Provenancing variscite beads: Pico Centeno (Encinasola, Spain) outcrop case study

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Abstract

In this study we discuss the exploitation and exchange of variscite at Pico Centeno mining district during the Copper Age. X-ray fluorescence and diffraction (XRF and XRD, respectively) analyses of the mineral recovered at Pico Centeno mining district provides a basic mineral signature for the source, which was then compared to variscite beads from 8 geological sources from different regions. In the Middle Guadiana Basin we analyzed beads from Perdigões (Reguengos de Monsaraz, Portugal) tholoi 1 and 2 (Valera et al., 2002) and La Pijotiella (Badajoz, Spain) T3 tholos (Hurtado, 1988, 1991). From the Andévalo Oriental in Huelva, Spain we analyzed beads from Dolmen 4 from Los Gabrieles (Linares Catela, 2006, 2009), Dolmenes de Puerto de los Huertos, Casullo and Mascotejo from El Gallego-Hornueco (Linares Catela, 2009) and, finally, Dolmen 2 from Pozuelo (Cerdan et al., 1975). Non-destructive compositional data were obtained using a μ-XRF, while non-destructive XRD patterns were recorded with a parallel beam. The variscite mineral group are orthorhombic phosphates with a general formula [MPO₄·2H₂O], where M=Al³⁺, Fe³⁺, Cr³⁺, V³⁺. 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. 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).

Materials and Methods

The Pico Centeno Silurian Al (Fe-Ca) phosphate deposits are located at the vicinity of Encinasola (Huelva, Spain). As previously described by [9], these SW Iberian deposits are associated with the silurian lidite which are found in the NW of the region in the vicinity of Encinasola. Encinasola is a part of the Hercynian mega-structure known as the Terena Synform. We have sampled two previously reported variscite types – concretionary and massive variscite (Moro et al., 1992, 1995) after the archaeological survey of the Terena Synform and the excavation of Pico Centeno (PCM 2). The sampling focused on mining and production debris (flakes and rough out nodules), although samples from the extraction scars were also taken, as well as samples other outcrops (Sierra Cocha & El Tejar) located in the Terena Synform in order to test source-to-source chemical differences and variance.

Variscite geological samples and beads from Middle Guadiana basin and Andèvalo Oriental megalithic contexts were analysed with an Eagle III EDAX μ-XRF, by means of X-ray diffraction with a Siemens D5000 diffractometer (Siemens, Munich, Germany), and with a Nicolet 510P Fourier transform infrared spectroscopy (FTIR).

A total of 38 geological samples were analysed. The reported data are the average five measurements. Furthermore, total of 44 beads were analysed from 8 Late Prehistoric burial of different architectural types and geographical regions in order to test distribution patterns and models.

Beads from Perdigões tholoi 1 and 2 were randomly sampled over 6000. Due to the variety of bead shapes, the major sampling criteria was to insure all bead shapes were represented in the sample. In contrast, although 502 beads were recovered from La Pijotiella tholos T3, only three were sampled based on their greenish colour, the rest of the beads were white. The beads recovered from Gabriels 4, Puerto de los Huertos, Casullo, Mascotejo and Pozuelo 2 megaliths from Andévalo Oriental were fully sampled. Although the Middle Guadiana megaliths are tholoi and the Andévalo Oriental ones are of dolmens, both
funerary architectural types can be chronologically ascribed to the 3rd millennium BC (Figure 2).

Results and Discussion

The mineralogical characterisation revealed that the sampled green rocks from these sites are all variscite and the XRD patterns from Pico Centeno (Figure 3) indicate all are orthorhombic cryptocrystalline type M variscite (International Centre for Diffraction Data card 25-18).

The µ-XRF analyses of different samples drawn from the same mine show considerable analytical variation for minor and trace elements. In some cases a coefficient of variation (CV) as high as 170% for a single element (Cr) (Moro et al., 1995). It is possible to observe in Figure 4 how the traditionally used as source-to-source discriminators (Odriozola et al., 2010; Querré et al., 2007) – mainly Cr and V – (Odriozola et al., 2010) cannot be used as source to source discriminator because their variability within a given source is bigger than a source to source variability for Iberian and French sources. Thus the repeated µ-XRF analysis for the same sample does not closely agree in most elements and, in fact, can exhibit tremendous variability, with M1-1 and M3-1 samples that accounts for CV’s as high as 87 (FeO), 62 (V) or 91% (Cr). These CVs prevent us of using these elements and their correlations as an indicator of provenance due to its high natural variability.

Thus, natural source mineral variability becomes an important barrier to variscite provenance analysis and therefore to its reliability in determining prehistoric exchange routes.

Variscite’s ideal formula is [AlPO4·2H2O] which means a P/Al atomic ratio equal to 1, although aluminium substitutions for other trivalent transition ions (Fe3+, Cr3+, V3+, …) may slightly increase this ratio. This is consistent with most of the previously reported data (Odriozola et al., 2010), however, in our case this ratio is much higher than 1, around 1.7. Despite this high ratio the XRD data unambiguously confirm that our material is type M variscite. For the El Tejar the measured P/Al ratio is closer to the one expected for pure stoichiometric variscite phase having a chemical composition equal to the ideal represented by AlPO4·2H2O formula. This value is consistent with the ones previously reported (Moro et al., 1992). If we consider partial substitution of aluminium by other transition metals in the P/M ratio, where M stands for the sum of the atomic percentages of aluminium and the rest of transition metals, the P/M ratio in our sample is still much higher than 1.

The existence of hydrogenphosphate anions in the variscite group minerals has been previously proposed. Frost et al. (2004) reported an...
Table 1. Mineral phase identification for the studied samples accomplished with bead type and measures.

| Code     | Megalithic tomb (mineralogy) | Tipology       | Length (mm) | Width (mm) | Perforation (mm) | Geographic area           |
|----------|------------------------------|----------------|-------------|------------|------------------|----------------------------|
| DP-2     | Pozuelo 2                  | Muscovite      | 8.61        | 7.22       | 1.78             | Andévalo Oriental          |
| DG-4     | Gabrieles 4                | Talc           | 10.48       | 13.61      | 6.89             | Andévalo Oriental          |
| DC-2144  | Calzado                    | Muscovite      | 11.99       | 16.10      | 10.00            | Andévalo Oriental          |
| DC-2180  | Calzado                    | Muscovite      | 14.63       | 13.91      | 6.48             | Andévalo Oriental          |
| DM-4016  | Mascotejo                  | Talc           | 11.24       | 12.01      | 6.19             | Andévalo Oriental          |
| DM-4031  | Mascotejo                  | Muscovite      | 12.00       | 8.62       | 1.79             | Andévalo Oriental          |
| DM-4049  | Mascotejo                  | Talc           | 14.59       | 13.91      | 6.18             | Andévalo Oriental          |
| DPH-1050 | Puerto Huertos              | Talc           | 13.68       | 11.49      | 4.99             | Andévalo Oriental          |
| DPH-1057 | Puerto Huertos              | Muscovite      | 12.49       | 12.37      | 2.78             | Andévalo Oriental          |
| DPH-1067 | Puerto Huertos              | Spherical      | 8.03        | 10.52      | 2.52             | Andévalo Oriental          |
| DPH-1076 | Puerto Huertos              | Cylindrical    | 15.11       | 13.98      | 4.68             | Andévalo Oriental          |
| DPH-1082 | Puerto Huertos              | Muscovite      | 7.69        | 6.27       | 2.39             | Andévalo Oriental          |
| DPH-1102 | Puerto Huertos              | Talc           | 8.34        | 10.66      | 3.99             | Andévalo Oriental          |
| DPH-1108 | Puerto Huertos              | Chlorite       | 0.91        | 5.26       | 2.03             | Andévalo Oriental          |
| DPH-1119 | Puerto Huertos              | Talc           | 6.89        | 6.88       | 2.31             | Andévalo Oriental          |
| DPH-1130 | Puerto Huertos              | Muscovite      | 6.99        | 11.01      | 2.76             | Andévalo Oriental          |
| DPH-1154 | Puerto Huertos              | Muscovite      | 10.00       | 8.31       | 2.79             | Andévalo Oriental          |
| DPH-1159 | Puerto Huertos              | Biconical      | 10.11       | 7.44       | 2.26             | Andévalo Oriental          |
| DPH-1164 | Puerto Huertos              | Muscovite      | 12.91       | 10.42      | 2.51             | Andévalo Oriental          |
| DPH-1165 | Puerto Huertos              | Muscovite      | 4.46        | 3.69       | 1.14             | Andévalo Oriental          |
| DPH-1175 | Puerto Huertos              | Muscovite      | 11.4        | 11.02      | 3.66             | Andévalo Oriental          |
| DPH-1177 | Puerto Huertos              | Chlorite       | 1.19        | 4.72       | 2.14             | Andévalo Oriental          |
| DPH-1184 | Puerto Huertos              | Muscovite      | 11.41       | 11.27      | 3.14             | Andévalo Oriental          |
| DPH-1238 | Puerto Huertos              | Cylindrical    | 13.34       | 11.64      | 5.33             | Cuenca media del río Guadiana |
| 4348     | T1 Perdigões                | Muscovite      | 2.24        | 5.89       | 1.59             | Cuenca media del río Guadiana |
| 4343     | T1 Perdigões                | Variscite      | 5.26        | 8.62       | 2.02             | Cuenca media del río Guadiana |
| 7163     | T1 Perdigões                | Variscite      | 3.87        | 6.24       | 2.06             | Cuenca media del río Guadiana |
| 7289     | T1 Perdigões                | Variscite      | 12.24       | 8.82       | 2.71             | Cuenca media del río Guadiana |
| 7547     | T1 Perdigões                | Muscovite      | 3.23        | 10.18      | 1.56             | Cuenca media del río Guadiana |
| 7784     | T1 Perdigões                | Variscite      | 11.09       | 15.22      | 4.54             | Cuenca media del río Guadiana |
| 7816     | T1 Perdigões                | Variscite      | 11.05       | 12.41      | 3.03             | Cuenca media del río Guadiana |
| 7942     | T1 Perdigões                | Variscite      | 13.85       | 6.69       | 2.73             | Cuenca media del río Guadiana |
| 7944     | T1 Perdigões                | Variscite      | 4.71        | 10.03      | 1.94             | Cuenca media del río Guadiana |
| 7906     | T1 Perdigões                | Variscite      | 5.12        | 7.76       | 2.66             | Cuenca media del río Guadiana |
| 11821    | T2 Perdigões                | Variscite      | 2.16        | 6.59       | 1.34             | Cuenca media del río Guadiana |
| 11822    | T2 Perdigões                | Variscite      | 3.99        | 5.94       | 2.18             | Cuenca media del río Guadiana |
| 11823    | T2 Perdigões                | Variscite      | 2.92        | 7.56       | 1.25             | Cuenca media del río Guadiana |
| 11825    | T2 Perdigões                | Variscite      | 3.64        | 8.09       | 1.73             | Cuenca media del río Guadiana |
| 11827    | T2 Perdigões                | Muscovite      | 5.20        | 6.27       | 2.14             | Cuenca media del río Guadiana |
| 11835    | T2 Perdigões                | Variscite      | 2.49        | 5.84       | 1.69             | Cuenca media del río Guadiana |
| 11824    | T2 Perdigões                | Variscite      | 3.58        | 5.24       | 2.18             | Cuenca media del río Guadiana |
| 11826    | T2 Perdigões                | Variscite      | 3.59        | 7.83       | 1.54             | Cuenca media del río Guadiana |
| 11838    | T2 Perdigões                | Variscite      | 2.48        | 5.41       | 1.02             | Cuenca media del río Guadiana |
| 11839    | T2 Perdigões                | Variscite      | 5.02        | 8.15       | 2.44             | Cuenca media del río Guadiana |
| P1       | T3 Pijotilla                | Variscite      | 25.00       | 7.50       | 3.80             | Cuenca media del río Guadiana |
| P2       | T3 Pijotilla                | Variscite      | 15.60       | 10.0       | 5.20             | Cuenca media del río Guadiana |
| P3       | T3 Pijotilla                | Muscovite      | 3.80        | 2.80       | 2.20             | Cuenca media del río Guadiana |

XRD, x-ray diffraction.
earlier model that considers non-hydrogen-bonded $\text{PO}_4^-$ and strongly hydrogen-bonded $\text{PO}_4^-$ units together with $(\text{Al(OH)}_2)_n(\text{H}_2\text{PO}_4)_m$ type species. These authors on the basis of the Raman spectra of variscite group minerals demonstrated the presence of multiple anionic species involving phosphate, dihydrogen-phosphate and mono-hydrogenphosphate species. The presence of hydrogenphosphate species in the variscite mineral would result in $\text{P/Al}$ atomic ratios higher than 1 depending on the exact value and the relative proportions of the different hydrogenphosphate species. Early studies have set up the existence of hydrogenphosphate species in the genesis of variscite minerals being the hydrogenphosphate solid phase the one precipitated earlier (Hsu, 1982).

In the infrared spectra of geological variscite samples and beads we observe bands at ca. 1100, 1150 and 830 cm$^{-1}$. These broad bands showing several shoulders are compatible with those described by Frost et al. (2004) in both the symmetric and antisymmetric stretching regions of the $\text{PO}_4^-$ units which are claimed by these authors as an indicator of multiple $\text{PO}_4^-$ species.

By obtaining the second derivative of the IR spectra we determine the position of the maxima corresponding to the overlapping vibrational modes, the obtained values are compared with those of the literature (Frost et al., 2004; Tejedor-Tejedor and Anderson, 1990; Farmer, 1977). The vibrational modes ascribed to librational modes of the water molecules present in the variscite structure are observed at frequencies below 900 cm$^{-1}$ and the modes between 1200 and 900 cm$^{-1}$ to the stretching frequencies of [30] the $\text{PO}_4^-$ coordination polyhedra. Our IR spectra are consistent with previously reported data and might be ascribed to a mixture of phosphate and hydrogenphosphate species. Therefore, the existence of these hydrogenphosphate species accounts for the $\text{P/Al}$ ratio reported previously.

These findings suggest the $\text{P/Al}$ atomic ratio recorded for Pico Centeno massive variscite arose during the genesis of the variscite deposits and resulted from the associated pH and nature of the host-rocks, modifying the concentrations of $\text{PO}_4^{2-}$, $\text{H}_2\text{PO}_4^-$ and $\text{PO}_4^{3-}$. Thus, the $\text{P/Al}$ 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 $\approx 1$.

The great majority of green beads from Perdigüés tholoi 1 and 2 match the ICDD card 25-18 card, as can be seen in Figure 5. There are only 3 beads that do not match variscite pattern and these appear to match muscovite XRD pattern (ICDD 6-263).

La Pijotilla’s beads match the variscite XRD pattern in two of the cases and muscovite for the third one. At Andévalo Oriental the use of variscite as raw material for beadwork is completely absent and the preferential mineral of choice is the use of the so-called soapstone (talc, muscovite and chlorite). Of the 25 beads analysed (Table 1), 9 beads were made with talc (ICDD 19-770), 13 with muscovite (Figure 5) and 2 with chlorite (ICDD 1-73-2376).

The compositional data show how it is not possible to discriminate between the three different variscite mines of Pico Centeno, or between the Sierra Concha, El Tejar and Pico Centeno sources according to minor and trace elements. This is contrary to what has been suggested in the literature. In our case study the above-mentioned $\text{P/Al}$ atomic ratio allows source provenancing between sources because it is a characteristic of the vein’s origins and as such can be used to link the prehistoric mine and the beads and is fully consistent with the beads found at the Middle Guadiana (Figure 6).

As shown in Figure 6 P vs $\text{Al}$ plot, the samples from the Pico Centeno mines are clustered together and clearly separated from the other outcrops. They also appear separated from the isolated nodules found distributed around the hill but outside the trenches debris and scars. Samples from Sierra Concha and El Tejar are closer to the mines’ cluster but are still separated enough from the core values of the cluster.

**Conclusions**

The sampled mineral found in the trench scars, the rough-out nodules, the worked flake scatter and the Middle Guadiana beads are all representative of a hydrogenphosphate species which results in a $\text{P/Al}$ ratio much higher than 1. Both the mineral sampled at Pico Centeno and the beads from the Middle Guadiana have similar $\text{P/Al}$ atomic ratios, which suggests that the raw material from which they are made comes from Pico Centeno.

The natural variability found in the elemental composition of the trench samples and the overlapping of minor and trace elements values in the mineral does not allow us to discriminate between trenches. It does, however, allow us to differentiate between different outcrops. In this paper we propose that differences in the $\text{P/Al}$ atomic ratio might be characteristic of the paragenesis of the mineral, and might constitute a fingerprint of each source.

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