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Long distance transport of Neolithic variscite ornaments along the European Atlantic arc demonstrated by PIXE analysis

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Abstract. The large grave mounds from the Carnac region in Brittany are among the most impressive funeral architecture of the Neolithic period in France. The exceptional quality of the adornments deposited in burials, such as polished stones axes and beads necklaces probably reflects the high status of the buried persons. Despite the importance of these artefacts, already pointed out by archaeologists during the early excavations of the 19th century, their origin has never been really established on the basis of objective criteria. This study focus on the beads, green in majority, similar to the turquoise colour. A combination of techno-typological study and chemical analysis by external beam PIXE has been performed on these archaeological artefacts. The composition in major elements gives the mineralogical nature of the material which turns out to be variscite, a hydrated aluminium phosphate. By comparison with the composition of variscite reference samples from various geological sources of Western Europe, the concentrations in trace elements allowed us to establish that the beads were originating from the Iberian Peninsula. The presence of these Iberian ornamental elements in archaeological sites in Western France thus reveals long distance relations between the Neolithic human groups during the fifth to the second millennium BC.

Keywords: Archaeology, Neolithic, Ornament, Variscite, chemical analysis, PIXE, Western Europe.

INTRODUCTION

In Prehistory, a fundamental question concerns the determination of contacts and exchanges between human groups and their evolution through space and time. This issue is often addressed by pointing out typological, stylistical and technological similarities between objects (lithic, ceramic artefacts…), arts (engravings, paintings…) or structures (housings, graves…).

Another way to highlight contacts is to identify for a specific geographic area, imported artefacts and to subsequently determine their origin. Prehistoric jewels, often made of precious material, are especially interesting due to their high symbolic value and their consequently long distance transport potentialities. For precious stone, chemical characterisation by PIXE is very powerful thanks to its high sensitivity and its totally non-destructive character required to investigate these prestige imports [1]. We applied external beam PIXE to variscite beads and pendants found during archaeological excavation of Neolithic graves from Western Europe to answer to the question of their origin.

ARCHAEOLOGICAL CONTEXT

Carnac region in Brittany (Morbihan, France) is famous for its megalithic monuments dated from the end of the Vth millennium to the beginning of the IInd millennium. Buildings consist of alignments of menhirs but also of large grave mounds among the most impressive architectural remains of the French Neolithic period. These graves were probably reserved to high-rank local dignitaries from the human groups who erected these monuments. Burials include high prestige objects, in peculiar stone axes in jadeite and fibrolite, or beads and pendants often made of green-coloured stone. In 1865, the mineralogist Damour described the material of a green-coloured bead excavated from the Neolithic mound of Tumiac (Arzon, Morbihan) as a new hydrated aluminium phosphate. He used the term of callaïs already proposed by Pliny the Elder (23-79 A.D.). Lacroix, the famous French geologist, determined in 1896 the formula of variscite, official name of this mineral [$Al PO_4.2H_2O$] [2]. However, no variscite deposit was known in Western Europe at that time and the hypothesis of a mysterious trade with the East was quite often suggested. In 1970, a deposit of variscite was found at Pannecé (Loire-Atlantique, France), nearby the Britannian Neolithic monuments. The local origin of variscite artefacts was therefore proposed but the discovery, in 1978, of the Can Tintorer mining complex in Gavà (Barcelona, Spain) with extensive traces of Neolithic exploitation reopened the debate on the provenance of the Brittanian jewels. All these uncertainties lead us to undertake a new analytical program on variscite ornaments based on PIXE to put an end to the debate [3].

PROPERTIES OF VARISCITE

Variscite is a hydrated aluminium phosphate of ideal formula [$AlPO_4.2H_2O$]. It crystallizes in orthorhombic system while clinovariscite, with same chemical composition, is monoclinic [4]. This mineral has a colour varying from green-blue to emerald green, sometimes white, and presents a waxy lustre. His hardness ranges from 4 to 5 on Mohs scale and its specific gravity is 2.5. Variscite is easily confused with turquoise which is also a hydrated aluminium phosphate, but contains copper [$CuAl_6(OH)_8(PO)_4$–$4H_2O$]. Variscite occurs more often in microcrystalline fibro-radiated aggregates. This supergene secondary mineral typically fills in fissures and cavities of argileous rocks, especially schist. Massive variscite nodules are of small size, rarely exceeding some centimetres. The mineral may contain iron in variable quantities. An isomorphic series exists with strengite [$FePO_4.2H_2O$], by substitution of aluminium by iron. Due to the formation processes and the presence of various chemical compounds different from alumina and phosphate (Fe, Ca, Mg…), variscite nodules often exhibit a heterogeneous composition and colour. Such heterogeneities are sometimes observed at the scale of a single archaeological beads or pendant, and these characteristics should be taken in account while interpreting data.

EXPERIMENTAL

Variscite artefacts were analysed with AGLAE IBA facility of the Centre of research and restoration of the museums of France [5] using an external 3 MeV proton micro-beam in PIXE mode.

Major and trace elements above Na were simultaneously determined by PIXE with two detection channels. This set-up and its improvements were described elsewhere [6]. The first detector, labelled "low energy" is a 10 mm² Si(Li) with an ultra-thin window and He flow. It permits detection of X-rays ranging from 0.5 to 10 keV, corresponding to the lines of major and minor elements ($10<Z<30$). The second one, labelled "high energy" is a 50 mm² Si(Li) with a 50µm Al filter for suppressing the K-line of Al and P, allows the determination of trace elements in the $20<Z<92$ range. The beam is extracted through a 100nm Si_3N_4 window, to a spot of about 0.1 mm diameter on the target placed at a distance of about 3 mm after the window. The beam intensity is monitored with an additional Peltier-cooled X-ray detector which collects the 1.74 keV Si signal emitted by the exit window. The beam current was 0.8 nA, with an integrated charge of about 0.5 µC per run. PIXE spectra were processed with the GUPIX 95 package [7].

With this approach, a single shot with 3 MeV protons permits the complete analysis of the variscite except the water content. The quantification procedure is the following:

(i) The "low energy" X-ray spectrum provides the matrix elements and some minor elements: Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_3 contents are quantified by setting a total sum of 100%.

(ii) An element (chromium, vanadium or iron) appearing in both "low energy" and "high energy" spectra with the highest intensity is used as an internal standard to inter-calibrate the two spectra.

The analytical procedure was controlled by the systematic analysis of an international geochemical standard (Diorite DR-N).

RESULTS AND DISCUSSION

The methodology used to determine the origin of archaeological artefacts compared the two sets of data, archaeological and geological, using statistical tools to point out similarities or differences.

Three PIXE analyses have been performed per object to take in account possible sample heterogeneities.

Reference Variscites

Variscite is not a common mineral in Europe: actually only about ten geological deposits are known on this continent. Samples from six sources have been analysed by PIXE, corresponding to the largest occurrences in Western Europe and to the space distribution of Neolithic variscite objects. The only one located in France is Pannecé (Loire-Atlantique), very close to Carnac, the five others being from the Iberian peninsula: Ensinsola in the South-West (Huelva), El Bostal, San Vincente de la Cabeza and Palazuelo de Las Cuevas in North-West (Zamora) and Can Tintorer, the Neolithic mine, in North-East (Barcelona). A total of 24 major, minor or trace elements have been measured with good accuracy (tab. 1).

Chemical discrimination between the different sources of variscite was well established on the basis of Cr and V variations (fig.1), but also with many other elements such as Si, Ga, U, As, Zn... Each deposit has a unique chemical fingerprint, except for one facies from Ensinasola which has a comparable chemical composition to variscite from Saint Vicente.

Archaeological Artefacts

22 beads and 2 pendants of variscite from six different archaeological sites from the Carnac region have been analysed. Multivariate statistical method such as hierarchical classification, including both archaeological and geological variscite analyses allowed us to propose the following conclusions.

Six analyses (① in fig 2) of two archaeological artefacts fall into the composition group of Can Tintorer. These two objects, one of them found in the famous “tumulus St Michel” at Carnac, likely come from Neolithic Cataluña mines.

Eight analyses (②) of three beads give a similar chemical composition to variscite from San Vicente or Encinasola. Further discrimination is not possible with the present data.

Nine beads (③) form a homogeneous group of composition very similar to variscite from El Bostal, the probable source for this group of Neolithic jewels.

Other beads present a large dispersion of values and cannot be associated to one of the six variscite deposits considered (④).

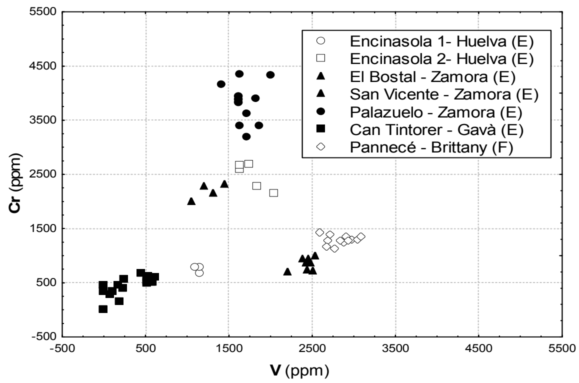

FIGURE 1. Discrimination of the six geological deposits of variscite from W-Europe by Cr and V concentrations.

A very important conclusion can be drawn from this statistical analysis: none of the archaeological beads and pendants comes from Palazuelos de Las Cuevas and, above all, from Pannecé in Brittany

This two compositional groups are indeed clearly isolated from others objects and geological deposits (⑤ and ⑥, fig. 2).

TABLE 1. Chemical composition of variscite [Mean and (standard deviation)] from six geological deposits: Encinasola (Huelva-E), El Bostal, San Vicente de la Cabeza, Palazuelos de Las Cuevas (Zamora –E), Can Tintorer (Gavà-E), Pannecé (Loire-Atlantique- F). Oxides are given in weight %, trace elements in ppm weight.

	Encinasola 1		Encinasola 2		El Bostal		San Vicente		Palazuelo		Can Tintorer		Pannecé	
SiO_2	0,0	(0,0)	0,0	(0,0)	0,1	(0,1)	0,7	(0,9)	0,5	(0,6)	27,2	(22,2)	0,0	(0,0)
Al_2O_3	39,8	(0,2)	40,3	(0,1)	39,9	(0,4)	39,4	(0,7)	39,3	(0,4)	27,9	(8,3)	39,9	(0,5)
MnO_2	0,0	(0,0)	0,0	(0,0)	0,0	(0,0)	0,0	(0,0)	0,0	(0,0)	0,0	(0,0)	0,0	(0,0)
Fe_2O_3	1,4	(0,1)	0,5	(0,1)	1,0	(0,5)	0,9	(0,4)	0,8	(0,5)	1,7	(0,5)	0,2	(0,1)
MgO	0,2	(0,1)	0,1	(0,1)	0,1	(0,1)	0,1	(0,1)	0,1	(0,1)	0,7	(0,6)	0,2	(0,1)
CaO	0,0	(0,0)	0,0	(0,0)	0,1	(0,0)	0,1	(0,0)	0,1	(0,1)	4,7	(6,7)	0,2	(0,2)
Na_2O	0,2	(0,1)	0,1	(0,1)	0,1	(0,1)	0,3	(0,2)	0,2	(0,1)	0,4	(0,4)	0,5	(0,4)
K_2O	0,1	(0,1)	0,0	(0,0)	0,1	(0,0)	0,1	(0,1)	0,1	(0,0)	0,5	(0,4)	0,1	(0,1)
TiO_2	0,2	(0,1)	0,0	(0,0)	0,0	(0,0)	0,1	(0,1)	0,2	(0,1)	0,5	(0,6)	0,0	(0,0)
P_2O_5	58,0	(0,1)	58,6	(0,1)	58,3	(0,2)	57,8	(0,5)	58,0	(0,4)	36,3	(17,2)	58,5	(0,4)
V	1130	(40)	1800	(160)	2430	(100)	1260	(170)	1630	(220)	280	(240)	2850	(160)
Cr	750	(60)	2450	(230)	840	(110)	2190	(140)	3590	(700)	420	(190)	1290	(90)
Cu	0	(0)	20	(30)	80	(10)	10	(0)	20	(20)	60	(80)	20	(10)
Zn	0	(0)	0	(0)	350	(50)	20	(0)	20	(10)	30	(20)	10	(0)
Ga	50	(20)	1	(1)	30	(20)	80	(10)	90	(60)	20	(10)	160	(10)
As	270	(30)	210	(20)	50	(10)	70	(10)	50	(10)	270	(120)	9	(3)
Rb	0	(0)	1	(2)	0	(0)	0	(0)	0	(1)	3	(14)	1	(2)
Sr	10	(10)	0	(0)	0	(0)	10	(10)	10	(10)	370	(270)	20	(30)
Zr	60	(30)	40	(20)	10	(10)	10	(0)	30	(20)	10	(20)	0	(0)
Ni	0	(0)	0	(0)	0	(0)	2	(4)	1	(2)	32	(37)	2	(2)
Y	0	(0)	0	(0)	20	(10)	0	(0)	10	(20)	10	(10)	0	(0)
Nb	0	(0)	3	(6)	0	(0)	1	(3)	0	(0)	0	(0)	0	(0)
Mo	70	(10)	30	(10)	90	(20)	10	(10)	10	(10)	0	(10)	20	(10)
U	10	(10)	0	(0)	310	(50)	10	(10)	10	(10)	10	(20)	10	(10)

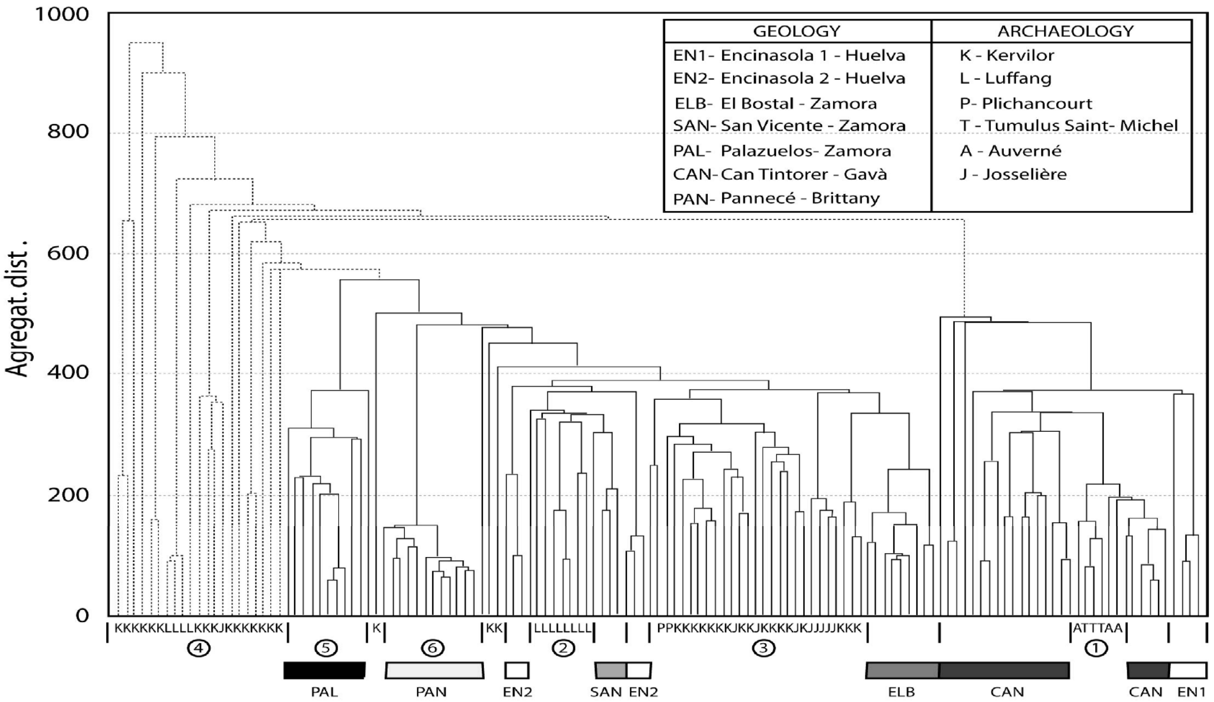

FIGURE 2. Dendrogram obtained from a hierarchical classification of data from Neolithic beads and geological references of variscite (minimum skip, Euclidian distances, 24 chemical elements).

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CONCLUSION

PIXE analysis of green-coloured beads and pendants from Neolithic graves from Carnac region confirms the nature of the mineral: variscite, and allow us to specify their Iberian origin and consequently, exclude a local provenance (Armorica). This study highlights exploitation of multiple Iberian variscite sources over a 2000-years period. Extensive analysis of well-dated objects should permit to identify change of supplies during this long period in connection with evolution of relationships, sphere of influence, breaking-off due to the exhaustion of a mine, local conflicts...

It has been previously demonstrated that the jadeite stone axes found in the same burials which contain variscite objects, come from the Italian Alps [8]. Thus, this work contributes to confirm the long distance circulation of precious stone, one element of the complex European network established during the Neolithic period.

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