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An elusive stone: the use of variscite as a semi-precious stone

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Summary The analysis of the stone beads from one of two gold necklaces found in a Romano-British grave near Gillingham, Kent, using non-invasive Raman microscopy showed that the beads are of garnet and emerald. The second gold necklace is set with seven green beads. These are very similar in appearance to weathered green glass but X-ray fluorescence analysis suggested that the beads are composed essentially of aluminium phosphate, leading to the interpretation that they may be variscite; this was confirmed by X-ray diffraction analysis.

Variscite has been reported only rarely from Romano-British contexts but polished beads and pendants of variscite (often referred to as *callais* or *callainite*) have been reported relatively frequently from Neolithic sites in Brittany and elsewhere in north west Europe. Visual identification of variscite is not straightforward and the ease with which it may be confused with weathered green glass (a material that is relatively common from Roman contexts) suggests that perhaps the striking difference in abundance between Neolithic and Roman contexts is apparent rather than real. The study emphasizes the need for analytical investigation of finds of 'weathered green glass' from Roman contexts, beyond visual examination.

INTRODUCTION

An archaeological investigation was undertaken by Pre-Construct Archaeology on land at Grange Farm, Gillingham, Kent, between October 2005 and May 2006. The site was positioned upon the northern slope of a hill, overlooking the River Medway and was continuously exploited from the Late Iron Age until post-Mediaeval times. Roman occupation of the site seems to have occurred soon after the conquest of Britain. In a tomb, constructed in the third century AD alongside a metalled road, necklace chain fragments were discovered on top of a collapsed tessellated surface.

The tomb contained the lead coffin of a teenage girl and "two gold necklaces were found overlying the grave but no further goods were found with the skeleton" [1; p. 3]. The two necklaces (illustrated in Figures 1 and 2) may have been placed as funerary offerings or be grave goods from another, robbed out, coffin within the same tomb.

In an unpublished report, Hobbs indicated several parallels for the necklaces from continental Europe [2], based in part on suggestions by Sas [3]. One parallel is provided by a child's grave from Bonn [4; No. 99e]; another is a more elaborate necklace from Pouilly-sur-Saône [4; No. 111]. Parallels for the terminals on the fragment of a necklace can be found on items from Archar, Bulgaria and from a third-century tomb in Lyon [5; pp. 212–213; Figure 30j].

The two items were declared under the terms of the Treasure Act and the original purpose of our investigation was to conduct analyses to form the basis of a report to the Coroner. It quickly became apparent however that these finds were of particular interest and, with the agreement of the excavators, a more detailed investigation of the materials used was undertaken. Several techniques were used including optical microscopy, X-ray fluorescence analysis, Raman spectroscopy and X-ray diffraction, as described below.

ANALYSIS AND INTERPRETATION

The gold chains

The metal of the two necklaces was analysed using non-invasive, non-destructive X-ray fluorescence (XRF) analysis.

FIGURE 1. Fragmentary necklace from Grange Farm, Gillingham, Kent. No. KKGF 03 (205). sf234, third century AD

FIGURE 2. Fragmentary necklace from Grange Farm, Gillingham, Kent. No. KKGF 03 (205). sf233, third century AD

A Bruker Artax micro-XRF spectrometer with a molybdenum tube (operated at 50 kV, 0.8 mA) was used. The areas to be analysed were not prepared in any way, so that the analyses may be subject to error due to the effects of surface enrichment of the gold alloy during burial. The long chain was found to contain 85–88% gold with 7–10% silver and 2–4% copper, the shorter chain, 90–93% gold, 3–6% silver and 1–3% copper.

Identification of the gemstones

The gemstones were analysed using Raman spectroscopy. This too was non-invasive and non-destructive and was carried out on unprepared surfaces of the red and green stones. A Dilor LabRam Infinity Raman microscope equipped with two lasers (a green Nd:YAG laser at 532 nm and a near infrared diode laser at 785 nm) was used. Spectra were compared with a British Museum in-house database of standards. Analyses of the red stones on necklace KKGF 03(205).sf234 showed that these are all garnets, probably close in composition to the magnesium-rich garnet, pyrope. Analysis of the bright green stones on the longer necklace fragment showed these to be emeralds. However, it was not possible to obtain useful spectra from the rather dull green stones of the shorter necklace fragment, probably because of surface alteration/contamination during burial.

Examination of these dull green stones using a binocular microscope revealed that they have pitted surfaces, with small cavities containing minute ‘globular’ (botryoidal) aggregates. The colour of the beads varies both from one bead to another and also within a single bead. Based upon these microscopical observations, it was thought that the beads might be of weathered green glass. However, the results of XRF analysis did not support this interpretation. Several beads were analysed using the Artax spectrometer: for these analyses helium gas was used to flush the analysis area in order to improve detection of light elements. The spectra obtained indicated that the proportion of silicon was very low, not consistent with the beads being made from glass. Instead, the XRF analyses indicated that the beads contained high proportions of aluminium and phosphorus, together with small amounts of potassium, titanium, chromium and vanadium. Consideration of this rather unexpected composition suggested that the beads might be variscite, a hydrated aluminium phosphate mineral. A very small sample was removed from one of the beads for analysis using a Debye-Scherrer X-ray powder diffraction (XRD) camera. Comparing the resulting diffraction pattern with the ICDD database (International Centre for Diffraction Data, Pattern 25-18) confirmed the identification of the material of the bead as variscite.

Variscite is a member of a group of minerals that includes several arsenates and phosphates with a general chemical formula $AXO_4{\cdot}2H_2O$, where A can be aluminium (Al^{3+}), iron (Fe^{3+}), chromium (Cr^{3+}) or indium (In^{3+}), and X may be arsenic (As) or phosphorus (P). The most commonly occurring minerals of this group are strengite ($FePO_4{\cdot}2H_2O$) and variscite ($AlPO_4{\cdot}2H_2O$); there is a compositional series between the two end-member compositions with varying proportions of iron and aluminium. Frost et al. have demonstrated that it is possible to distinguish between the various minerals of the variscite group on the basis of their Raman spectra [6].

DISCUSSION

Previous reports of variscite in Romano-British jewellery

Necklaces and bracelets of Roman date, comprising gold chains set with emeralds and garnets are relatively well known throughout the Roman Empire, including Britain [7; pp. 96–99]. Emeralds, in particular, were highly regarded by the Romans and Pliny wrote in his *Natural history* "… no colour has a more pleasing appearance. … there is nothing whatsoever that is more intensely green. … engravers of gemstones find that this is the most agreeable means of refreshing their eyes: so soothing to their feeling of fatigue is the mellow green colour of the stone" [8; book 37 XVI]. Sources of emerald are few and it is thought that emeralds used in the Roman world were obtained from the Eastern Desert of Egypt – see, for example, Aston et al. [9; pp. 24–25] or Sidebotham et al. [10]. In her account of these Roman gold necklaces, Johns commented on the use of green glass as a substitute for emerald and also on the use of other coloured glasses to imitate amethyst, sapphire and pearl [7]; see also Murdoch [11; Figures 168 and 169]. Johns [7], however, makes no mention of variscite and the number of published examples of the use of variscite in Roman jewellery from Britain is very low, as discussed below.

Most recently (but now almost 20 years ago!), Hooley reported the recovery of a small bead identified as variscite from excavations at the General Accident Head Office Extension site in York [12; p. 20]. In a fuller, unpublished report (we are grateful to its author for providing this report and for alerting us to previously published reports of variscite beads from Roman contexts), the bead (Find No. 1983/4.32 sf1044) is described as being octagonal in section and is dated to the late second to early third century AD [13]. The material of the bead was identified as variscite by Wilthew using a combination of elemental analysis (by XRF) and XRD. In his report, Hooley also refers to a second variscite bead from York (1981.12 sf35) that was found at the Rougier Street site; this faceted cuboid bead was dated to the mid-fourth century or later. Other reported finds are very few and Hooley commented that, "only half a dozen items of this material are known from Roman Britain". One example, a fragment of a stone finger ring (included amongst 'Miscellaneous objects of bronze') from excavations at Gadebridge Park, Hemel Hempstead was identified as variscite by Bimson [14; Figure 60; p. 138 item 151]. She used a combination of qualitative spectrographic analysis, which showed that the ring consisted mainly of aluminium and phosphorus, and XRD, which produced a diffraction pattern that could be matched with variscite. In Bimson's analytical report, published by Neal [14], it was noted that variscite is a rather rare mineral and that "this is the first time it has been identified [in Britain] in an archaeological artefact". The only other published report of variscite artefacts from Roman Britain that could be located is a record of three beads with octagonal cross-sections that were recovered amongst the small finds from Balkerne Lane, Colchester [15; p. 34 Nos. 1444–1446].

Variscite from Neolithic contexts in Brittany

For some time, pale to bright green beads and pendants (Figure 3) have been reported from many prehistoric sites in western Europe, especially in Brittany [16]. These beads are often described as being of *callais* or *callainite* but now are usually referred to as variscite. The terms *callais* and *callaina* were used by Pliny [8; book 37 LVI and XXXIII], but it is thought that Pliny was referring to turquoise, hydrated copper aluminium phosphate, rather than to variscite [16; pp. 227–229, 17]. Damour made chemical analyses of some *callais* beads from a tomb at Mané-er-Hroek, Locmariaquer and showed that they consisted of a hydrated aluminium phosphate [18]. Later analyses of some Breton beads by Lacroix (referred to by Forde [16; p.228]) confirmed Damour's finding that the Breton beads were made from a hydrated aluminium phosphate, similar to variscite. A further complication is added by analyses of a sample of *callainite* from Montebras, France reported by McConnell;

FIGURE 3. *Callais* beads from Lannec-er-Ro'h (British Museum Reg. No. 1875,0403.552–561) and a triangular pendant from Mané-er-Hroek, Morbihan, Brittany (1875,0403.823), *c*.4700–4300 BC

XRD analysis gave a powder diffraction pattern that could be "satisfactorily accounted for only by assuming a mixture of wavellite [another hydrated aluminium phosphate mineral] and turquois [*sic*; hydrated copper aluminium phosphate]" [19].

The 10 perforated beads and the sub-triangular, perforated pendant shown in Figure 3 were analysed using the Raman microscope. The resulting spectra are consistent with them being made from minerals of the variscite group, based upon comparison with spectra published by Frost et al. [6]. Thus, whilst not all of the green beads from Neolithic contexts that have been described variously as *callais*, *callaina*, *callainite* or variscite may be variscite in the narrow sense, rather than another closely related member of the variscite group of minerals, the term variscite would seem to be a useful way to describe the material that was exploited by Neolithic peoples and later by the Romans. More detailed mineralogical study may permit characterization of different geological sources and provenancing of particular archaeological finds – see below.

Geological occurrence and possible sources of variscite

Variscite is a naturally occurring, hydrated aluminium phosphate mineral. Typically, it is deposited under near-surface conditions in situations where phosphate-bearing waters are available. It occurs usually as nodules or veins of fine-grained material, ranging in colour from very pale green to a bright emerald green; less commonly it may be brown, yellow and (rarely) red [20]. It has been shown that the green colour arises from the presence of Cr^{3+} ions in the structure; small amounts of iron and/or vanadium found in some samples do not contribute to the colour [21]. Variscite is relatively widespread geologically, with several occurrences in Europe (it was named for Variscia, now Voigtland, in Germany); a particularly rich deposit near Fairfield in Utah, USA supplies much of the modern material that is used for jewellery (see, for example, Webster [22; pp. 365–366]).

It was suggested by Jobbins that the variscite used to make the beads found at Balkerne Lane, Colchester may have come from central Europe (see Crummy [15; p. 34]). Harrison and Orozco Kohler record that sources of variscite have been reported in Austria and the Czech Republic [23], quoting the observations of Meireles et al. [24]. A central European source for the variscite used for both the Neolithic and the Roman artefacts cannot be excluded, but the most probable source for the variscite used during the Neolithic is now thought to be northern Spain.

In north east Spain (Catalonia), at Can Tintorer, spectacular mines were dug during the Neolithic to extract variscite, which was worked into beads at a settlement adjacent to the mines (see Harrison and Orozco Kohler [23] and references therein). However, recent analytical work to characterize the various geological sources suggests that variscite for the beads and other ornaments found in Morbihan, Brittany was probably obtained from north western Spain in the provinces of Zamora or Galicia [25, 26].

Is there really so little Roman variscite?

It appears that the use of variscite in early north west Europe was extensive, with many beads and other worked items being recognized from Neolithic contexts. In later periods, however, the use of this material seems to have all but ceased, with very few published reports of its identification from archaeological contexts. Even during the Roman period, when there is evidence from Palazuelo de las Cuevas, Zamora in Spain that variscite was being exploited [23], the number of finds is very low. There are no obvious reasons why variscite should have survived better in Neolithic sites compared to later sites, so the observed difference in abundance may simply indicate that the quantities of material extracted and worked by the Romans (and other post-Neolithic cultures) were very small. However, it may be that the apparent difference in abundances between the Neolithic and later periods reflects a failure to identify variscite from the later contexts. But why should recognition of variscite from Roman sites be less reliable than from Neolithic contexts?

Underlying any failure to recognize variscite in artefacts from Roman contexts may be the ease with which it may be confused visually with weathered glass – a point made by Hooley [13]. As described above, glass is a material that is known to have been used by the Romans to imitate natural gemstones in jewellery. On Roman sites, glass is perhaps perceived as a more likely material than variscite and it is perhaps significant that in each of the published instances when variscite has been recognized from Roman contexts in Britain, its identification has depended upon a combination of chemical and mineralogical analysis. Thus, critical to the identification of variscite from Romano-British contexts has been a recognition of the need for some analysis beyond visual observation. When considering the nature of such material from Neolithic contexts, however, the choice is more limited and glass is certainly not a contender!

SUMMARY AND CONCLUSIONS

The present study of two items of Roman jewellery from Gillingham in Kent has shown that the chains are of gold alloyed with a small proportion of silver and a trace of copper. One of the necklaces (Figure 1: No. KKGF 03 (205).sf234) is set with emeralds and garnets. The stones from the second item (Figure 2: No. KKGF 03 (205).sf233) have been identified as variscite. The identification of variscite in Roman jewellery – and in post-Neolithic material generally – is unusual, whereas it is well known (though often referred to as *callais* or *callainite*) from Neolithic contexts in north west Europe. A review of previously reported finds of variscite, together with the present observations, suggests that the rarity of variscite in Romano-British contexts may be apparent rather than real and arise from the ease with which it may be confused with weathered green glass, a material that was used widely in the Roman world. This emphasizes the need for careful scrutiny of such finds and the application of techniques for chemical and mineralogical analysis.

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MATERIALS AND SUPPLIERS

- Raman microscope: HORIBA Jobin Yvon Ltd, 2 Dalston Gardens, Stanmore, Middlesex HA7 1BQ, UK. Email: info@jobinyvon.co.uk
- Micro XRF: Bruker AXS Ltd., Banner Lane, Coventry CV4 9GH, UK. Email: info@bruker-axs.co.uk
- XRD database: The International Centre for Diffraction Data, 12 Campus Boulevard, Newtown Square, PA 19073-3273, USA. Email: info@icdd.com

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