

# PERDIGÕES' GREEN BEADS PROVENANCE ANALYSIS

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## Resumo:

### Análise de proveniência das contas verdes dos Perdigões

A variscite é um mineral raro que oferece uma excelente oportunidade de estudo dos padrões de comércio e troca na Europa durante a Pré-História através da determinação da sua fonte de proveniência.

No presente texto será discutida a proveniência das contas de colar verdes com base em análises de XRF e XRD, através das quais se criou uma identidade geoquímica passível de ser comparada com as das fontes de variscite conhecidas.

## Abstract:

Variscite is a rare mineral that offers an excellent opportunity to study trade and exchange patterns in prehistoric Europe through proveniencing of source material.

In this paper we discuss the provenance of Perdigões' green beads by means of XRF and XRD analyses, thus creating a geochemical baseline that is compared with that of the known variscite sources.

## 1. Introduction

A major research question in the study of prehistoric Iberia is the analysis of traded objects and their implications for understanding social interaction, in a period, 3<sup>rd</sup> millennium BCE, known by its importance in the discussion of a set of social changes of structural relevance -i.e. the appearance of permanent hierarchies, class societies or the state, the development of the social inequality and more institutionalised forms of power, ... Exchange and mobility patterns are, thus, of outmost importance in the understanding of prehistoric Iberia.

The study of the green beads from *tholos* 1 and 2 from Perdigões will help to understand the Rivera do Alamo complex net of interactions in which Perdigões would have act as a central place of an aggregated network, as claimed by Valera (2006) and further evidenced by pottery studies performed by Dias et al. (2008).

The idea under our study is to understand the details of Prehistoric exchange patterns, towards what exchange theories developed since the mid 1970's (i.e., Earle and Ericson, 1977, Weigand et al., 1977) have been highly successful, specifically in terms of scarce resources such as rare minerals and ores. The more rare the resource, the more successfully its source can be tracked simply due to the fewer number of potential sources available. Rare minerals and ores, then, offer an excellent opportunity to study trade and exchange patterns in prehistoric Europe through provenance of source material.



Figure 1 – Location of the Iberian variscite sources and location of Perdigões.

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Variscite is, thus, a wonderful resource for provenance study as it is a scarce naturally occurring hydrated aluminium phosphate. In the Iberian Peninsula, only five main sources occur (figure 1): *Can Tintorer* (Gavá, Barcelona), *Palazuelos/El Bostal* (Aliste, Zamora), *Punta Corbeiro* (Sanxenxo, Pontevedra), *Pico Centeno* (Encinasola, Huelva) in Spain and *Bragança* (*Tras-o-Montes*) in Portugal. Thus, a high degree of precision and accuracy can be achieved due to the limited number of available geological outcrops in which the mineral is found.

## 2. Materials and methods

In this paper we performed a provenance analysis of 20 green beads (figure 2) from Perdigões' (Reguengos de Monsaraz, Portugal) *tholoi* 1 and 2 (Valera et al., 2002). X-ray fluorescence and diffraction analyses of the beads provided a baseline mineral signature that if compared to sources outlines the origin of the raw material used for bead working. Non-destructive compositional data were obtained using a  $\mu$ -XRF, while non-destructive XRD patterns were recorded with a parallel beam using a Goebels mirror set.

Beads were analysed with an Eagle III EDAX  $\mu$ -XRF and by means of X-ray Diffraction with a Siemens D5000 diffractometer.

**X-ray diffraction** patterns were obtained using a Siemens D5000  $\theta/2\theta$  diffractometer with Cu K $\alpha$  source operating at 50 kV, 35 mA. A parallel Goebel-mirror beam from a Cu K $\alpha$  source was used and the data were collected on transmission mode with a 2D detector. Patterns were obtained using a step width of 0.02° 2 $\theta$  between 3° and 65° 2 $\theta$  and a counting time of 10 s per step at ambient temperatures.

**X-ray fluorescence** compositional data was obtained by focusing directly over the sample with an optical microscope; an area of 100  $\mu$ m was analyzed using a K $\alpha$  radiation produced by a Rh tube operated at 40 kV. The elemental composition of the samples is expressed as weight percentage of the corresponding oxides.

Beads from Perdigões *tholoi* 1 and 2 were randomly sampled from the more than 3000 turquoise-green beads recovered in each tomb. Due to the variety of bead shapes that occurred in the *tholoi*, the major sampling criteria was to insure all bead shapes were represented in the sample.

## 3. Results and discussion

Variscite is also known as '*callaite*'. This term was first used by Pliny (Natural History XXXVIII) to describe all green rocks with a shiny luster, which then also became attached to variscite. Since the mid 1970s the term '*callaite*' has been strongly criticized in its general use when alluding to variscite beads (Dominguez Bella, 2004), although only recent studies (Edo et al., 1995, Pozo et al., 2002, Villalba, 2002, Querré et al., 2007, 2008) have proven that not all green or green-bluish shiny lustrous rocks used in bead production were made of variscite. In fact, the raw material for bead



Figure 2 – Bead from Perdigões *tholoi* 1.

production was much more varied than expected, and strengite, muscovite, chlorite, sericite and talc have all been noted as raw materials. The mineralogical characterization of Perdigões' beads revealed that the great majority of green beads from *tholoi* 1 and 2 match the variscite ICDD 25-18 card (fig. 3); and that only 3 beads do not match variscite pattern which appear to match muscovite XRD pattern (ICDD 6-263) –table 1.

ID	Site	XRD
4348	T1 Perdigões	Muscovite
4343	T1 Perdigões	Variscite
7163	T1 Perdigões	Variscite
7289	T1 Perdigões	Variscite
7547	T1 Perdigões	Mucovite
7784	T1 Perdigões	Variscite
7816	T1 Perdigões	Variscite
7942	T1 Perdigões	Variscite
7944	T1 Perdigões	Variscite
7906	T1 Perdigões	Variscite
11825	T2 Perdigões	Variscite
11821	T2 Perdigões	Variscite
11822	T2 Perdigões	Variscite
11823	T2 Perdigões	Variscite
11827	T2 Perdigões	Muscovite
11835	T2 Perdigões	Variscite
11824	T2 Perdigões	Variscite
11826	T2 Perdigões	Variscite
11838	T2 Perdigões	Variscite
11839	T2 Perdigões	Variscite

Table 1 – Mineral phase identification for the studied beads.

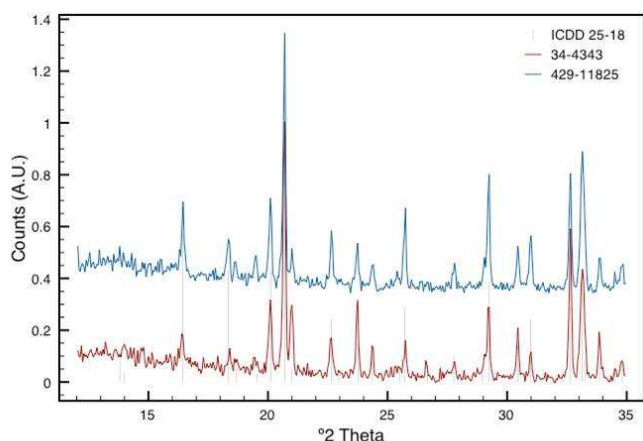


Figure 3 – XRD patterns of Perdigões beads with indication of peak position for ICDD card 25-18.

XRD card 25-18 from a Palazuelos variscite sample matches all of the peaks appearing in our variscite samples, while card 33-33 from Utah presents a peak shift to higher 2θ degrees. This might be due to the higher purity of the mineral phase of Utah variscite and to the presence of Fe, Cr, Ni, ... substitutions as well as for the intergrowth with metavariscite and quartz as reported for Palazuelos and Pico Centeno sources (Arribas et al., 1971, Salvador and Fayos, 1972, Moro Benito et al., 1992, 1995). XRD patterns, thus, indicate that all variscite beads are orthorhombic cryptocrystalline type M variscite (ICDD 25-18).

Once secure that we are dealing with variscite beads, we can return to see whether there are groups of beads that show similar chemical composition and whether they can be associated with a specific source. The relationship between beads and source is established by comparison of the chemical components of the beads and those of the sources. The validity of this approach rests in the fact that '[...] differences in chemical composition between different natural sources exceed, in some way, the differences observed within a given source' (Weigand et al., 1977).

The variscite mineral group are orthorhombic phosphates with a general formula  $[MPO_4 \cdot 2H_2O]$ , where  $M = Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}$ . Variscite is a secondary mineral formed by direct deposition of phosphatic groundwater descending along open fissures and reacting with aluminium-rich rocks (Larsen, 1942). It occurs as fine-grained masses in nodules, cavity fillings and crusts associated with clay rocks, typically of schist. Variscite's pure phases are white and transparent, however its colour ranges from yellow to green hues and massive variscite usually have a waxy, lustrous turquoise-green colour. Colour is, however, dependent on the formation process and the presence of chemical compounds other than P and Al are responsible for the colour that variscite nodules exhibit. Recent spectroscopic studies claim that Chromium ( $Cr^{3+}$ ) and Vanadium ( $V^{4+}$ ) are the uniquely responsible for the colour of variscite (Calas et al., 2005).

Recent studies show considerable analytical variation for source minor and trace elements. In some cases a coefficient of variation (CV) as high as 1.7 for a single element (Odriozola et al., 2010). These CVs prevents us of using minor and trace elements and their correlations as an indicator of provenance due to its high natural variability. Thus, source natural variability becomes an important barrier to variscite provenance analysis and therefore to its reliability in determining prehistoric exchange patterns.

Variscite's ideal formula is  $[AlPO_4 \cdot 2H_2O]$  which means a P/Al atomic ratio equal to 1, although aluminium substitutions for other trivalent transition ions ( $Fe^{3+}, Cr^{3+}, V^{3+}, \dots$ ) may slightly increase this ratio. This is consistent with most of the reported data, however, in our case this ratio is much higher than 1, around 1.7 (table 2).

The presence of hydrogenphosphate species in the variscite mineral would result in P/Al atomic ratios higher than 1 depending on the exact value and the relative proportions of the different hydrogenphosphate species. These findings suggest the P/Al atomic ratio recorded for Pico Centeno massive variscite and Perdigões beads arose during the genesis of the variscite deposits and resulted from the associated pH and nature of the host-rocks, modifying the concentrations of  $PO_4^{3-}, H_2PO_4^-$  and  $HPO_4^{2-}$  (Odriozola et al.,

ID	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	V	Cr	Mn	Fe <sub>2</sub> O <sub>3</sub>	Cu	Zn	Ga	As	Rb	Zr
4343	25,59	7,96	64,62	0	0	-	0,15	0,48	-	1,13	0,01	0,01	0,02	0,01	-	0,01
7163	28,32	-	69,2	0,22	0,43	0,12	0,10	0,28	-	1,25	0,02	0,01	0,01	0,03	0,01	0,00
7906	27,86	-	68,84	0,21	0,65	0,21	0,13	0,23	-	1,79	0,02	0,01	0,02	0,03	-	0,01
7944	27,9	-	68,7	0,16	0,43	0,23	0,13	0,73	-	1,57	0,02	0,01	0,05	0,08	-	0,01
7942	27,69	-	68,81	0,04	0,32	0,41	0,20	0,55	0,01	1,87	0,01	0,01	0,02	0,02	-	0,03
7289	27,53	-	67,47	0,15	0,19	0,19	0,11	0,56	-	3,68	0,02	0,00	0,03	0,04	-	0,02
7816	27,11	-	67,59	0,28	1,46	0,54	0,16	0,61	-	2,18	0,01	0,01	0,03	0,01	0,01	0,01
11821	28,67	-	69,13	0,15	0,52	0,33	0,09	1,02	-	0	0	0,01	0,02	0,03	0,00	0,01
11822	27,06	-	65,02	0,1	0,29	0,26	0,07	0,42	0,00	6,54	0,02	0,01	0,02	0,16	0,01	0,02
11823	27,56	-	68,23	0,1	0,52	0,39	0,10	1,32	0,00	1,69	0,01	0,00	0,02	0,03	0,00	0,02
11824	27,32	-	68,00	0,09	0,45	0,29	0,09	1,13	0,01	2,52	0,02	0,01	0,02	0,03	0,00	0,01
11825	27,96	-	67,73	0,11	1,73	0,30	0,14	0,71	-	1,24	0,02	0,01	0,01	0,02	0,01	0,01
11835	24,47	10,74	61,74	0,13	1,08	0,15	0,13	0,62	-	0,88	0,01	0,00	0,01	0,03	0,00	-
11838	28,26	-	69,45	0,16	0,37	0,08	0,10	0,33	-	1,17	0,01	0,00	0,01	0,03	0,01	0,01
11839	28,32	-	68,82	0,05	0,25	0,17	0,10	0,80	-	1,6	0,01	0,00	0,01	0,03	0,00	0,03
11826	28,28	-	69,11	0,1	0,45	0,28	0,16	0,50	0,00	1,03	0,01	0,01	0,02	0,02	0,00	0,01

- not detected.

Table 2 – chemical composition of the variscite beads from Perdigões

2010). Thus, the P/Al atomic ratio should be an indication of provenance as it is established during mineral genesis. This issue has not been addressed in any of the other studied sources where this ratio seems to be  $\approx 1$ .

Assuming the above-mentioned hypothesis, if compared, the variscite beads and the variscite sources P/Al atomic ratio should establish Perdigões beads origins. To what the non-parametric density estimation (figure 4) allows the recognition of the origin of Perdigões variscite beads in Pico Centeno source. Figure 4 shows how the overall sample of Perdigões beads fits into natural Pico Centeno clusters, and therefore can be interpreted as a match between Perdigões beads and Pico Centeno source.

#### 4. Conclusion

Based on beads P/Al ratios recorded in the data set and the match with Pico Centeno's ratio, we claim that the raw material procurement for bead working at Perdigões was Pico Centeno.

#### 5. Acknowledgements

The authors acknowledge the Junta de Andalucía, Consejería de Innovación, Ciencia y Tecnología for the financial support (P06-HUM-02159). C.P. Odriozola acknowledges a PhD grant from I3P fellowship program. We must thank the permission to study beads from Perdigões to ERA-Arqueologia S.L. and especially to A.C. Valera.

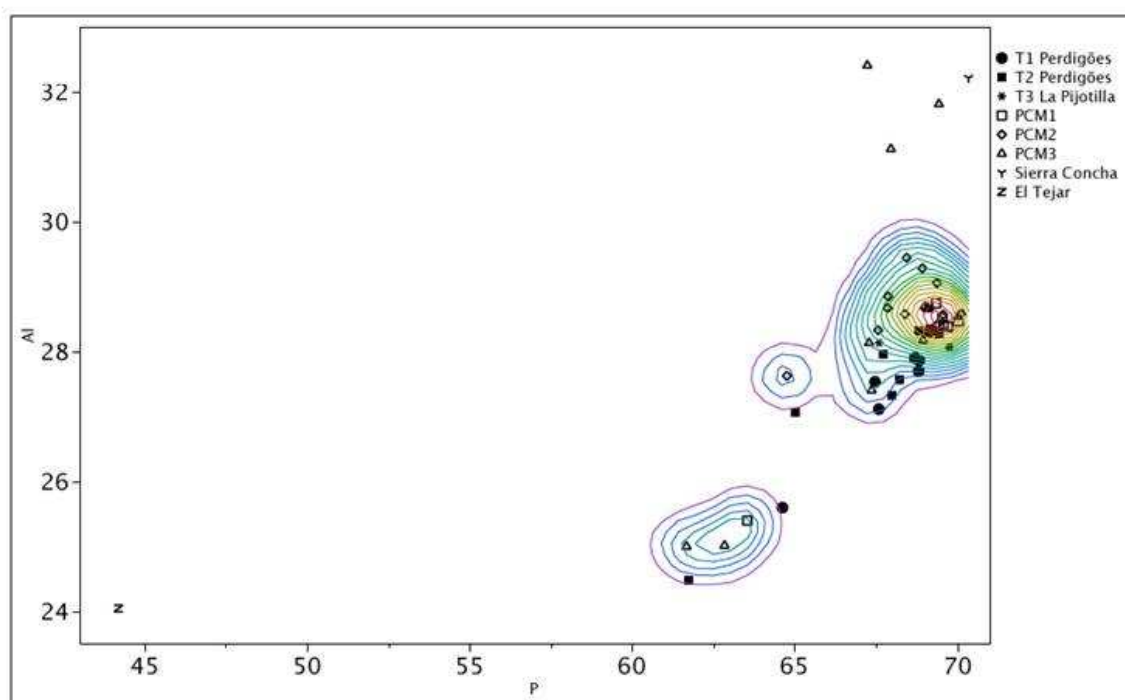


Figure 4 – P vs. Al plot with non-parametric density estimation.

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