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Focus article

Earliest evidence for asbestos composites linked to Byzantine wall paintings production

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ABSTRACT

Evidence suggests that asbestos, a fibrous form of serpentine or amphibole was discovered and used in Cyprus since ancient times. In the first century AD, Pedanius Dioscorides in his treatise *De Materia Medica* V.138, refers to "λίθος ἀμίαντος" [lithos amiantos], a fibrous stone from Cyprus, cleansed by fire that was mainly used to manufacture fabrics. Other ancient Greek and Latin authors make reference to the use of this natural resource mainly for the production of textiles and oil-lamp wicks. Additional known uses of asbestos in antiquity include ceramic production as evidenced by the discovery in Finland of 2000 BC asbestos-tempered ceramic ware. The exploitation and use of this fibrous rock in the manufacture of cements, however, was thought to be a novelty of the late nineteenth century. Here we show that 'amiantos' composites were in existence in Byzantine Cyprus, emerging much earlier than the start of the modern asbestos industry. The identification of chrysotile mineral in $CaCO_3$-rich uppermost plaster coatings, just beneath the paint layer, in twelfth century Byzantine wall paintings in the Enkleistra – place of reclusion – of Saint Neophytos, provides direct evidence for the earliest use of asbestiform fibres in wall-painting finish coatings. We demonstrate that Byzantine monks were familiar with the fabrication of asbestos-fibre composites and their superior properties over more common $CaCO_3$/organic fibre plasters, traditionally used in Byzantine wall painting. We support that chrysotile fibres were exploited for their good physical, flexural, and insulating properties.

1. Introduction

The use of asbestos fibres in Byzantine Cyprus during the twelfth century as reinforcement to finish-coatings in the production of wall paintings marks an important technological development and innovation in the use of this mineral resource. Asbestos (Bowles, 1955; Ross and Nolan, 2003) was known since ancient times for its resistance to destruction under extreme conditions and particularly for its fireproof and cleansing properties when exposed to fire (Dioscorides, 2005). It was also believed to have magical power and was associated with mythical creatures as recounted by medieval alchemists (Laufer, 1915; White, 1954). Historic accounts from the Classical world, China and India provide written testimonies on its exploitation and use (Laufer, 1915; Browne, 2003). Remarkably, it was mainly employed in the production of woven textiles. In the second century AD, Pausanias in his book *Description of Greece* I.26, refers to a golden lamp for Goddess Athena made by Callimachus (400 BC?) burning all year round with a wick made of "Carpasian flax" with fireproof properties (Jones et al., 1918). In his book *Natural History* XIX. 4, Pliny the Elder (AD 23–79) also refers to linen cloth, incombustible by flame, used to make napkins and wrappings for the bodies of monarchs during cremation, separating their ashes from those of the woodpile. In the thirteenth century, Marco Polo describes in *The Travels* a special cloth used by the Tartars made of spun and woven wool-like fibres dug from a mountain that were thrown in the fire to whiten (Polo, 2009). In the Christian era, asbestos seems to have been valued and traded in exchange of goods along the silk routes (Loewe, 1971). According to Maines (Maines, 2005), Ibn al-Fatiq recorded that tenth-century Christian pilgrims travelling to Jerusalem were sold presumably pieces of asbestos as fragments of the True Cross having magical properties as proved by their incombustibility. Two major natural resources of asbestos are mentioned in ancient texts: Cyprus (Plutarch, 1936; Beck, 2005) and the

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ancient city-state of Carystus (Gilroy, 1853; Evans, 1906; Plutarch, 1936; Jones, 1969; Hammar and Dodson, 2011; Richard, 2011) in Euboea, Greece. According to Gilroy, in an extract from the book of Sotacus *Περί λίθων* [Peri lithon] (On Stones) preserved in the accounts of Apollonius Dyscolus (or Alexandrinus Minor) *Historiae Commentitiae*, there is a passage referring to Carystus stone similar to that found in Cyprus that can be spun and woven into napkins that are cleansed when thrown in flames and twisted into wicks that could burn but not consumed by fire. The Greek geographer Strabo (c. 64BC – after AD 21) in *Geography* 10.1, also refers to a fibrous stone from Carystus that is combed and woven and used to make towels cleansed by fire when soiled (Jones, 1969). This information is also supported by Plutarch, in his essay *De defectu oraculorum.43* (Plutarch, 1936), who, equally, mentions a filamentous rock from Euboea that was used to make towels, nets and women's head coverings that was unaffected by fire. He also states that at his time the fibrous veins were almost extinct giving a *terminus ante quem* for the exploitation of asbestos in this locality.

The admixture of asbestiform minerals in pottery as temper to provide tensile strength to the clay as early as 4500 years ago (Lavento, 1992), demonstrates another important usage of this fibrous rock, beside textile manufacture. However, the incorporation of asbestos fibres in plasters and finish-coatings, appears for the first time much later, during the second half of the nineteenth century following the industrial revolution, with the introduction of asbestos cement composites. There are no other known instances, particularly of the Byzantine period or earlier, denoting the use of asbestos in wall plasters, joint compounds or floors. The discovery of the asbestiform fibres in Byzantine wall paintings in Cyprus provides the earliest known precursor to the modern engineered cementitious composites. It further provides insight on the chemistry and origin of painting materials as proxies to infer technological innovation and craftsmanship in the late twelve-century in Cyprus.

Compared to other contemporary religious places in Cyprus and elsewhere in the Byzantine world, the Enkleistra of Saint Neophytos is rather unique. It was first hewn out of the limestone cliff and occupied by Saint Neophytos in AD 1159. The saint gradually dug his abode into a complex that consisted principally of three caves: the cell with his tomb, the bema and the naos (Fig. 1). His fame soon spread and in 1170 he was forced by the bishop of Paphos to accept a disciple. He thus started a monastery and composed the rules, which he called "Τυπική Διαθήκη» [Typike Diatheke]. Neophytos composed not only his biography and the rules of the monastic community he founded, but also an account of the conquest of Cyprus by "Richard the Lionheart" in 1191 and several theological treatises. However, the increasing amounts of pilgrims made him dig another cave, above the first cave complex, in seek of solitude and inner peace that was completed by the end of 1196.

According to written testimonies including an inscription by the painter, Theodore Apseudes, giving the date AD 1182/1183 and a statement by Saint Neophytos himself asserting: "in the twenty-fourth year of my confinement [1183] the Enkleistra was painted throughout" (Mango and Hawkins, 1966, p.124), the date for the extended painted phase of the original nucleus of chambers has been established as AD 1182/1183, while, the final phase of the paintings (mainly in the naos) was attributed to a different and unknown painter around AD 1196. Between the earlier and the later wall paintings, there are important stylistic differences: the earlier style resembles that of "court" painting or the "rococo" manner which appears to have evolved in Constantinople in the last quarter of the twelfth century (Mango and Hawkins, 1966), whereas the later paintings are depicted in a far more austere and linear manner that may reflect a deliberately "monastic" asceticism, or a reversion

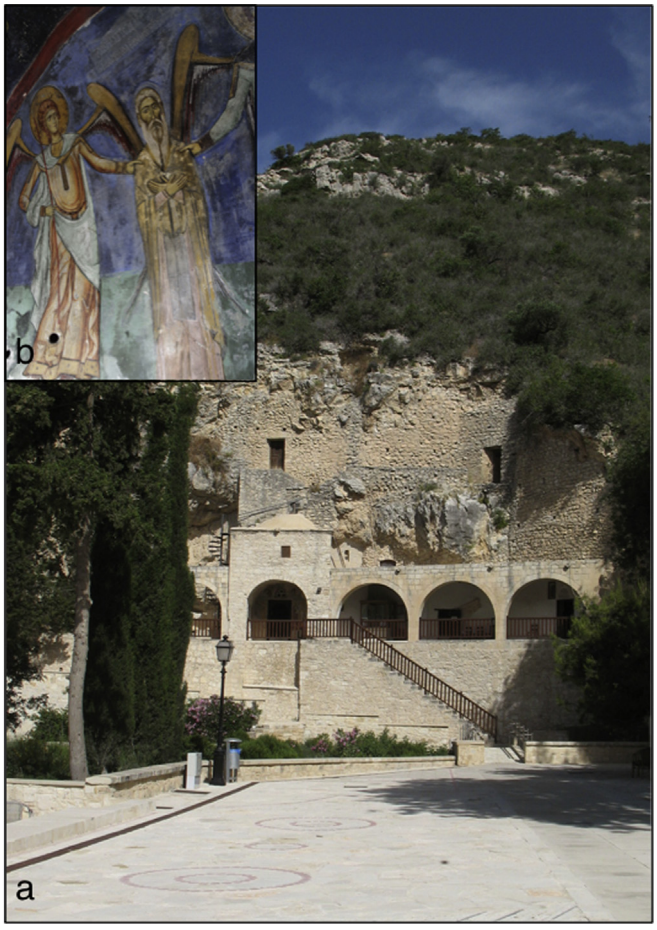

Fig. 1. The Enkleistra of St. Neophytos. Context of the cliff and the façade of the Enkleistra of St. Neophytos leading to the naos, bema and the cell (a). Detail of a twelfth century wall painting in the bema (b) depicting St. Neophytos between the two archangels (only the one to the left is showing here) who hold him by the shoulders.

to less sophisticated painters using the "Comnenian provincial" or "linear style" (Mango and Hawkins, 1966). The Enkleistra also preserves wall paintings of later centuries with a prominent phase of the sixteenth century surviving in the naos and bema.

2. Materials and methods

A non-invasive/minimally invasive methodology was employed for the characterization of the wall paintings at the Enkleistra of St. Neophytos. Analyses were performed in situ and on paint stratigraphic micro-samples (~2–3 mm^3) first on unmounted samples to record morphological and topographic information and subsequently on polished sections (embedded in epoxy resin following established analytical protocols) providing spatially resolved data at the microscopic and molecular scale. Hundreds of spot measurements were taken on site using X-ray fluorescence spectroscopy (XRF) revealing major, minor and trace elements and UV/Vis/NIR reflectance spectrometry providing fingerprint identification of organic and inorganic compounds (Kakoulli and Fischer, 2009; 2011). In addition, 45 micro-samples were analysed using combined techniques including digital microscopy, Fourier transform infrared spectroscopy (FTIR), gas chromatography mass spectrometry (GC/MS) and field emission gun (FEG) variable pressure (VP) scanning electron microscopy (SEM) coupled energy dispersive X-ray spectroscopy (EDS) and Raman spectromicroscopy (μRS) with laser excitation wavelengths at 785, 532 and 405 nm.