-univocal response: 2 different sources ? to consider separately

Txotxinkoba: Sepulchral cave in the Lea river basin. Excavated by J.M. Apellániz and E. Nolte in 1967. With carinated ceramic. Estimated dating at the “Last Aeneolithic”

| site        | no | na |     | Na   | Mg  | Al     | Si   | P      | K    | Ca   | Ti   | V    | Cr   | Mn | Fe    |
|-------------|----|----|-----|------|-----|--------|------|--------|------|------|------|------|------|----|-------|
| Txotxinkoba | 4  | 4  | max | 2695 | 0   | 209761 | 0    | 242586 | 1474 | 1283 | 65   | 652  | 1041 | 4  | 5283  |
|             |    |    | X   | 8460 | 633 | 213920 | 1866 | 246776 | 5872 | 5351 | 1510 | 2028 | 7646 | 29 | 14815 |
|             |    |    | σ   | 4952 | 158 | 211557 | 467  | 243713 | 3030 | 3018 | 998  | 1167 | 3442 | 18 | 8085  |
|             |    |    | δ%  | 2756 | 317 | 1987   | 933  | 2045   | 2002 | 1906 | 640  | 598  | 3096 | 12 | 4509  |
|             |    |    |     | 56   | 200 | 1      | 200  | 1      | 66   | 63   | 64   | 51   | 90   | 65 | 56    |

|     | Co | Ni | Cu  | Zn  | Ga  | As  | Rb  | Sr  | Y   | Zr | Nb | U   | V* | Cr* | Fe* | Cr/V  | Cr+V |
|-----|----|----|-----|-----|-----|-----|-----|-----|-----|----|----|-----|----|-----|-----|-------|------|
| max | 0  | 2  | 63  | 22  | 2   | 107 | 0   | 2   | 0   | 4  | 0  | 3   | 5  | 12  | 41  | 0,51  | 1833 |
| X   | 23 | 5  | 309 | 293 | 138 | 170 | 12  | 35  | 32  | 74 | 0  | 391 | 24 | 53  | 78  | 8,08  | 8592 |
| σ   | 12 | 3  | 129 | 96  | 80  | 138 | 4   | 12  | 10  | 38 | 0  | 103 | 11 | 25  | 64  | 3,54  | 4609 |
| δ%  | 10 | 1  | 120 | 132 | 66  | 26  | 5   | 16  | 15  | 37 | 0  | 192 | 9  | 19  | 17  | 3,31  | 2947 |
|     | 85 | 47 | 94  | 137 | 83  | 19  | 128 | 133 | 153 | 98 |    | 186 | 81 | 76  | 26  | 93,46 | 64   |

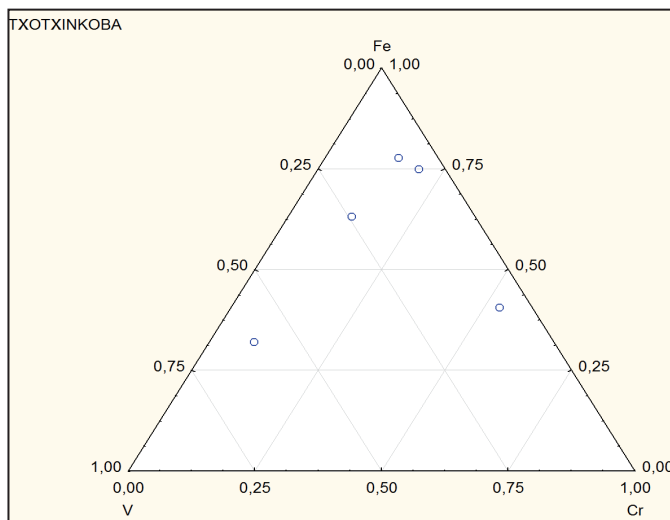
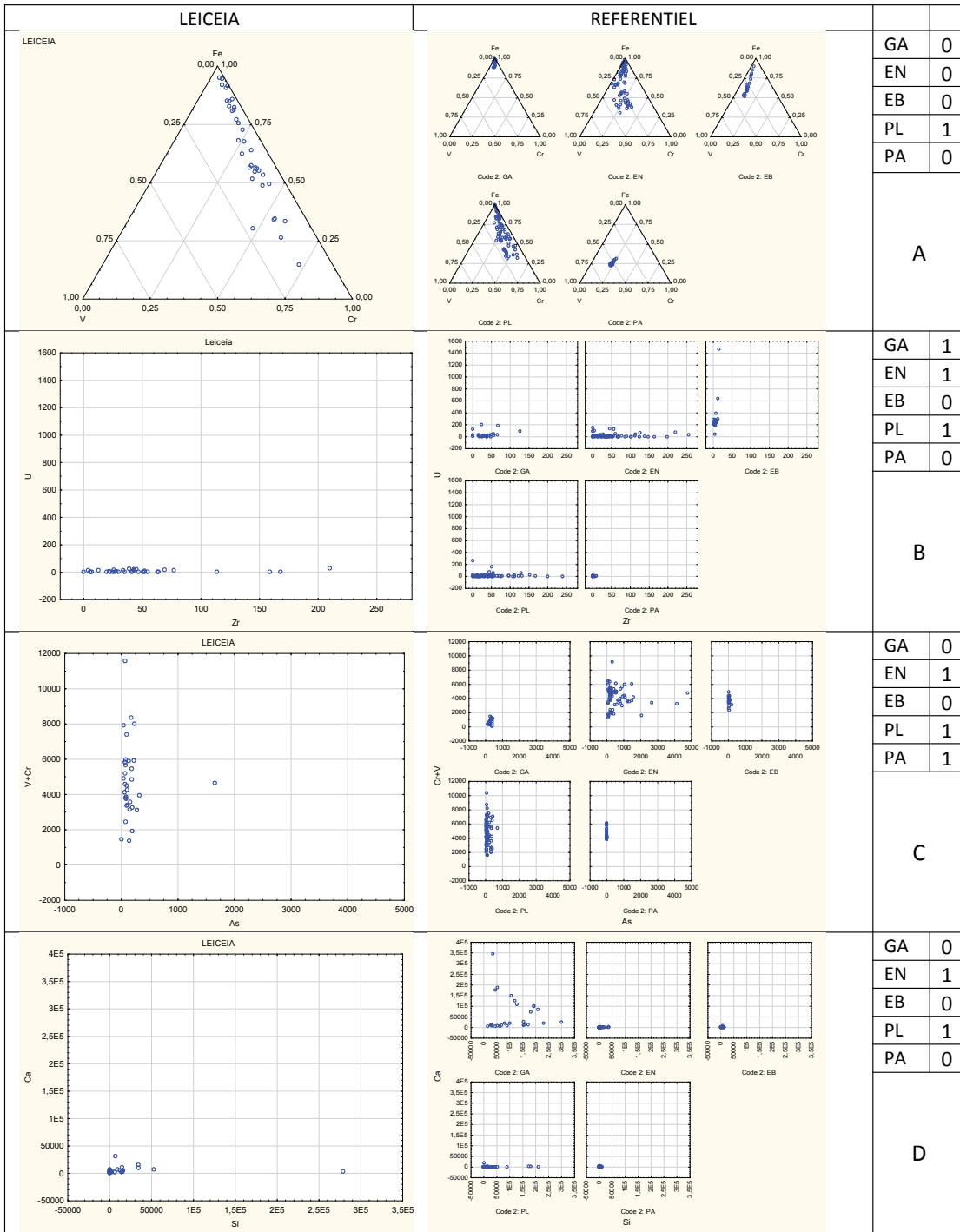


Fig. 16: - A: Chemical composition table of variscite objects from Txotxinkoba Cave, North Spain. B: Comparison of chemical analyses of variscite objects with the chemometric model reference frame applied to the site. C: Medium-Long distance mobility and possible provenance for the variscite samples in this site.



Variscite probably arrived to Bizkaia (N. Spain) specially after the Chalcolithic. It is possible that in the Neolithic existed a punctual “entrance” for variscite in dolmens with a Bell-Beaker phase (as Errekatueta) and in collectives sepulchral caves, with a Chalcolithic-Bronze Age sequence, between the end of the IV millennium and the end of II millennium Cal. BC.



| LEICEIA |   |   |   |   |       |            |
|---------|---|---|---|---|-------|------------|
|         | A | B | C | D | Bilan | Provenance |
| GA      | 0 | 1 | 0 | 0 | 0     |            |
| EN      | 0 | 1 | 1 | 1 | 0     |            |
| EB      | 0 | 0 | 0 | 0 | 0     |            |
| PL      | 1 | 1 | 1 | 1 | 1     | Palazuelo  |
| PA      | 0 | 0 | 1 | 0 | 0     |            |

SITE NAME: LEICEIA  
 Number of objects total :34  
 Number of analyses :34

Univoque response: Palazuelo

**3.2. PIXE analysis Sites from Portugal**

Leceia, Lisbonne Region: Chalcolithic fortified settlement.

| site   | no | na |            | Na   | Mg   | Al     | Si    | P      | K    | Ca    | Ti   | V    | Cr   | Mn | Fe    |
|--------|----|----|------------|------|------|--------|-------|--------|------|-------|------|------|------|----|-------|
| Leceia | 34 | 34 | min        | 1253 | 0    | 170092 | 0     | 213018 | 84   | 533   | 207  | 408  | 902  | 0  | 1367  |
|        |    |    | max        | 8587 | 2987 | 212032 | 52884 | 254925 | 5234 | 30892 | 2811 | 3590 | 7963 | 67 | 79698 |
|        |    |    | X          | 3222 | 347  | 200848 | 7154  | 243327 | 1564 | 4506  | 1177 | 936  | 3910 | 25 | 13892 |
|        |    |    | $\sigma$   | 1529 | 728  | 9812   | 12291 | 10604  | 1150 | 5603  | 618  | 553  | 1629 | 16 | 15791 |
|        |    |    | $\delta\%$ | 47   | 210  | 5      | 172   | 4      | 73   | 124   | 53   | 59   | 42   | 67 | 114   |

|            | Co | Ni  | Cu  | Zn   | Ga  | As   | Rb  | Sr  | Y   | Zr  | Nb | U   | V* | Cr* | Fe* | Cr/V | Cr+V  |
|------------|----|-----|-----|------|-----|------|-----|-----|-----|-----|----|-----|----|-----|-----|------|-------|
| min        | 0  | 0   | 199 | 8    | 19  | 39   | 0   | 0   | 0   | 0   | 0  | 0   | 1  | 3   | 15  | 1,98 | 1357  |
| max        | 30 | 34  | 728 | 1033 | 333 | 1660 | 22  | 218 | 10  | 210 | 0  | 28  | 22 | 73  | 95  | 7,91 | 11553 |
| X          | 12 | 6   | 292 | 82   | 133 | 178  | 3   | 19  | 2   | 50  | 0  | 6   | 7  | 30  | 63  | 4,46 | 4845  |
| $\sigma$   | 8  | 8   | 101 | 178  | 76  | 272  | 5   | 38  | 3   | 47  | 0  | 8   | 4  | 18  | 21  | 1,42 | 2053  |
| $\delta\%$ | 68 | 123 | 34  | 216  | 57  | 153  | 183 | 196 | 127 | 94  |    | 135 | 63 | 60  | 34  | 31,9 | 42    |

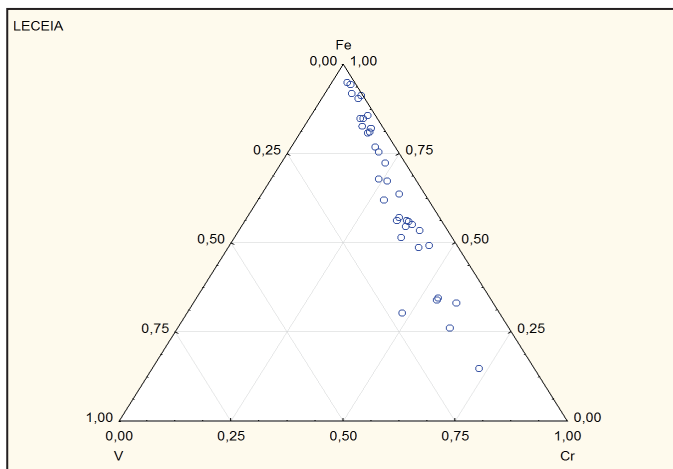
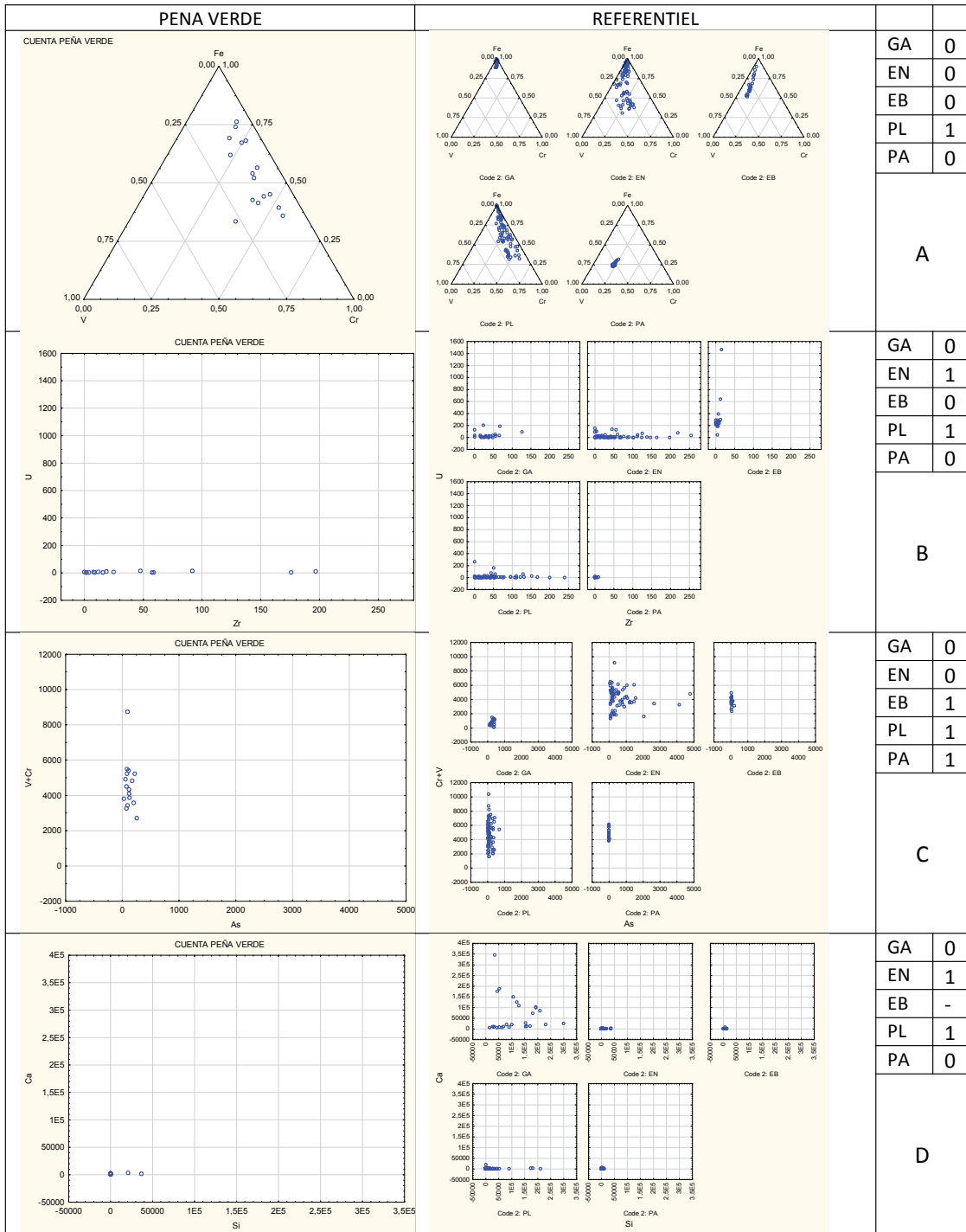


Fig. 17: - A: Chemical composition table of variscite objects from Leceia archaeological site, Portugal. B: Comparison of chemical analyses of variscite objects with the chemometric model reference frame applied to the site. C: Medium-Long distance mobility and possible provenance for the variscite samples in this site.





| PENA VERDE |   |   |   |   |       |            |
|------------|---|---|---|---|-------|------------|
|            | A | B | C | D | Bilan | Provenance |
| GA         | 0 | 0 | 0 | 0 | 0     |            |
| EN         | 0 | 1 | 0 | 1 | 0     |            |
| EB         | 0 | 0 | 1 | - | 0     |            |
| PL         | 1 | 1 | 1 | 1 | 1     | Palazuelo  |
| PA         | 0 | 0 | 1 | 0 | 0     |            |

SITE NAME: PENA VERDE  
 Number of objects total: 15  
 Number of analyses : 16

Univocal response: Palazuelo

Pena Verde, Lisbonne Region: Chalcolithic.

| site       | no | na |            | Na   | Mg | Al     | Si    | P      | K    | Ca   | Ti   | V    | Cr   | Mn | Fe    |
|------------|----|----|------------|------|----|--------|-------|--------|------|------|------|------|------|----|-------|
| Pena Verde | 15 | 16 | min        | 370  | 0  | 191852 | 0     | 231809 | 203  | 322  | 266  | 595  | 1991 | 14 | 2240  |
|            |    |    | max        | 5893 | 0  | 213970 | 36946 | 253269 | 2668 | 3553 | 1775 | 1824 | 7604 | 83 | 10164 |
|            |    |    | X          | 2625 | 0  | 209506 | 3631  | 248653 | 1137 | 1300 | 865  | 1058 | 3517 | 36 | 5728  |
|            |    |    | $\sigma$   | 1543 | 0  | 5209   | 10333 | 6349   | 687  | 836  | 480  | 354  | 1339 | 18 | 2500  |
|            |    |    | $\delta\%$ | 59   |    |        | 2     | 285    | 3    | 60   | 64   | 56   | 34   | 38 | 50    |

|            | Co | Ni | Cu  | Zn | Ga  | As  | Rb  | Sr  | Y   | Zr  | Nb | U   | V* | Cr* | Fe* | Cr/V  | Cr+V |
|------------|----|----|-----|----|-----|-----|-----|-----|-----|-----|----|-----|----|-----|-----|-------|------|
| min        | 6  | 1  | 190 | 6  | 33  | 32  | 0   | 0   | 0   | 0   | 0  | 0   | 5  | 19  | 33  | 1,47  | 2693 |
| max        | 37 | 9  | 558 | 34 | 366 | 263 | 9   | 246 | 20  | 197 | 0  | 12  | 27 | 56  | 76  | 6,72  | 8736 |
| X          | 16 | 4  | 317 | 15 | 135 | 125 | 2   | 37  | 6   | 45  | 0  | 4   | 11 | 35  | 54  | 3,64  | 4574 |
| $\sigma$   | 8  | 2  | 105 | 8  | 93  | 63  | 2   | 67  | 6   | 61  | 0  | 4   | 5  | 12  | 14  | 1,57  | 1389 |
| $\delta\%$ | 52 | 65 | 33  | 55 | 69  | 50  | 124 | 183 | 108 | 134 |    | 105 | 49 | 34  | 26  | 43,25 | 30   |

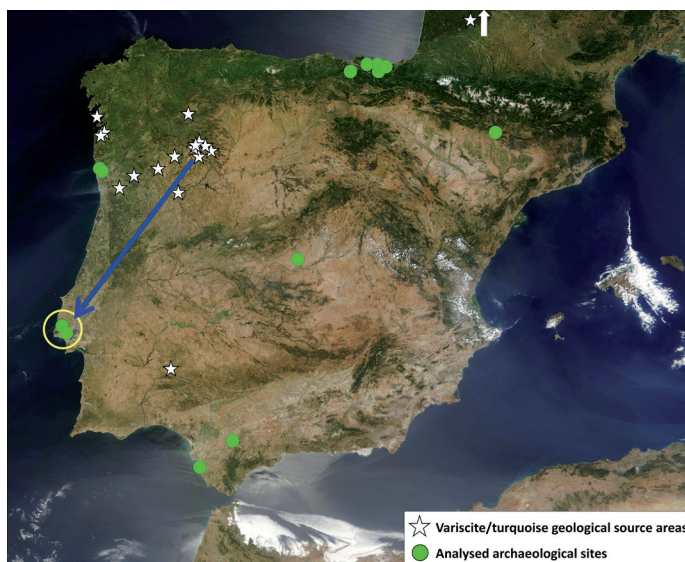
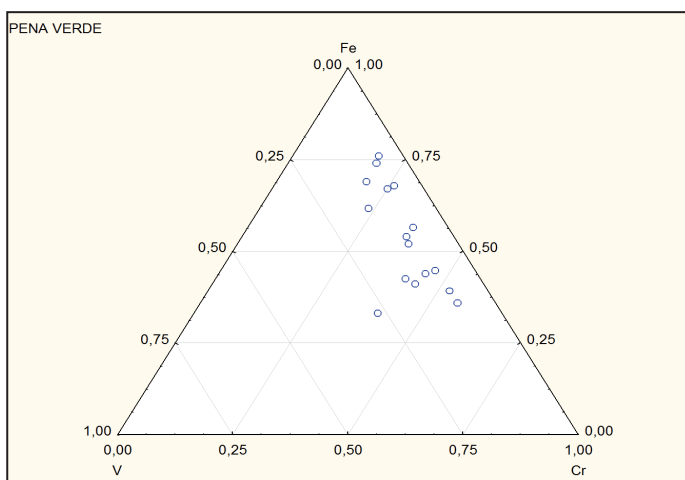
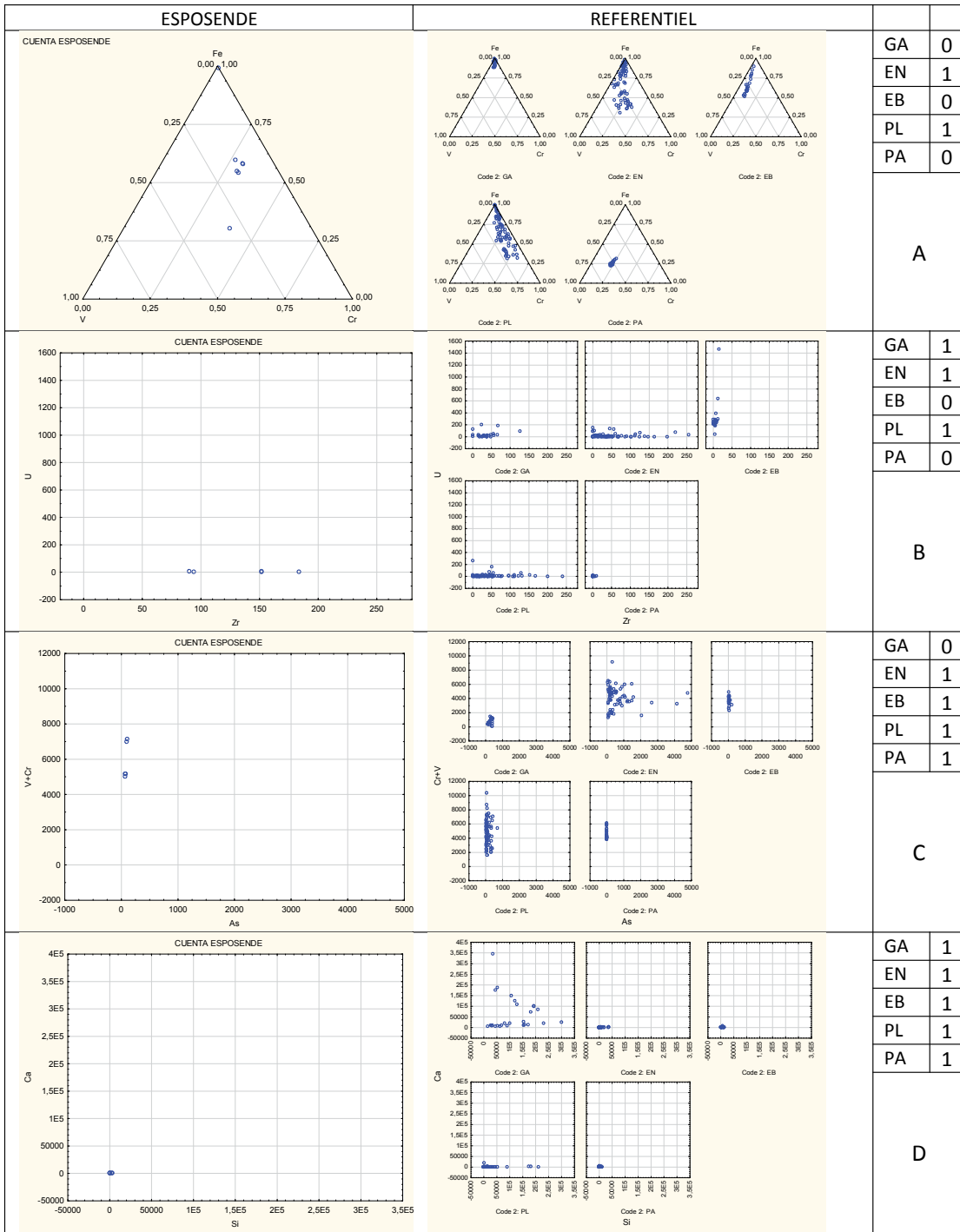


Fig. 18: - A: Chemical composition table of variscite objects from Pena Verde archaeological site, Portugal. B: Comparison of chemical analyses of variscite objects with the chemometric model reference frame applied to the site. C: Medium-Long distance mobility and possible provenance for the variscite samples in this site.



| ESPOSENDE |   |   |   |   |       |   |
|-----------|---|---|---|---|-------|---|
|           | A | B | C | D | Bilan | Provenance                                    |
| GA        | 0 | 1 | 0 | 1 | 0     | Indétermination<br>(Palazuelo<br>/Encinasola) |
| EN        | 1 | 1 | 1 | 1 | 1     |   |
| EB        | 0 | 0 | 1 | 1 | 0     |   |
| PL        | 1 | 1 | 1 | 1 | 1     |   |
| PA        | 0 | 0 | 1 | 1 | 0     |   |

SITE NAME: ESPOSENDE  
 Number of objects total : 2  
 Number of analyses : 6

Non-Univocal response: indétermination - Palazuelo and/or Encinasola

Esposende. North Portugal. Two collar beads.

| site      | no | na |     | Na   | Mg  | Al     | Si   | P      | K    | Ca   | Ti   | V    | Cr   | Mn  | Fe   |
|-----------|----|----|-----|------|-----|--------|------|--------|------|------|------|------|------|-----|------|
| Esposende | 2  | 6  | min | 379  | 0   | 207972 | 0    | 247792 | 409  | 111  | 292  | 1696 | 2560 | 0   | 1968 |
|           |    |    | max | 3416 | 804 | 210429 | 3294 | 253598 | 1331 | 1146 | 1635 | 1961 | 5164 | 34  | 9787 |
|           |    |    | X   | 1452 | 134 | 209528 | 1166 | 251178 | 889  | 423  | 1234 | 1833 | 3832 | 13  | 6883 |
|           |    |    | σ   | 1034 | 328 | 1012   | 1488 | 2605   | 397  | 377  | 491  | 132  | 1048 | 13  | 2911 |
|           |    |    | δ%  | 71   | 245 | 0      | 128  | 1      | 45   | 89   | 40   | 7    | 27   | 101 | 42   |

|     | Co | Ni | Cu  | Zn | Ga  | As  | Rb  | Sr  | Y   | Zr  | Nb | U  | V* | Cr* | Fe* | Cr/V  | Cr+V |
|-----|----|----|-----|----|-----|-----|-----|-----|-----|-----|----|----|----|-----|-----|-------|------|
| min | 1  | 0  | 235 | 6  | 100 | 69  | 0   | 0   | 0   | 2   | 0  | 0  | 12 | 27  | 30  | 1,31  | 4521 |
| max | 26 | 5  | 479 | 20 | 168 | 107 | 3   | 8   | 8   | 184 | 0  | 8  | 30 | 39  | 60  | 2,63  | 7124 |
| X   | 13 | 2  | 293 | 11 | 126 | 83  | 1   | 2   | 4   | 112 | 0  | 4  | 16 | 31  | 53  | 2,09  | 5665 |
| σ   | 11 | 2  | 92  | 5  | 30  | 16  | 1   | 3   | 4   | 65  | 0  | 3  | 7  | 4   | 11  | 0,5   | 1109 |
| δ%  | 82 | 89 | 31  | 50 | 24  | 19  | 245 | 214 | 111 | 58  |    | 88 | 43 | 14  | 21  | 23,79 | 20   |

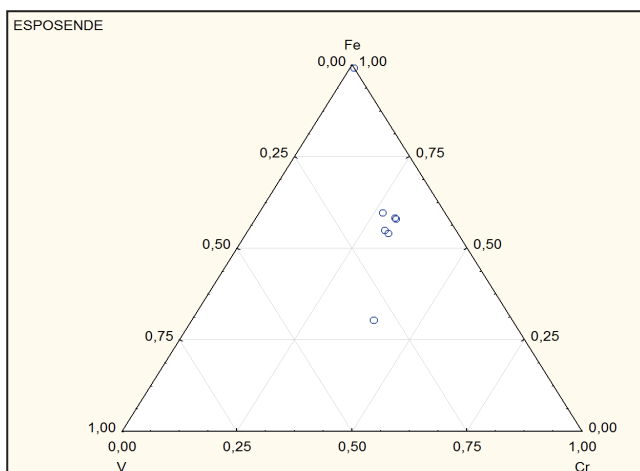


Fig. 19: - A: Chemical composition table of variscite objects from Esposende archaeological site, Portugal. B: Comparison of chemical analyses of variscite objects with the chemometric model reference frame applied to the site. C: Medium-Long distance mobility and possible provenance for the variscite samples in this site.

## Conclusions

Using techniques for geochemical analysis with a non-destructive or minimally invasive character for the sample, such as PIXE-PIGE and LA-ICP-MS spectroscopy, we have analysed a broad set of archaeological samples from the Recent Prehistory in the Iberian Peninsula and practically all the European geological deposits of phosphate minerals as variscite and turquoise, that appear associated with them.

We have confirmed that a relatively good discrimination has been obtained through an interactive geochemical model using specially the Fe-Cr-V relationship, represented by a triangular diagram, joined to the study of elementary relationships between the Zr-U, Si-As, Mg-Ca contents and another chemical elements presence.

These geochemical results, on these archaeological samples obtained especially by PIXE and confirmed by LA-ICP-MS techniques, were discussed in relation to their possible provenance areas, related with the three main geological areas with variscite and turquoise outcrops in the Iberian Peninsula: Palazuelo de las Cuevas-San Vicente area, that included other sites as El Bostal and Bragança district in Portugal; Pico Centeno mines, Encinasola area, in Huelva province, SW Spain; and Gavá mines in Catalonia, NE Spain. Other possible sources in Iberia and the rest of Europe have also been checked.

Some of the provenances of the groups of archaeological objects of a particular site and chronology have been very clearly identified.

Thus, the variscites of the Dolmen de Alberite I, in Cadiz province, South Spain, seem to come from the area of Encinasola, Huelva, the outcrop geographically closest to that dolmen. However in the Dolmen del Tomillo, we do not have a great information from a statistical and geochemical point of view as there is only a single bead necklace, and it could come from Encinasola or Palazuelo.

The only necklace bead in variscite found in the Middle Neolithic necropolis of the Campo de Hockey, Cádiz, an object very interesting for presenting a reuse, seems to come from the Encinasola, Huelva source-area.

At the sites of Leceia and Pena Verde, in the region of Lisbon, variscite beads come from the area of Palazuelo de las Cuevas, Zamora, when they are actually closer to the source-area of Encinasola geological area.

At the archaeological site of Valle de las Higueras, Toledo, in the peninsular central area, the provenance seems to be the area of Palazuelo de las Cuevas, Zamora.

The analytical data of other authors for the origin of the ancient Neolithic necklace beads of Cueva del Moro, Olvena, South of the Pyrenees are confirmed, with a possible origin in the mines of Gavá, Barcelona, although these samples could have been burned, which seem to have modified partially their geochemistry, showing some anomalous data.

The different sites of the Basque Country present a great diversity, with many analysed beads of different nature to the phosphate minerals, there are several cases of compositions based on talc and other ferromagnesium silicates.

The variscites appear to come from Palazuelo, although in some cases it is difficult to determine its origin since they have a high degree of surface chemical alteration and patinas.

An apparent relationship between some of the chronologies of archaeological objects and the origin of the variscite used for its production is observed.

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variscite ornaments in Western Europe. (CALLAIS)". (2010) developed in the UGEA-PHAM/SCCYT, UCA and the AGLAE Laboratory, Centre de Recherche et de Restauration des Musées de France- UMR 171, Musée du Louvre, Paris, France. Also, thanks to a grant of the Research Coordinate Action ACC-241-RNM-2001, granted by Junta de Andalucía government and to Dr. Jesús de la Rosa, UHU, for his help in the LA-ICP-MS determinations. I wish to thank for their help and comments as well as for access to samples of museums to: Prof. Joao Luis Cardoso, (Universidade Aberta de Lisboa), Prof. Primitiva Bueno (Univ. Alcalá de Henares), Prof. Pilar Utrilla (Univ. Zaragoza), Dr. Vicente Baldellou (Museo de Huesca), J.M. Gutiérrez (Museo de Villamartín), Dr. I. García Camino (Bilbao Archaeological Museum), Braga Museum (Portugal), and for their help in sampling and field trips over the last 20 years to Mr. Emilio Sastre, Mr. Carmelo Bermejo, Ms. Trinidad Hernández, Mr. José María Carrascal, Ms. Ana Durante, Ms. María J. Bóveda and Ms. Susana Rodríguez.

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