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PIXE analyses over a long period: the case of Neolithic variscite jewels from Western Europe (5<sup>th</sup>-3<sup>th</sup> millennium BC).

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## Abstract

PIXE analysis of archeological variscite beads and pendants from the Neolithic period that were excavated in Spain, Portugal and France and of variscite geological references samples from European occurrences were carried out from 1999 to 2013 in order to trace back the circulation of this precious gemstone over three millennia. Transformations of the AGLAE external beam system and progress in spectrum processing have induced some apparent compositional variation, affecting in particular the phosphorus/aluminum ratio. This long term evolution has been taken into account with the help of geostandards to build a large and coherent geochemical database of minor and trace elements in variscite. This database allowed us to determine the provenance of the raw material and thus of the circulation of the jewels.

**Keywords:** PIXE, variscite, calibration, provenance, Prehistory.

## Introduction

The provenance and the circulation of variscite - a precious stone resembling turquoise with  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  formula with iron traces - that was employed for ornaments of Early Neolithic to Chalcolithic periods (5<sup>th</sup> - 3<sup>rd</sup> millennium BC) in Western Europe represent a main archeological issue (fig.1). On one hand, many Prehistoric occupations with variscite artifacts have been excavated, and on the other several occurrences of this mineral have been located (fig.2). The question of the provenance of the archeological variscite has motivated two research programs in Spain and France that were undertaken simultaneously and independently in the 1990. The first results obtained using LA-ICP-MS and PIXE showed that the variscite of the studied artifacts from Western France Neolithic graves were mined from Iberian deposits [1,2]. However, it was necessary to extend this work to a larger number of archeological artifacts and geological references samples to confirm this hypothesis and to establish on statistically significant grounds the origin of each bead and pendant from all archeological sites [3]. It was decided to further analyze samples from France and Spain using the transnational access to the AGLAE facility of the C2RMF because of its high analytical performance, central location and secure environment for the investigation of these precious artefacts.

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The delays required to organize the transport of artifacts from museums and archaeological deposits in Spain, Portugal, United Kingdom and France to the C2RMF, to complete field missions in Western Europe variscite deposits to collect geological references from Spain, Portugal, France, Italy, England, and lastly to regularly apply to the "Call for Proposals" for the transnational access to the AGLAE facility explain the long duration of this program. Overall, 1720 analyses of major, minor and trace elements in variscite and in geostandards were carried out in thirteen runs from one to four days each distributed over 13 years, from 1999 to 2013. During this period, almost all Neolithic jewels from France and a large number of archeological artifacts from Iberian Peninsula were analyzed by PIXE. Variscite reference samples from all known ancient mines and from other geological outcrops identified in Western Europe were also analyzed.

## **Experimental**

During that period, the AGLAE external beam line underwent experimental and spectrum processing improvements and consequently, the measuring conditions have evolved over time [4, 5]. Some parameters have been kept constant, such as the proton beam energy (3 MeV) and intensity (about 2 nA to avoid any beam-induced damage), the geometry (low and high energy detectors placed 45° relative to the beam axis), the filters used (a helium flux of 1-2 l/min, permanent magnets to deflect backscattered particles away from the low energy detector, 50- $\mu$ m thick aluminum absorber for the high energy detector). The mean analysis time per sample was about 4 minutes and 24 chemical elements were quantified: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, U. A 5-mm<sup>2</sup> pellet of the international geostandard Diorite DR-N [6] was analyzed at the beginning and the end of each run, and regularly within the sequence. In addition, from 2004 onwards, a variscite archaeological bead (MeH40) coming from the archaeological site of Mane-er-Hroek, Locmariaquer (Morbihan, France) was promoted to a standard status and was systematically analyzed. The beads and pendants were directly submitted to the beam without preparation apart from cleaning with alcohol. On the other hand, some experimental parameters have evolved during the period [4, 5]. The Si(Li) detectors were replaced subsequently to failures or improvements: the first Si(Li) detectors employed were from KeveX, the crystals of which were later replaced by ones from Gresham. Eventually the Si(Li) detectors were replaced by SDD detectors. All detectors featured different crystals specifications: thickness and active surface, windows technology (1-2  $\mu$ m carbon absorber to block light in front of the SuperQuantum and MOXTEK thin entrance windows) and finally an ice layer buildup in front of the detector crystal. During the 1999-2005 period, the measuring strategy was to carry out single spot analyses (100- $\mu$ m diameter) which was later changed to scanned area (20  $\mu$ m, 500x500 $\mu$ m area) to better reflect the concentration of such heterogeneous samples. The spectrum treatment strategy was to process the low energy spectra with GUPIX in iterative mode with a fixed H value, forcing the concentration of main elements in oxide form to sum up to 100%. The iron value determined in this step was subsequently used to calibrate the trace elements concentrations from the high energy spectra. The filters thickness parameters were continuously adjusted. During the period of 13 years, the GUPIX program was upgraded several times (from DOS-based GUPIX to GUPIXWIN v 2.3) using incompatible parameter and data file formats.

## **Results and discussion**

### Reproducibility and reliability

Two main conclusions were deduced from the evolution of concentrations for major and minor elements obtained on 151 DR-N analyses (fig.3). First, concentrations variations were more important before 2005 for most elements: Na, Mg, Al, Si, K, Ca and Fe. These variations are explained by the fact that the external beam is fixed and the grain size of the powder too coarse compared to the beam diameter (30- $\mu$ m spot size). Indeed diorite is a multi-phased rock containing quartz, plagioclase, alkali feldspar, micas and minors minerals. After 2005, the grain effect was removed by scanning the pellet under the beam; the results obtained were then more representative of the average composition and the reproducibility was thus improved. Whereas this problem of heterogeneity exists for DR-N powder pellet, it is not the case for variscite samples. Indeed, this mineral occurs in homogeneous nodules or veins in micro- or cryptocrystalline form, with sub-micronic crystal grains much smaller than the beam size. The size of the scanned variscite area was 0.5x0.5mm. Note that the scanning was obtained exclusively by a mechanic displacement of the sample before 2012 and after, by a combination of vertical magnetic beam deflection and mechanic translation [5]. Overall, the PIXE concentration of major and minor elements obtained on the DR-N pellet varied within 5% from the recommended values. Natural variscite should exhibit a variable composition as it result from a solid solution of pure variscite [AlPO<sub>4</sub>.2H<sub>2</sub>O] and strengite [FePO<sub>4</sub>.2H<sub>2</sub>O] end-members according to Al and Fe substitutions. Stoichiometry of pure variscite is Al<sub>2</sub>O<sub>3</sub>=41.8% and P<sub>2</sub>O<sub>5</sub>=58.2% on anhydrous base and mass atomic P/Al ratio of 1.148. The substitution of Al atoms by Fe atoms induces an increase of P/Al ratio. Variscite also incorporates transition elements like Cr, V, As and its green color is generally ascribed to the presence of Cr<sup>+++</sup> [7]. Note that important elements like P or Cr, V and As are not present in the DR-N standard and thus cannot be checked.

Let us first comment the major elements in the variscite, i.e. Al and P. When the P/Al ratio for all variscite samples is plotted as function of time (fig.4), a variation between 1.1 and 1.5 is observed despite that the DR-N data from the same runs present a good reproducibility and reliability. In particular, three marked sequences of analyses can be noted, corresponding to the use of different detectors. This variation is probably related to the detection efficiency for P, because variscite is mainly composed P and Al in a dependent way (P<sub>2</sub>O<sub>5</sub>+Al<sub>2</sub>O<sub>3</sub>=100%) so that a small variation of P<sub>2</sub>O<sub>5</sub> will induce *de facto* a variation of Al<sub>2</sub>O<sub>3</sub> that will be amplified in the P/Al ratio. Two hypotheses can be proposed to explain this long-term variation: first, an instrumental effect like a change of in the low energy detector efficiency for P and/or Al (e.g. ice layer buildup or variable carbon filter thickness). Second, this effect could also derive from the spectrum processing using GUPIX, more precisely by selection of inadequate parameters in the detector description (e.g. dead layer thickness of Si(Li) detector, tailings). For example, a 1- $\mu$ m dead layer of would reduce the detector efficiency for P by 20%, which would be left unnoticed in the DR-N composition.

This effect is well illustrated in table 1 where analyses of the variscite bead standard (MeH40) during three periods extending over 9 years are reported. Compared to period 1, in period 2 we note a 1.4% decrease of P<sub>2</sub>O<sub>5</sub> and in period 3 a further 3% decrease that induce an apparent increase of Al<sub>2</sub>O<sub>3</sub>, while Fe<sub>2</sub>O<sub>3</sub> concentration is stable. The corresponding P/Al ratio decreases from 1.321 to 1.242 and finally to 1.176. If in the final campaign the strengite molecule is discarded (1.83% of Fe<sub>2</sub>O<sub>3</sub>), the P/Al ratio closely approaches the value for pure variscite (P/Al=1.148). Note that this run was the first performed using SDD detectors (no dead layer) and GUPIXWIN with parameters adjusted in accordingly [5].

As for the trace element concentrations, the variations are less pronounced than for major elements, as is shown in figure 5 which depicts the evolution of Cr, V, Fe and Ga in the MeH40 variscite bead for over 9 years. This can be explained by the fact that the Fe pivot element value extracted from the major element spectrum used to normalize the trace element

concentrations is less affected. The geochemical database based on the PIXE analyses of archeological and geological variscite over a period of 13 years appears to be coherent. All elements except P and Al, the two major elements of variscite, can be used to compare composition of the gemstone for provenance purposes.

### Geographical references

Variscite is a rare mineral in Western Europe and the potential sources available to Neolithic people are limited (fig. 2). Three ancient exploitations are known, all located in Spain: Gavà - Can Tintorer Neolithic mines (Gavà, Barcelona), Encinasola - Pico Centeno mines (Encinasola, Huelva) and Palazuelo de las Cuevas-San Vicente de la Cabeza-El Bostal (Aliste, Zamora). All reference samples of these three ancient exploitations were collected in archaeological mining waste. Their chemical composition obtained by PIXE is probably very similar to the rocks used in the Neolithic to make jewelery. A single occurrence is known in France, Pannecé (Loire-Atlantique), discovered in 1970 in La Floquerie quarry that do not show any trace of ancient mining. Other occurrences might exist but were probably not exploited either because the deposit was too poor in variscite or yielded nodules too small to produce jewelry: Ervedosa, Deilao and Guadramil (Bragança, Portugal), Sarrabus (Cagliari, Italy).

It is worth noting that several geological samples studied proved to be made not of variscite but of turquoise  $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ : Punta Corveiro (Pontevedra, Spain), Montebras (Soumans, France), St Austell (Cornwall, England). Overall, 194 PIXE analyses were performed on variscite and on a few strengite or turquoise samples from 14 localities.

In general, the composition for minor and trace elements in variscite samples from a particular deposit exhibit a correlated spread of values. This phenomenon is well known in geology by which specific petrogenetic processes in rocks induce during their formation characteristic geochemical trends that can be used as provenance fingerprints.

The ternary diagram representing chromium, vanadium and iron concentrations illustrates such fingerprints. In figure 6 is represented the values measured in several samples from the three Spanish variscite mines and from the Pannecé modern quarry (Brittany, France). The deposits from North-West Spain which comprise Palazuelos de las Cuevas and San Vicente de la Cabeza sources is characterized by a very large and correlated range of Cr and Fe concentrations whereas V appears always in low concentrations, leading the Cr/V ratio lying between 1.6 and 8. The variscite samples from Encinasola exhibit large range with important Fe concentrations and a large spread of Cr and V values, with the Cr/V ratio ranging between 1.6 to 0.2.

Contrary to the two previous mines, the variscite from Can Tintorer at Gavà and from Pannecé in Brittany (France) present an homogeneous composition that explains the strong regrouping of their points in the Cr-V-Fe diagram. Conversely, Gavà samples appear almost completely deprived in Cr and V and proportionally enriched in Fe. The Pannecé deposit yields variscite samples richest in vanadium and the most depleted in chromium and iron with a Fe/Cr ratio equal to 1.

On the base of three minor and trace elements, Cr, V and Fe, we could confirm that each deposit present geochemical characteristics including large variation of concentrations. Other features of trace element not discussed here, allowed us to further differentiate variscite sources: for example, high concentrations of Ca and As for Gavà samples, low Ga, high Zn concentrations for Deilao, Ervedosa and Sarrabus and high U level in El Bostal variscite.

## Examples of provenance of archaeological artifacts

PIXE analyses were carried out on 851 beads or pendants from 39 archaeological sites. Archaeological sites are characterized by their localization and their dating and many variscite beads and pendants were discovered during their excavation. Their provenance could be inferred by comparison with the reference database obtained on reference samples. We present here three examples highlighting the usefulness of the Cr, V and Fe fingerprints discussed previously.

The first example deals with the dolmen Kervilor Mané Bras (La Trinité-sur-Mer, Brittany, Western France), a grave dated 4300-4000 BC of "Tombe à couloir" type located in the Carnac region, rich in megaliths [8]. A selection of 41 beads and pendants from this monument has been analyzed. The Cr, V and Fe concentrations show a large spread and overlap in the Cr-V-Fe ternary diagram, the representative points being dispersed along a line from iron pole to the centre of the triangle (fig.7a). The Cr/V ratios vary from 0.2 to 1.6 and Fe reaches up to half of the sum of the three elements. This pattern matches the fingerprint of Encinasola deposit and never corresponds to the Pannecé deposit (fig.6). Artefacts found in the grave of Kervilor probably come from the Encinasola prehistoric mine located in South Spain, more than 1000 km away and unexpectedly not from the Pannecé deposit located 100 km from the site (fig. 8).

The second archaeological example is the Chalcolithic occupation of Leceia (Oeiras, Portugal), a fortified village located on the Tage estuary, West of Lisbon. People occupied this site during a long period corresponding to the beginning of copper metallurgy in Portugal, but variscite jewels are dating from the Chalcolithic initial period 2800 BC [9].

The Fe and Cr concentrations of the variscite artifacts show a large range whereas the V levels are always very low (fig.7b). The line drawn in the Cr-V-Fe diagram appears to be very similar to that of variscite samples from Palazuelo-San Vicente mines (fig.6). The jewels from Leceia probably come from these deposits located about 400 km to the North and surprisingly not from the Encinasola mine, distant only 200 km to the East direction (fig. 8).

The third example deals with the site of Villeneuve-Tolosane/Cugnaux (France) near Toulouse, South of France dated 4,500-3,500 BC [10]. This characteristic Neolithic village was occupied by the first farmers of the "culture chasséenne" and provided numerous remains, among which variscite beads. Their compositions showed a high compositional homogeneity: all the representative points are grouped at the Fe pole and don't show any measurable Cr or V content (fig.7c). This typical fingerprint matches that of variscite from Can Tintorer mine at Gavà. The source of variscite jewels is the nearest to the village, being accessible by a 100-km trip to in the north (fig. 8).

These examples confirm that the determination of minor and trace element concentrations in variscite are useful for the determination of the provenance of the archaeological variscite jewels. The results obtained here contradict the conclusions of Odriozola and co-workers who analysed variscite samples from Encinasola (Pico Centeno mines) and isolated archaeological beads from south Iberian Peninsula using  $\mu$ -XRF technique [11]. On one hand these authors concluded that the strongly scattered minor and trace elements composition measured within the deposit prevent deducing any information about their origin. On the other hand, they claim that the P/Al atomic ratio might reflect the paragenesis of the mineral and could constitute a fingerprint. The P/Al ratio reported in their work (P/Al=1.7) is questionable as it is much higher to what we have observed for years in hundreds of samples. In addition, such a high excess of P is hardly conceivable in a properly crystallised variscite as it can be seen in XRD and in thin section under polarizing light microscope. On the other hand, our PIXE analyses of samples from the same mines ( $P_2O_5=56\%$   $Al_2O_3=40\%$ ) agree with theoretical

composition and with most published analyses of variscite from Encinasola.

## Conclusions

The constitution of a long-term geochemical database using PIXE is a real challenge. Because of instrumental changes among years (often related to improvement in detectors and in measurement strategies) and of the constant progress and refinement in spectrum processing (new program releases, changes of format and parameters) data collected over a long period might exhibit virtual variations. The choice of adequate reference targets and application of systematic quality control are essential to reach proper reproducibility and the reliability. It is under these conditions that the intrinsic qualities of the PIXE technique can be reached, namely accuracy for determination of major constituents and high sensitivity for the measurement of trace element. These qualities can then be the strongest assets of the use of PIXE in archaeological studies, like in the present case the determination of the circulation of a variscite from precious ornaments of the Neolithic and Chalcolithic periods in Western Europe.

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### Table captions

Table 1. Evolution of Al, P and Fe and P/Al ratio over 9 years obtained using PIXE of the same archaeological variscite bead (MeH40) (n: number of analyses, X: mean value and  $\sigma$ : standard deviation).

Table

Analysis period	n		Al <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	Total	P/Al
period 1 Jul 2004 - Jul 2005	8	X	36.64	58.67	1.83	98.37	1.321
		$\sigma$	0.13	0.20	0.11	0.07	
period 2 Oct 2008 - Jan 2009	9	X	38.40	57.82	1.85	98.07	1.242
		$\sigma$	0.19	0.25	0.16	0.14	
period 3 Jul 2013	5	X	39.29	56.05	1.81	98.39	1.176
		$\sigma$	0.24	0.21	0.09	0.05	
pure variscite			41.80	58.20	0.00	100.00	1.148

### Figure captions

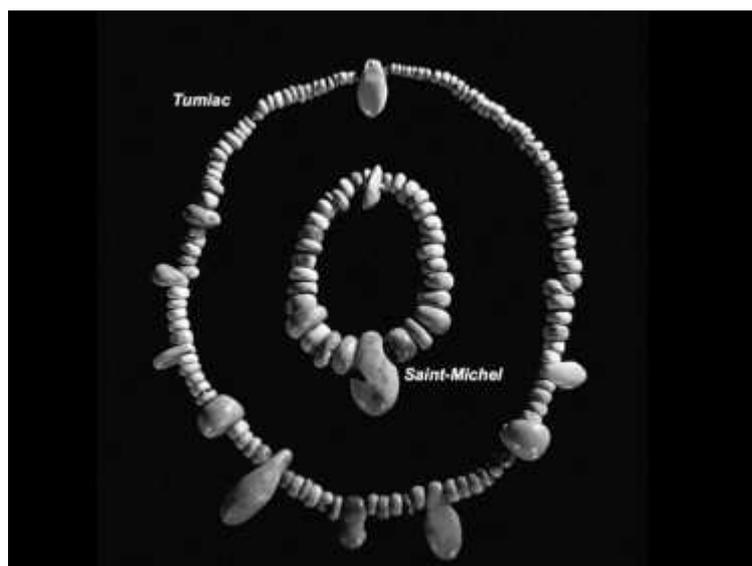


Figure 1. Beads and pendants made of variscite from Neolithic graves of Brittany: Tumulus St Michel (Carnac, France) and Tumiac (Arzon, France).

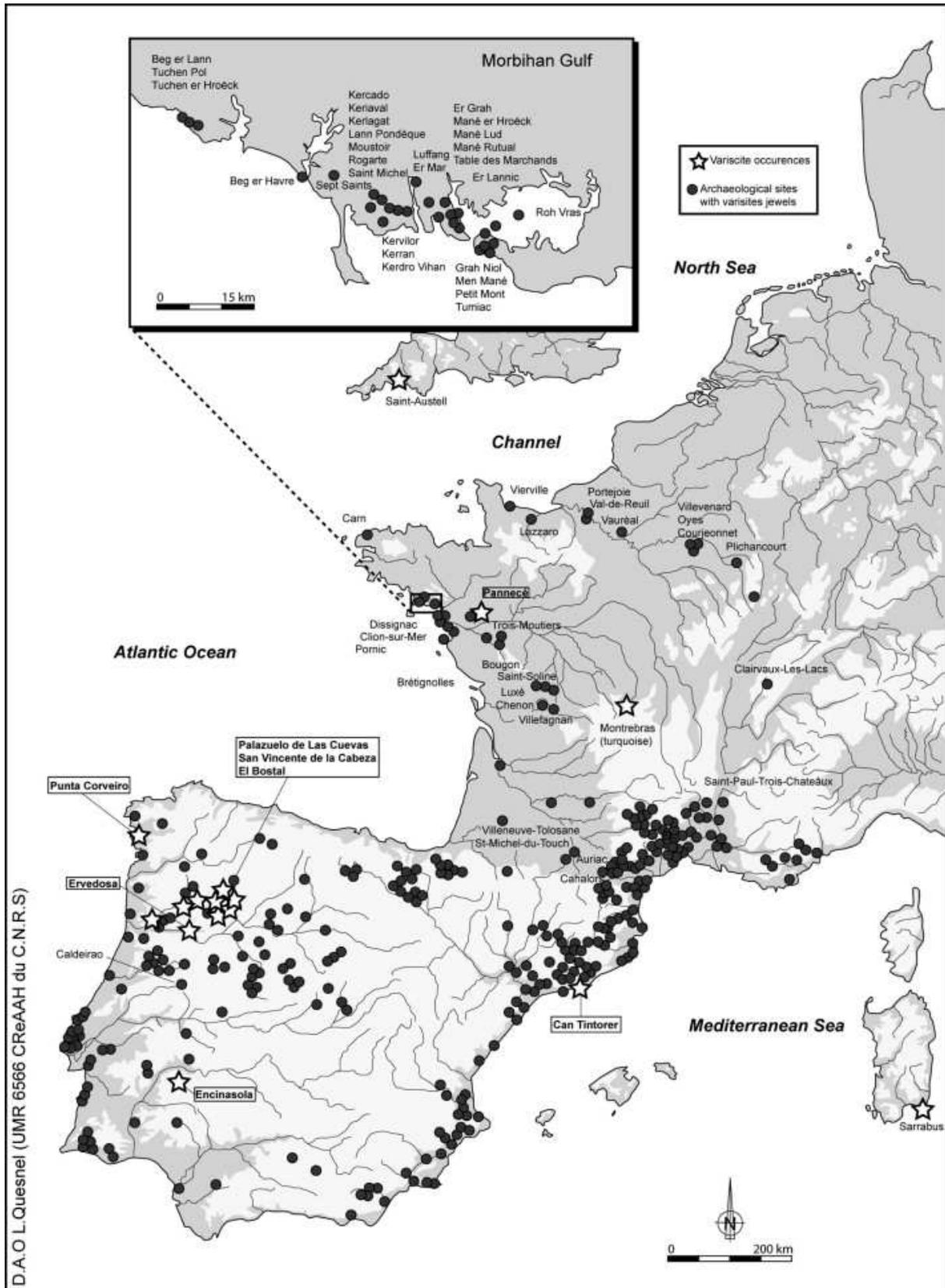


Figure 2. Location of Prehistoric occupations with variscite artifacts exclusively concentrated in Western Europe with Prehistoric mines and geological occurrences of the region.

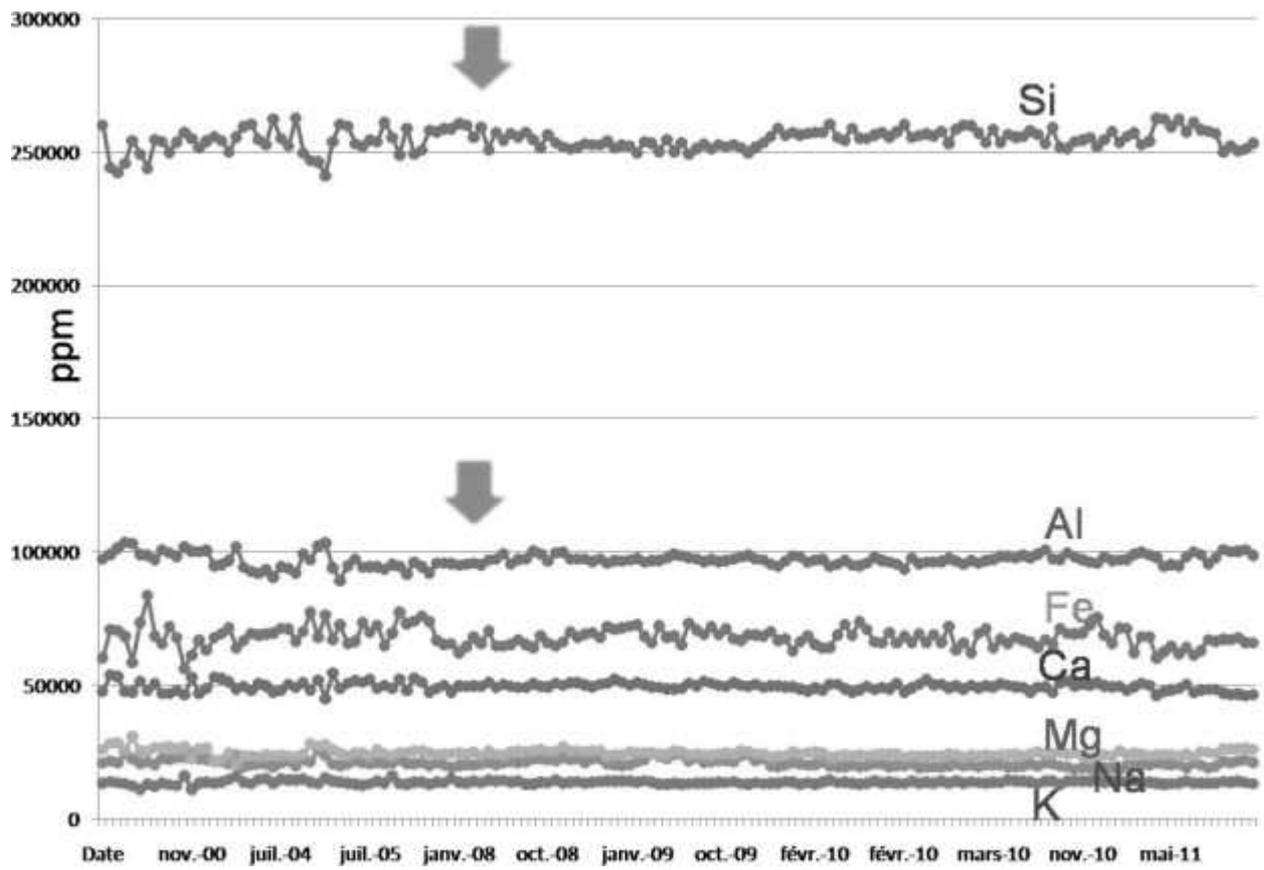


Figure 3. Stability of analysis of the DR-N geostandard over 14 years of PIXE analysis of variscite artifacts. Arrows indicate the change from punctual analysis to area scanning analysis.

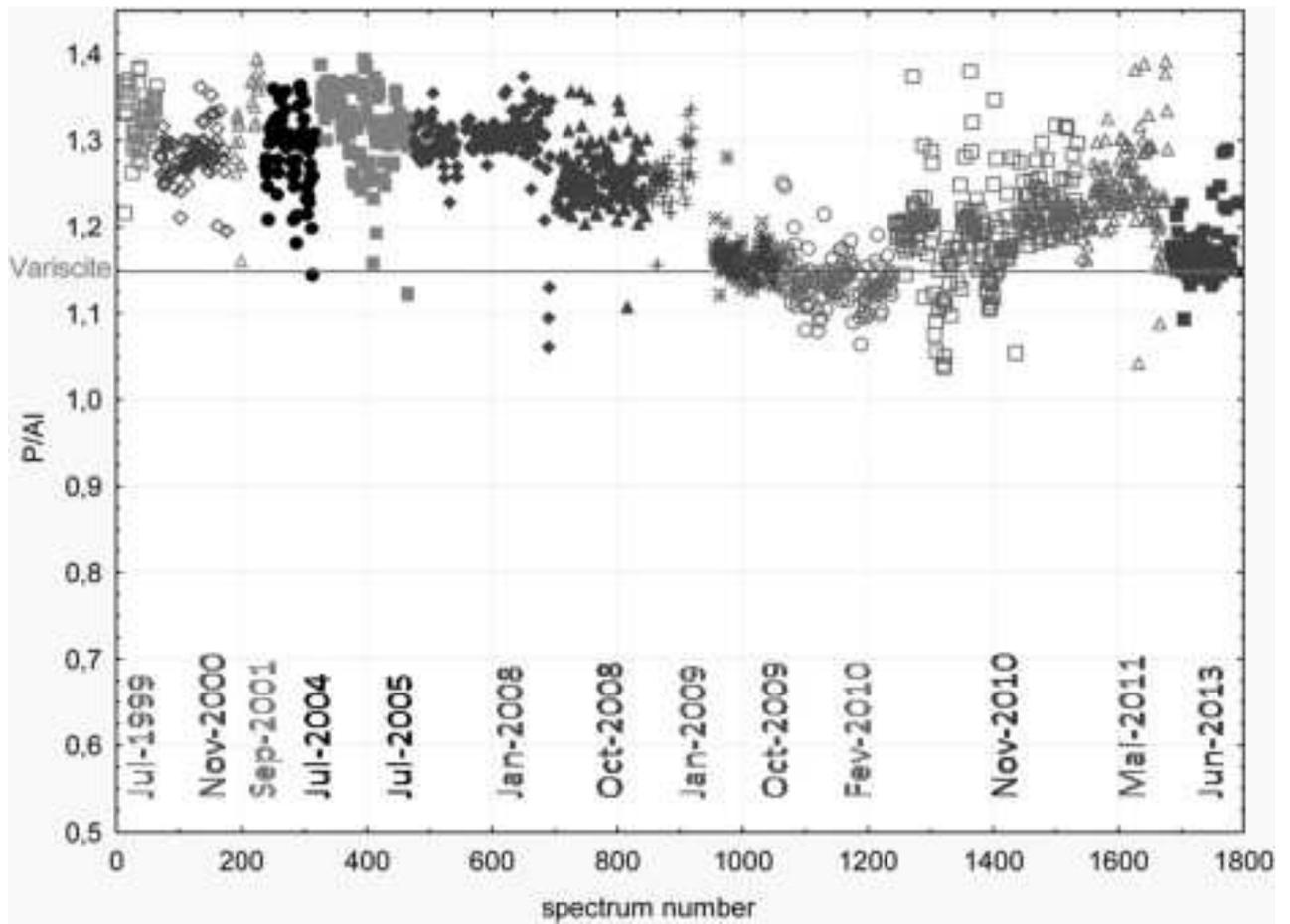


Figure 4. Evolution of P/Al ratio from archaeological and geological variscite samples over 14 years of PIXE analysis. Each group of symbol corresponds to the date of analysis specified in the bottom of the diagram.

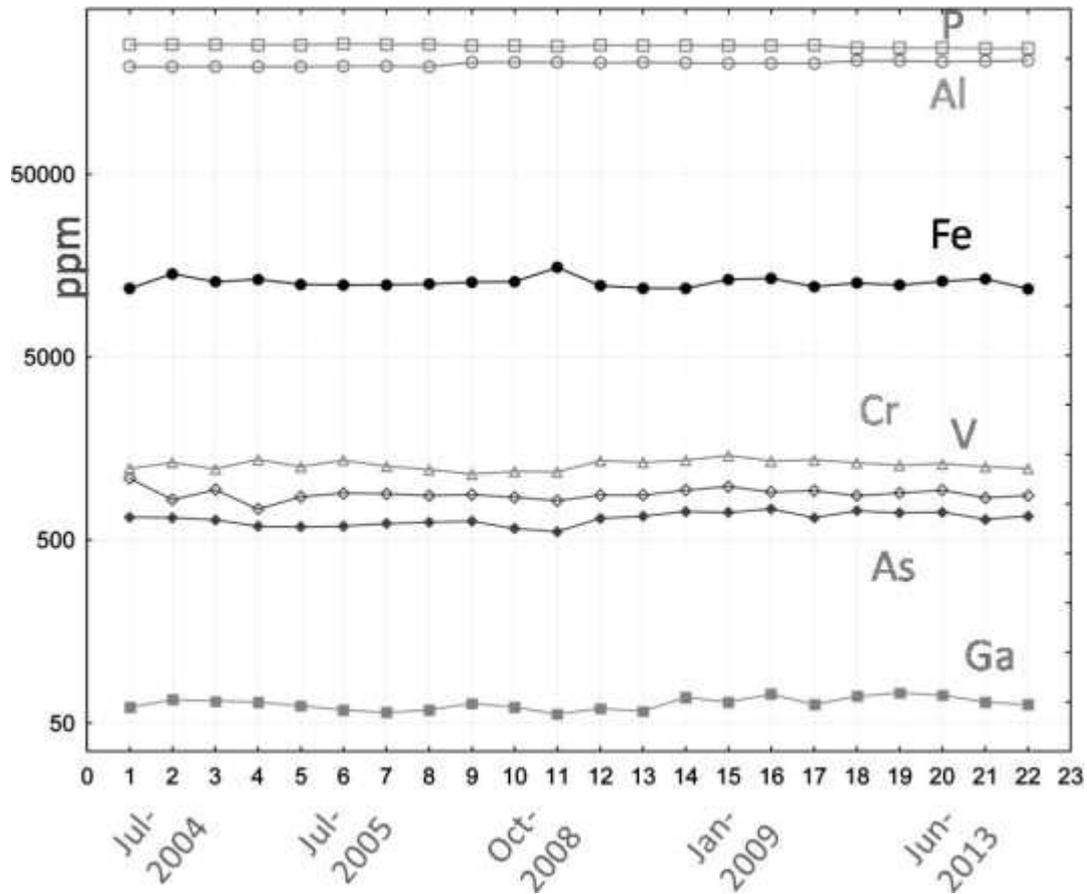


Figure 5. Stability of minor and trace element concentrations of MeH40 variscite bead from Mane er Hroeck, Locmariaquer (Brittany, France) over 9 years. Each point corresponds to one analysis - 1: July 2004; 2-8: July 2005; 9-11: October 2008; 12-17: January 2009; 18-22: January 2013.

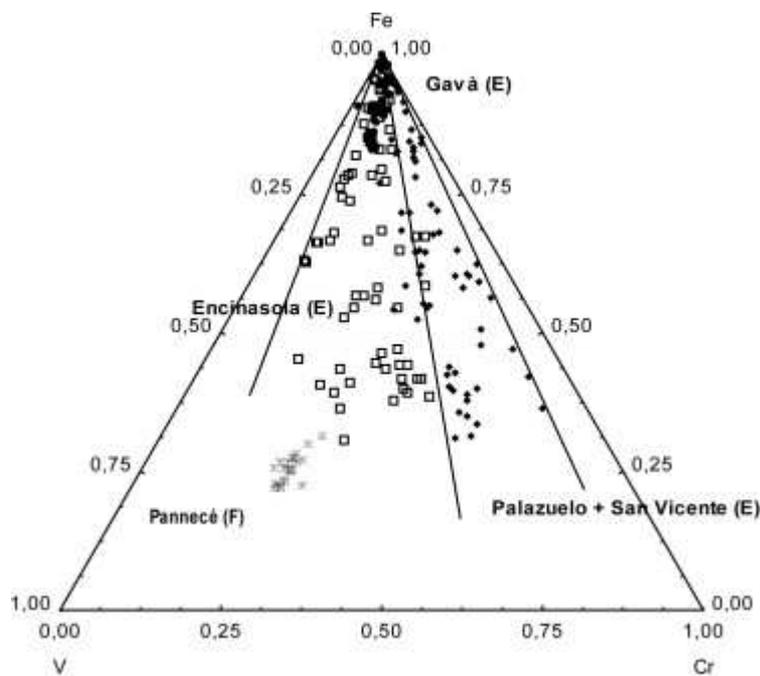


Figure 6. Variscite from the 3 main Iberian prehistoric mines and Pannecé quarry in France

plotted in a ternary diagram V-Cr-Fe, showing marked different composition ranges (empty squares: Encinasola - full diamonds: Palazuelo de las Cuevas + San Vicente de la Cabeza - full circles: Gavà - stars: Pannecé).

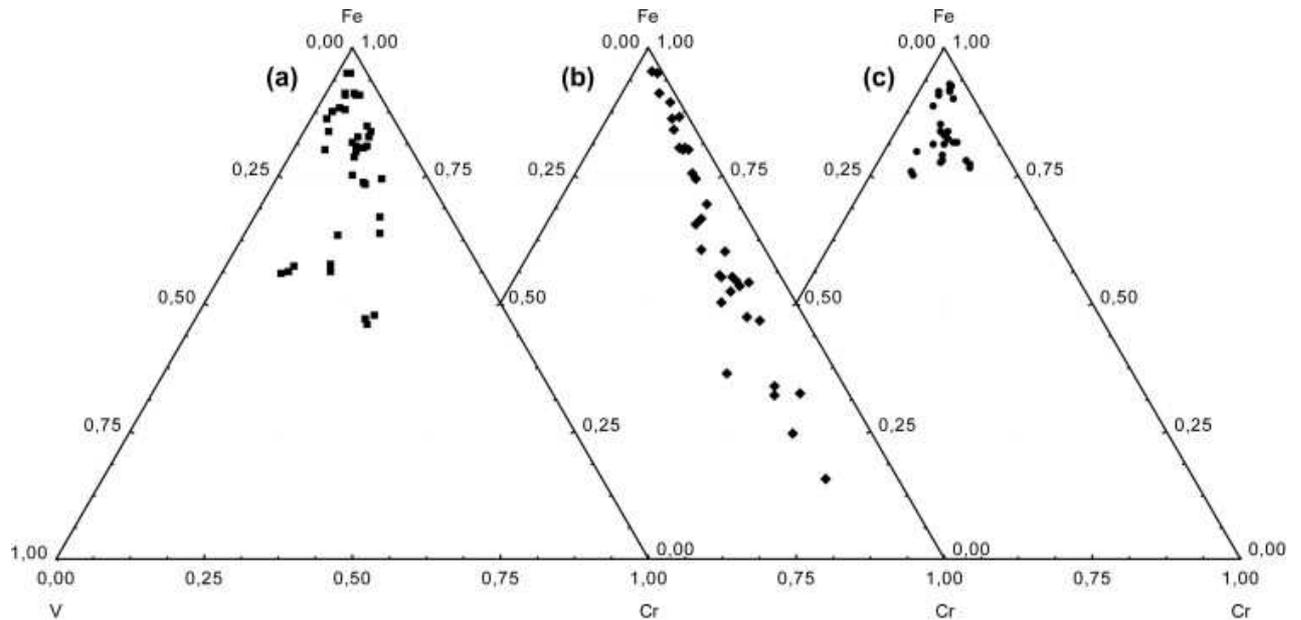


Figure 7. Ternary diagram V-Cr-Fe for 3 different groups of variscite jewels. (a) Dolmen from Kervilor, La Trinité-sur-Mer (Brittany -France) (b) Chalcolithic occupation of Leceia, Oeiras (Lisbon-Portugal) (c) Neolithic village of Villeneuve-Tolosane (Languedoc, France).

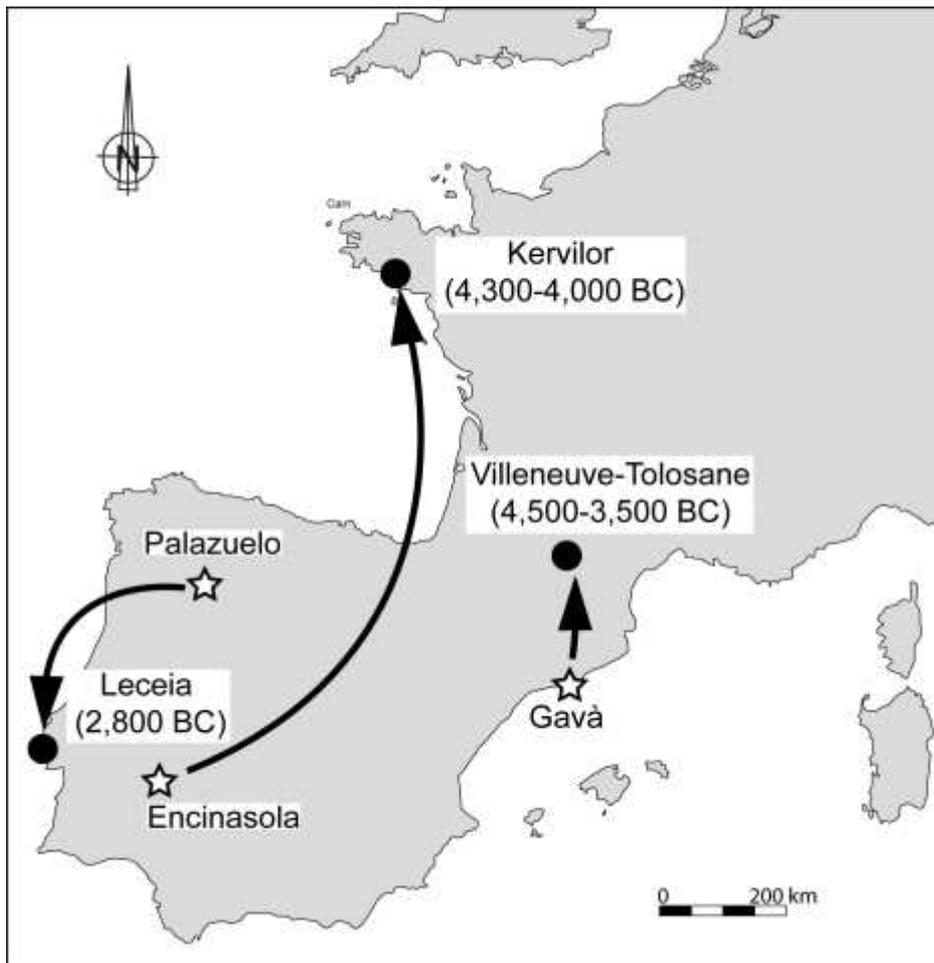


Figure 8. Location of the three archaeological sites where variscite beads come, Kervilor, Villeneuve-Tolosane, Leceia and geographical origin of the raw material proposed, respectively Encinasola, Gavà, Palazuelo.