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SCIENTIFIC CULTURE, Vol. 8, No. 1, (2022), pp. 95-113
Open Access. Online & Print

DOI: 10.5281/zenodo.5717172

ARCHAEOLOGICAL AND HISTORICAL STUDY OF *LYKION* COMPLEMENTED BY IR AND RAMAN SPECTROSCOPIC INVESTIGATION

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Received: 08/11/2021
Accepted: 23/12/2021

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ABSTRACT

The present study explores issues of production, distribution and application of *Lykion*, a renowned and widely used medicine of the ancient world, by synthesizing literary archaeological and scientific evidence. Lykion has astringent and antimicrobial properties and was used to cure various skin and several other diseases. Miniature vessels have been characterized by researchers as carriers of medicinal and/or cosmetic substances; amongst these, a special category distributed in various areas of the Eastern Mediterranean and South Italy bear inscriptions or stamps identifying *Lykion* as the vessels' content and sometimes provide the name of the manufacturer as well. A comparative study of their typology with their unlabelled counterparts indicates similarities in terms of their content and use. The unlabelled examples are mostly characterised as vessels of storage and transportation of an alternative non-certified medicine produced by using a local plant variety with similar medicinal properties. In the latter case, the shape of the container could signal both the place of origin and the content. Hitherto analytical investigations that would confirm the validity of this hypothesis had yet to be conducted. The present research attempts, for the first time, to trace evidence regarding the content of 15 published ceramic vessels whose biconical and pear-shaped shapes are mostly associated with this particular medicine. The assemblage under study was excavated in ancient Abdera, a coastal city in Western Thrace, Greece. In order to investigate any absorbed content into the ceramic matrix of these vessels, 42 samples were extracted from their inner unglazed walls. The powder samples were then analysed by the complementary Infrared (IR) and Raman spectroscopies and consequently compared to spectra acquired from certified Greek plant varieties. Here we have detected remnant which bear similarities with the spectra of the species *Rhamnus lycioides.*

KEYWORDS: *Lykion*, ancient Abdera, Infared, Raman, ancient botany, ancient pharmacology, miniature clay pots

1. INTRODUCTION

The significance of the ancient medicine *lykion*, which takes its name after the homonymous plant, is confirmed by the frequent references of it in ancient and medieval medical treatises, as well as by the widespread distribution of its miniature stamped clay and lead containers in various areas of the Eastern Mediterranean and South Italy (Zahn 1904; Sjöqvist 1960; Calvet, 1982; Hershkovitz 1986; Mitsopoulos-Leon 1991; Taborelli, Marengo 1998; Rotroff 1997; Işin 2002; Vivliodetis & Giannopoulou, 2014; Taborelli 2014, 2015; Kallintzi 2016; Lajtar, Poludnikiewicz 2017; Taborelli & Marengo 2017, 2018).

Map 1. Distribution of lykion pots in the Eastern Mediterranean and South Italy based on the up to today published findings (map produced through Google Earth by V. Boura)

It is one of the few medicines with no origin in Pharaonic Egypt, whose discovery and application is credited to the Greeks (Sjöqvist 1960, 81, ft. 7). Despite the fact that the medicinal micro-containers of *lykion* begin to circulate in the last quarter of the 4th c. BC (see the earliest example "Type I" from the Athenian Agora in Rotroff 1997, 198), the first appearance of it in literary sources as a healing substance, described in parallel to the *lykion* plant, occurs in the 1st A.D, and it is attributed to Pedanius Dioscorides (*De materia medica* I.100) and to Pliny the Elder (*Naturalis Historia* XII.15, XXIV.75-76). Based on the information provided by the above-mentioned authors, we can deduce, however, that the 5th c. BC physicians of the Hippocratic Corpus were already aware of the healing properties of the different varieties and/or species of plants used to produce the medicine under study. *Lykion* is also cited by Galen, the father of pharmacy, (*De simplicum medicamentorum temperamentis* 12.63-64) as well as by other Roman physicians and pharmacognosists such as Celsus (*De medicina* e.g., 4.9, 5.26, 5.28, 6.6), Scribonius Largus (*Compositiones* 19, 23, 113, 115, 142) and Aelius Promotus (*Dynameron* e.g., 27.5, 31.6, 96.5, 99.1, *Περί των ιοβόλων θηρίων και δηλητηρίων φαρμάκων* 10.50-52, 35.1-10). Furthermore, the literary medical tradition demonstrates that the use of *lykion* survives the Late Antiquity and the Middle Ages. Famous Late Antique doctors, such as Oribasius (*Collectiones medicae*, 11.17, 14.1), Alexandros Tralianus (*Therapeutica* 2.12-13) and Paul of Aegina (*Epitomae Medicae* 7.3) account for its uninterrupted use in time, while it appears that it was still in circulation during the Middle Byzantine period as the *Dynameron* of Nikolaus Myrepsus (13th c. AD) affirms (*Dynameron* e.g. 1, pinax 441, 3.69, 6.8, 19.24g).

It should be understood that the term *lykion* was used to signify both the raw material and the finished product and that both materials were traded. Literary testimonies do not clarify whether *lykion* circulated in the form of raw material or medicine. Archaeological testimonies confirm at least the circulation of the medicine by the discovery of relevant stamped examples. More specifically, research has brought to light stamped medicinal carriers of limited capacity and of various handless (biconical, angular biconical, globular, tall cylindrical) and handled shapes (amphora-shaped, pear-shaped, jug-shaped) that come from religious, burial, public, and domestic contexts. The stamped examples usually bear the name of the medicine or the name of the medicine and that of its producer; the latter consists a "formula of guarantee" for any medicine (Guarducci 2008, 139-140, Taborelli 2018, 177). Current scholarship has identified general distinct groups based on the geographical spanning of the pots from west to east (cf. Type 1A-B, Type 2A-B, Type 3A-B, Type 4, in, Sjöqvist 1960, 79-81; Types A-B-C-D, in, Hershkovitz 1986, 46-49; A. Sicilian, B. Magna Graecian, C. Athenian or Central Mediterranean and D. Eastern Mediterranean, in, Taborelli & Marengo 1998, 222-226; Type I (Athenian Agora), Type II (Morgantina), Type III (Eastern Type, Patara), Type IV (Jerusalem-Masada-Samaria, Tell Anafa, and Jaffa; Syrio-Palestinian), Type V (Athenian Agora Louvre), Type VI, (Priene), in, Işin 2002, 89-91; Lajtar & Poludnikiewicz 2017, 317-326 published from Tell Abrid, Egypt, local variations of the already proposed groupings). The variety of stamped vessels proves that the medicine in question was not stored and/or transported in a pot of a unique shape (Işin 2002, 88), while, specifically for the Morgantina findings, it has been also suggested that the different forms may have served different purposes in separate occasions (Sjöqvist 1960, 78).

Nevertheless, it should be stressed that the vast majority of the "*lykion*" pots under consideration are either unlabelled or the manufacturer remains anonymous. Although it has been suggested that the vessel's form may indicate the production centre of its content, to identify these pots as carriers of *lykion* cannot be acceptable without conducting any chemical analysis (Işin 2002, 88, ft. 31; Lajtar & Poludnikiewicz 2017, 326).

The present study attempts for the first time to trace evidence for the content of a group of vessels whose shape is associated with *lykion* by combining archaeological, literary and scientific evidence, responding to the call for more collaborative studies between historians and archaeological scientists (Totelin 2016). These vessels come from Abdera and are considered products of trade due to their content. This first attempt aims at filling a well admitted gap in our knowledge regarding the function of these pots. The botanical identity of the basic raw material is a prerequisite for the experimental part of this study, hence, this paper also aims at elucidating its controversial identity by reviewing and reflecting on relevant classical literature quotes.

2. HISTORICAL CONSIDERATIONS

The material from Abdera examined in the present case study, consists of 15 miniature vessels, 12 of which were found in various domestic contexts of the ancient city. The excavator connects the miniature vessels with the "packaging, transportation and usage of cosmetic or medical substances, mainly the medical ointment named "*lykion*" (Kallintzi 2016, 490). All of them are handless and feature thick walls and a rough appearance. Only one of these vessels bears an inscription that identifies its manufacturer and /or its owner (ΣΤΡΑΤΩΝΟΣ) but not the medicine, and stands apart from its non-inscribed counterparts, both in terms of overall quality and size (see Fig. 1, no MA 6480). Their date ranges from the 3rd c. BC to the middle of the 1st c. AD, and they are classified by their body shapes into two main types: 1. Biconical, which constitute the largest group (10 vessels) and 2. Pear-shaped. Type 2 corresponds, according to the excavator, to similar shapes mainly from Corinth, but also from Palestine, Ephesos, Morgantina, Vardarski Rid, Thebes and Orchomenos (Kallintzi 2016, 512-514 with bibliography). Type 1, however, which includes the inscribed example, stands apart from the findings that belong to type 2 due to its striking resemblance to a similar group of vessels from Patara in Lycia (Işin 2002, 90, type III, subtypes 1, 2, 3, fig. 5-6, which correspond to Hershkovitz's (1986) group B) (Fig. 1).

More than 100 examples of miniature vessels of biconical shape dating from the mid-2nd to the 1st c. AD have been brought to light in the Tepecik Nekropolis, the largest known group up to present day. All of them are uninscribed but based on typological similarities to other published examples, the excavator characterizes them as medicinal/ointment jars and it is speculated that they could be associated with the medicine in question (Işin 2002, 88). Similar finds have been discovered in Athens, Piraeus, Corinth, Delos, Samos, Ephesus, Perge, Tarsus, Jerusalem, Masada, Dor, Paphos, Samaria (Işin 2002, 90 with bibliography; to these we may add two examples for Tell Abrid in Lajtar & Poludnikiewicz 2017, 326-327, cat. nos 13-14, where they mention further examples from Pylos, Kenchreai, Naxos and Alexandria, see 326, ft. 33). It is observed that when these finds come to light, the hypothesis about their *lykion* content is constantly reproduced.

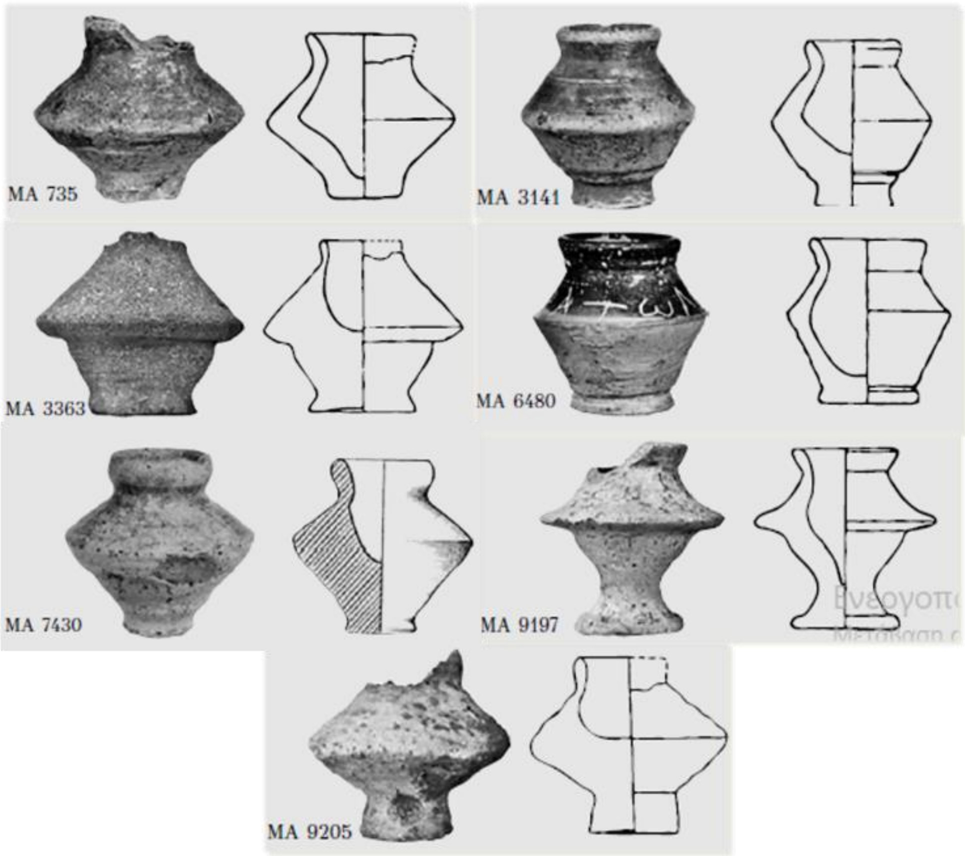

Figure 1. Biconical miniature pots from Abdera (Type 1). After: Kallintzi 2016, 497-498, figs. 1-2

Interestingly, *lykion* was a medicine produced by a plant of the same name, so-called because it flourishes abundantly in Lycia and in Cappadocia of Asia Minor, although it grew in other places too, mainly in rough terrains. Literary evidence describes it as a thorny shrub which some call *pyxacantha* (Pedanius Dioscorides, *De Materia Medica* 1.100; Galen, *De simplicum medicamentorum temperamentis* 12. 63-64; Oribasius 11, *lambda*, 17). Moreover, Latin authors such as Scribonius Largus (*Inscriptiones* 142) and Marcellus (*De Medicamentis* 28.3) distinguish a specific plant-based medicine from Asia Minor, the so-called *lycium pataricum*, a testimony that points to Patara as one of the production centres of the *lykion* medicine.

On another note, Dioscorides describes an additional medicinal plant variety of *lykion* that flourishes in India and he reports that it comes from a similar thorny shrub called λογχῖτις. *Lycium Indicum* would reach the Greco-Roman world through long-distance trade. The two varieties of *lykion* plant demonstrate the simultaneous use of different trade routes and the circulation of more than one version of the medicine: a Mediterranean variety would come from Asia Minor, and a more exotic and effective one would come from India. The *Periplus of the Red Sea* accounts for the availability of *lykion* from the north Indian ports of Barbarikon and Barygaza (Casson 1989 §39 and §49) while Pliny the Elder (*Naturalis Historia* XII.15) reports that the Indian *lykion* was transferred from India in special leather containers made of rhinoceros's or camel's skin. Galen in his *De simplicum medicamentorum temperamentis (*12. 215-216) tells us that because of the extensive adulteration among precious substances, he would travel to Phoinike to obtain from a caravan the authentic Indian variety himself. In these networks, the Levant played an important role in the production and circulation of goods. Diodorus Siculus in his *Bibliotheca Historica* (5.42.2) informs us about the numerous intermediaries involved in this complex trade network maintaining that merchants would come to Arabia to buy precious commodities and convey them to Phoenicia, Coele-Syria, and Egypt. From these places, they were exported to the rest of the world (Frangié-Joly 2016, 40).

Considering that *lykion* was traded both as medicine and raw material we may speculate that its containers would be stamped in specific production centres of the Greco-Roman world. For example, Taborelli and Marengo maintain that Akragas and Syracuse are candidate production centres of *lykion* due to the significant number of stamped and uniform micro-containers that have been discovered in these sites. They also believe that Syracuse might have exported its products to various Mediterranean regions

(2017, 42-43). Moreover, Taborelli has suggested that the producers of the medicinal preparation commissioned a batch of containers from a potter and lent him the stamp (or mould); then they would have collected the containers ready to be filled, packed and sold, directly or through a merchant who would specialise in this sector (Taborelli 2018, 177).

Studying the up to day known examples, we can deduce that several individuals were certified manufacturers of *lykion* between the 3rd c. BC and the 1st c. AD. The preserved stamped inscriptions carry their name along with the name of the medicine. Zahn (1904) reports the names Krates, Proteos, Isidoros, Charidemos, Thrasys, Aristeos, and Straton;-it is noteworthy that the name of Straton appears in our pot from Abdera too. Other characteristic examples include Dionysios (Rowe 1942), Demeas (Calvet 1982), Simakon and Nymfodoros (Taborelli & Marengo 2018), Nikias, Herakleios (Taborelli, Marengo 2017), Iason, Mousaios, Artemidoros, Kleanthis, Akestias, Oiniades (Sjöqvist 1960); Lykias (Taborreli, Marengo 1998), Ermaphilos, Moschion (Taborelli 2018, 175, ft. 28). Some of the inscriptions bear also the phrase "επ'εγγυη" or "επ'εγγυαι" ('that guarantees") to further warranty the content of the pots (see characteristic examples from Athens in Rotroff, 1997, 198, 424, cat. no 1775 and 1776; from Mirmeki in Taborelli, Marengo 1998, 262). It should be understood that the names of the ancient pharmacists sometimes appear more than one time in the archaeological record, while the findings may come from different places. Moreover, same names often signal different individuals since their chronological framework ranges between the 3rd c. BC and the 1st c. AD. For example, the name of Nikias appears on pots that span the 3rd through the 1st c. BC (Zmeikova 1982, 74; Georgaki-Zografou 2001 and Rotroff 1997, 198 respectively). Perhaps, the 3rd c. BC examples point to the poet-physician Nikias, a friend of the poet Theocritus (cf. *Idyll* 28 that was written by Theocritus before or during a voyage from Syracuse to Miletus, and presented with the gift of a carved ivory distaff to the wife of his friend, the poet-physician Nikias). We should add here the most recent finding from the island of Kythnos in Greece, which belongs to Sjöqvist's (1960) type 2 and carries the inscription NIKIAS LYKIOS ("Nikias from Lycia", Tsilogianni 2018, 427, table 4d). The repetition of the names may also point to the passing of knowledge from generation to generation within the context of family tradition. This can be further supported by the reference of a pharmacist who is the son of a pharmacist (Ermaphilos son of Moschion) on stamps of *lykion* containers from Athens and Tell Abrid (Gossen 1913; Nutton 2000; Lajtar, Poludnikiewicz 2017, 324; Taborelli 2018, 175, ft. 28). Moreover, the names of the medicine and/or the pharmacist are sometimes disposed around stamped healing symbols such as the head of Asclepios or the tripod of Apollo, which link to the healing properties of their content (Krug 1997, 112).

It is observed that the name of the medicine under study appears only on stamped examples which are not biconical. Only one pot of biconical shape from the island of Delos bears a painted inscription which mentions "ΟΠΩΡΑ ΛΥΚΙΟΥ", that is "fruits of *lykion*" (Chatzidakis 2014, in *Iasis*, 283, no149). Nevertheless, the fact that the inscription is painted and not stamped questions the validity of this information. Similarly, the painted inscriptions on 3 containers of biconical shape that report substances other than *lykion* may have been added to the miniature pots at a later stage: ΑΛΥΠΟΥ, ΚΕΝΤΑΥΡΙΟΝ (Vivliodetis-Giannopoulou 2014, in *Iasis*, 55, fig. 5; Chatzidakis 2014, in *Iasis*, 278, no 143); ΩΡΑΣ ΑΝΘΟΣ (Smith 1992). Overall, only stamped examples can be treated as solid evidence for the presence of *lykion* in them. It is proposed that the stamped examples represent a high-quality certified product traded for its content. The unlabelled examples might have contained a medicine produced by local pharmacists using available alternative raw materials (Sjoqvist 1960, 32, Krug, *op.cit.*, Guarducci 2008, 139-140). Perhaps the producers of the content of these vases were not authorized to mark their non-genuine products. However, regarding the assemblage from Patara and all associated examples including our case study, we assume that the form of this special category of vessels signals both the place of origin and the content.

Regardless the provenance of the raw material, *lykion* had astringent and antimicrobial properties and was used to cure various skin diseases (for references see above, p. in introduction) oedemas, dysentery, hemoptysis, cough, tonsillitis, otitis, haemorrhoids, liver disorders, rabid dog bites, itching and psoriasis of the eyelids and torn gums. It was used in several forms: as infusion, injection, clyster, pill, ointment, collyrium. Indian *lykion* was considered especially beneficial and effective for eye disorders. In this case, it had the form of a collyrium or of an ointment and could be used pure or as part of a medicinal compound. Galen includes *lykion* in his *Simples medicines* where he mentions various natural ingredients – plants, minerals and animal products- that could be used uncompounded due to the effectiveness of their healing properties (Koutroubas 2010, 113). On a similar note, Paulus of Aegina (*Epitomae medicae* 7, 3) classifies *lykion* in a section dedicated to the properties of simple medicines. Scribonius Largus (*Compositiones* 19) further indicates that the use of *lycium indicum per* *se* is much more effective in the treatment of eye disorders than the use of any other compounded collyrium (Jocks 2013, 70).

According to Dioscorides and Pliny the Elder the extract of *lykion* derives from the roots and the shrubbery after they soak for several days in water and then boil. This liquid product is again boiled until it reaches a honey-like consistency. The foamy substance that floats on top during the boiling is stored for eye meditations and the rest for other purposes. Similarly, the extract may derive from the fruit when pressed out and left in the sun. We may hypothesize that these preparations/products were stored in the miniature vessels in question. It is notable that, especially for the liquid medicinal formulas, Dioscorides states that they should be stored among others, in clay and metal wares (*De material medica*, praef. 6), which is consistent with the current archaeological record.

3. ON THE BOTANICAL IDENTITY OF *LYKION*

The botanical identity of *lykion* is of particular importance to the experimental part of this study but it remains a rather puzzling issue. As stressed by Hardy and Totelin (2016, 93-95) the main issue arising when exploring ancient botany is the identification of plants that have been catalogued and described by ancient writers. Even in antiquity, the nomenclature of plants differs, depending on the writer (Riddle 1985, 28), while Renaissance scholars admit that Pliny sometimes made errors when he identified species found in the Italian peninsula with plants cited in ancient Greek sources (Touwaide 1998, 2). We should also underline that when the term *lykion* is translated into modern languages, there is no consensus among scholars regarding its modern name; they usually adopt one term without considering that the exact botanical identity of *lykion* is debatable.

The descriptions of the *lykion* plant as appear in the literary sources are informative but they don't point out a particular species. Similarly, the illustrated manuscripts are not completely reliable towards that end (e.g., Pierpont Morgan Library. MS M.652). The Mediterranean variety of *lykion,* as mentioned above, is described by Dioskorides (*De material medica,* I, 100) as a thorny shrub. Its shoots are three cubits long or even longer and are surrounded by dense foliage similar to that of the boxwood. It features many firms and very bitter black fruits similar to those of pepper, a pale-colored bark, and woody roots. Concerning the Indian variety, information is more limited regarding its appearance. If we are to trust Pliny, the Indian variety resembles to *lykion* from Asia Minor described by Dioscorides. Moreover, Pliny names or describes various plants which could be used to produce the medicine *lykion* and render it effective. He mentions the *pyxacanthum Chironium* (*Naturalis Historia* XII.15; XXIV.77), which flourished in Mount Pelion in Greece and was according to him of equal quality to the Indian variety. This might be a local variety of the plant called *pyxacantha* or *lykion* by Dioscorides. Pliny also mentions that this plant was used as a substitute for *lycium indicum*. The root of the asphodel, the ox-gall, the wormwood, the sumach, and the amurca of olive oil, are also employed for a similar purpose but the final product is adulterated. Alternatively, Pliny proposes a wild (dark/reddish) variety of *rhamnos* that would produce a *lykion* of inferior quality. He also indicates that the leaves of this kind of *rhamnos* -as well of the paler one- raw or boiled, are made up into a poultice with oil.

Several varieties of *rhamnos* are reported by Dioscorides (*De material medica* I, 90) while four centuries before him they were cited by Theophrastus (*Historia plantarum* III.18.2). Their medicinal properties as well as its uses had been identified and recorded earlier by the Hippocratics. The latter recommend the use of the plant's leaves in the form of poultice over wounds and menstrual cramps and the medicine in liquid form for the treatment of various gynaecological issues (Hippocrates and Corpus Hippocratium Med., *De affectionibus*, 38; *De mulierum affectibus* 78; 193; *De natura muliebri*, 29). These applications are in common with the ones reported for *lykion* from the time of Dioscorides onwards.

Moreover, Pliny reports a *lyкion* medicine prepared with *gentian* (*Naturalis Historia,* XXV, 87) or *centaurium* (*Naturalis Historia,* XXV, 30), appropriate for wounds, while these plants are cited by Dioscorides (III, 3 and 6) as substitutes of *lykion* for the treatment of several diseases.

All the above testimonies allow us to speculate that the base-raw ingredient for the production of the medicine *lykion* could vary. This could in turn result in the circulation of medicines with similar healing properties but with different strength and efficacy as the latter would be largely dependent on the natural state of the plant used.

We believe that if the unstamped vases from Abdera carried the medicine *lykion*, this would have been the by-product of a Mediterranean plant variety. Generally speaking, regarding the basic ingredient of the Mediterranean *lykion*, there have been proposed plant species of three different families: a) Solanaceae, b) Ramnaceae, c) Berberidaceae.

P.G. Gennadios in his botanical dictionary (Gennadios, 1914, 624), uses the scientific name lycium barbarum, a species that belongs to the genus *Lycium* of the family of Solanaceae, in order to characterize *lykion*, specifically the *lykion* of Lycia and Cappadocia or else the *pyxakantha* of Dioscorides**.** Some recent publications are based solely on this piece of information (Valiakos et al. 2017, table 1); other scholars, classify this plant into the Solanaceae family, but, at the same time, they associate *lykion* with the Ramnaceae family (Doga-Toli, in *Iasis* 2014, 46). Furthermore, the ancient *lykion* has also been connected with goji berry–a bush producing red fruits widely known nowadays for its antioxidant properties– whose scientific name is *lycium barbarum* (Chatzidakis, in *Iasis* 2014, cat. no 149). It has been suggested that the ancient *lykion* should not be confused with the genus *lycium*, and particularly with the species *lycium barbarum* which is found nowadays from the Southeastern Europe to the Far East (Ernout 1949, 75-76, Valliakos 2014, 211). Probably, the confusion around the identity of the ancient plant and its recent questionable identification is related to a more recent plant nomenclature that was introduced by Linnaeus, the father of taxonomy, in the 18th c. of our era (Amigues 2000).

Likewise, *lykion* is connected with the species lycium europaeum (Sprengel 1807, vol. I, p. 162= Royle 1833, 85, Varella, 2006) belonging to the genus *lycium*. However, according to Sibthorb (*Flora Graeca,* I, 156, no 542), *lycium europaeum* is linked with the *rhamnos* of Dioscorides.

Gennadios further notes that the common name of the plant in question is *loutsia* in Crete, and *zyliki* in Cyprus. While investigating the botanical identity of these plants based on their vernacular names, we came to the conclusion that they belong to the family of Berberidaceae –and not to that of Solanaceae– and that they belong to the species berberis cretica (Harber, von Raab-Straube 2015: Berberidaceae. – In: Euro+Med Plant base) which nowadays grows in Crete, Pelion and other regions of Greek mainland and the islands, as well as in other parts of eastern Mediterranean, such as in western and in southern Anatolia and in Cyprus, while related species grow in Syria and Lebanon (Dimopoulos et al. 2013, 326). Moreover, "*berberis*" in the Gennadios' dictionary (Gennadios 1914, 189-190), is associated with the vernacular name *loutsia* among other names that point to the thorny form of the bush (e.g., *sagathia*, *oxagathia*). Gennadios refers also to the dual properties of the plant: "all parts of these plants and especially their roots contain a pharmaceutical and colouring substance, the berberine", which is in accordance with the information we possess from historical evidence. Similarly, in Heldreich's dictionary (Heldreich, Miliarakis 1925, 4, 81) the vernacular names *loutsia* and *loutzia* correspond to the scientific names: *berberis cretica* and *lycium barbarum.*

The study of John Forbes Royle (Royle 1833) regarding the botanical identity of *lykion,* especially of the Indian one, became an article-reference mostly in papers of archaeological interest. According to him, the *Indian lykion* was still in use to produce the medicine in the 19th c., while different parts of the plant in dried form could be easily found in Indian markets. Royle refers also to the Arabic and the Persian translations of Dioscorides and concludes that the Arabic *hooziz*, is a synonym of the Greek *loofyon* or *lookyon*, that was produced by the shoots of the trunk and the roots of a berberis species. Therefore, he concludes that the Indian *lykion* is connected with the family of berberidaceae, most probably with the species *berberis asiatica, berberis aristata,* berberis lycium, rejecting its connection with the *acacia catechu*, suggested by other scholars. Furthermore, commenting on earlier bibliography, he states that the *lykion* of Asia Minor may have been produced by different species of *rhamnus*, such as the rhamnus infectoria[1] or even by the species *berberis vulgaris*, stressing that "the family of berberidaceae possesses so many of the many properties as some species of the genus rhamnus". According to Sibthorb, *lykion* is related to the family of Rhamnaceae and particularly with the species *rhamnus infectoria* or *cathertica* (*Flora Graeca,* I, 157, no.547). Royle also quotes Shibthorp's handwritten notes regarding *lykion*, where it is suggested that it should be identified with the species rhamnus oleoides, which agrees very well with the description of Dioscorides (Royle 1833,87). In later times, the translators of ancient texts, classify the *lykion* of Lycia/Cappadocia into the family of Rhamnaceae and relate it to the following species, depending on the scholar: rhamnus cathartica*/rhamnus infectoria/*rhamnus lycioides*/rhamnus oleoides/*rhamnus petiolaris*/rhamnus punctata* (e.g., Ernout 1949, 76, André, 1972, 136, André 1985, 149, Beck 2005, 71,) or into the family of berberidaceae. Amigues (1993, 14), based on Boissier (*Flora Orientalia*) and Davis (*Flora of Turkey*), claims that the species found in abundance in Lycia and Cappadocia and described by Dioscorides should be identified with berberis crataegina. Similarly, the *pyxacanthum chironium* that grows on Mount Pelion, mentioned by Pliny as related to the *Indian Lykion*, should be identified with *berberis cretica*. Finally, the *Rhamnos* cited in the ancient texts as one of the plants used for the medicine *lykion* is identified with *rhamnus oleiodes,* (André

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[1] According to Euro-Med Plant Base this species grows nowadays in Sicily, France and Spain but not in Modern Greece.

1972, 137), *rhamnus cathartica* (Beck 2005), and *rhamnus lycioides sbsp oleoides/* rhamnus lycioides sbsp graeca (Amigues 2003).

Despite the different identifications provided by ancient and modern scholars, there is an overall consensus regarding the antimicrobial activity of the medicine *lykion*. Riddle (1985, 50) refers to the "antibiotics" produced by the plants mentioned by Dioscorides, and, he notes particularly for *lykion* that: "we are unsure whether *lykion* is a yellow-berry buckthorn (*Rhamnus infectorius* Sibth., Rhamnaceae family) or one of the several barberries (*Berberis* spp., Berberidaceae family), but in this case it matters little. Plants of both families contain berberine, a quaternary alkaloid that possesses antimicrobial (antibiotic) activity". The efficacy of *lykion*, mainly as medicine for eye and skin infections (Boon 1983; Jackson 1996) should be attributed to this substance. Consequently, it appears that plants of both families were in use in Antiquity and they should be both exanimated in conjunction to the content of the vessels of our case study.

4. INFRARED AND RAMAN SPECTROSCOPIC INVESTIGATION

4.1 *Materials, Sampling and Methods*

The 15 miniature vessels from Abdera, the material of our case study, do not constitute a specific group of finds spotted at a specific area of the ancient site. Most of them are isolated finds discovered primary in the area of the so-called south precinct of the ancient city, in structures characterized by the excavator as houses, "terracotta workshop", and perhaps shops (Kallintzi 2016, 502). With the hope to identify preserved organic matter that would enable us to understand the function of the containers from Abdera, we extracted samples from the sub surface of the inner walls of the 15 vessels. The acquisition of organic residues absorbed into the unglazed ceramic matrix of pottery vessels is methodologically approved by current scholarship (Roffet-Salque et al., 2017, 627). These samples were then powdered and studied using the infrared Attenuated Total Reflectance (ATR) and micro-Raman techniques. Our sampling strategy included also the extraction of samples from the outer walls of the ceramic vessels. The idea was to be well aware of the nature of the ceramic matrix in order to subsequently isolate any signals of organic substances. We also attempted to demonstrate whether these pots are of local or foreign origin and used as reference material the spectroscopic data of two clay samples identified as local to the region of Abdera. Only one sample yielded evidence for the existence of organic matter (see Fig. 1, no MA 9205) which was compared with spectra acquired from certified local *Ramnacae* varieties kindly provided to us by the director of the Botanical Museum of the University of Athens. Moreover, we analysed and compared the spectra of our organic matter with a Goji Berry seed and with parts of the leaves of a Berberis Cretica plant. Both of the latter were products of contemporary commercial activity.

The ATR spectra were acquired with a 45° single bounce diamond crystal ATR accessory (Pike Technologies, MIRacle) attached to a mid-infrared spectrometer (Bruker, Equinox 55) set to operate at 4 cm^{-1} resolution.

A total of 36 ATR spectra were acquired from 17 samples. The sample quantity from each of the 3 container areas was not sufficient for a measurement in some cases.

Raman spectra were acquired with two bench systems (a) a dispersive confocal Renishaw InVia Reflex Raman system (resolution 2 cm^{-1}) equipped with a microscope and a ×5 (N.A. = 0.12) and a ×50 long working distance (N.A. = 0.50) objective lenses using 5 different laser lines and (b) a Bruker RFS 100 FT-Raman macro-system set to 4 cm^{-1} resolution with a fixed low magnification lens using a 1064 nm laser line. For the acquisition of Raman spectra, the sample quantity was never a problem and a total of 401 Raman spectra were acquired from 17 samples; the number of sampling spots investigated was around 235, as more than one spectrum was usually taken from each spot.

As a general rule, baseline subtraction was not applied to either ATR or Raman spectra shown here, except when explicitly stated in the figures. For reference and identification/confirmation purposes we use Raman and ATR spectral data from the mineralogical database RRUFF (Lafuente et al., 2015).

4.2 *Infrared measurements*

As in any infrared technique, the spatial (xy) resolution in Attenuated Total Reflectance (ATR) is of the order of the average wavelength of the radiation (ca. 10 μm), while the average probing depth (wavelength dependent) is of the order of a few μm due to the evanescent field of the infrared beam total reflection from the diamond crystal, which is in contact with the sample. The sampling area of our ATR accessory is a circular disk of 1.8 mm (1800 μm) diameter, making ATR a surface-sensitive bulk characterization spectroscopic method, very convenient for the study of powders. In contrast to typical infrared transmittance measurements, it requires no sample preparation and does not suffer from absorption saturation or hydrolysis/ion-exchange effects, the latter may be due to mixing with the KBr or similar matrix (Kamitsos et al., 1997). This is why the first series of measurements were acquired with a 45° single bounce diamond crystal ATR accessory (Pike Technologies, MIRacle) attached to a mid-infrared spectrometer (Bruker, Equinox 55) set to operate at 4 cm^{-1} resolution. In the figures that follow, data are shown from the low (500-1950 cm^{-1}) and the high (2700-4300 cm^{-1}) frequency region, separated by a region including artefacts of the diamond accessory and carbon dioxide from the atmosphere. In Fig. 2 we compare the powders from the outer wall of the pots to the local clay sample (the latter is a surface sample of archaeological remains and was kindly provided to us for comparison purposes). The strongest envelope, centered at ca. 1035 cm^{-1} for the local clay and ca. 1010 cm^{-1} for most of the samples (shoulders are also seen in this composite envelope), can be attributed to a combination of Si-O stretching modes in silicate glassy and mineral phases of composition with ca. 50-70 mol% SiO_2, while other phases cannot be excluded (Fig. 2a). Most of these spectra have similarities with spectra of silicate-based glasses as well as spectra of zeolites either natural or chemically treated studied earlier by some of us (silicate glasses: Kamitsos et al., 1994; Ingram et al., 2000; Möncke et al., 2013; zeolites: Wondraczek et al., 2013; Mitrogiannis et al., 2017; Markou et al., 2018). Nevertheless, this comparison is not meant to imply that there is a one-to-one structural similarity between e.g. the silicate component of the two groups of samples. In any case, as indicated by the appearance of narrow low intensity peaks at ca. 780, 795 and 870 cm^{-1}, the present spectra indicate the co-existence of a crystalline phase(s) with a silicate glassy phase. The 693 cm^{-1} peak (hardly visible) and the 777 – 796 cm^{-1} doublet seen in the Abdera clay (but also in various other samples) can be assigned to the stretching-bending vibration of Si-O-Si bridges in quartz. In the high frequency region (Fig. 2b), the wide envelope corresponds to the O-H stretching vibrations of water (3000 to 3700 cm^{-1}), with bending vibration of water seen at 1640 cm^{-1} (Fig. 2a). The high-frequency narrow bands like the one at ca. 3620 cm^{-1} in sample 3362 correspond to structural OH stretching vibrations (see also Fig. 3b).

The measurements of the samples from the inner bottom are overall similar to the ones of the outer surface. There is however one striking difference in more than half of the samples: the detection of varying amounts of a carbonate phase, most probably of calcite-type $CaCO_3$, as designated by bands are observed at ca. 712, 874, 1415 and occasionally 1795 cm^{-1} which in the terminology of the CO_3^{2-} anion group theoretical description are attributed to vibrational modes v_4, v_2, v_3 and v_1+v_4, respectively (Fig. 3a). The presence of $CaCO_3$ could manifest the degradation of the interior as a result of corrosion of the original clay leading to formation of Ca-hydroxide, which reacts with atmospheric CO_2 to form $CaCO_3$. This process is favored at the interior surfaces due to the presence of the humidity of the material enclosed. In the high frequency region below 3000 cm^{-1} we are fortunate enough to observe weak peaks at ca. 2855 and 2925 cm^{-1} and in some cases also at ca. 2960 cm^{-1}, which are safely identified as remnants of an organic substance (**Fig. 3b**). The peaks at ca. 2855 and 2925 cm^{-1} are respectively the in-phase and out-of-phase C-H stretching vibrations of aliphatic methylene groups (CH_2), while the peak at ca. 2960 cm^{-1} is the out-of-phase (and the hardly discernible peak at ca. 2880 cm^{-1} is the in-phase) C-H stretching of methyl groups (CH_3) (See e.g. Larkin, 2011). Here we have selected samples showing the strongest organic residue signal.

Comparing the powder spectra of the interior and the exterior vessel areas, we see that samples 839 and 3362 have significantly diminished organic residue at their external surfaces, while the opposite stands for sample 9199. This signals either a leakage from the interior or a possible contamination from the environment for sample 9199.

The differences in the band shape and/or center for both the silicate (ca. 1000 cm^{-1}) and water (ca. 3400 cm^{-1}) bands between the Adbera local clay and the rest of the samples can in principle support their different origin, but they are rather small to eliminate the possibility of variations from sample to sample as a result of the burial environment. Spectra from the interior of sample 9205 (as well as sample 7430 which is not shown) clearly reveal that it belongs to a distinct group when compared with the rest of the samples (outliers) – this is evident from the wider 850-1100 cm^{-1} composite envelope. It is not clear whether this is to be interpreted as evidence of corrosion (e.g., formation of silicate phases with more depolymerized network) or of different composition (and hence, possibly, different sample origin).

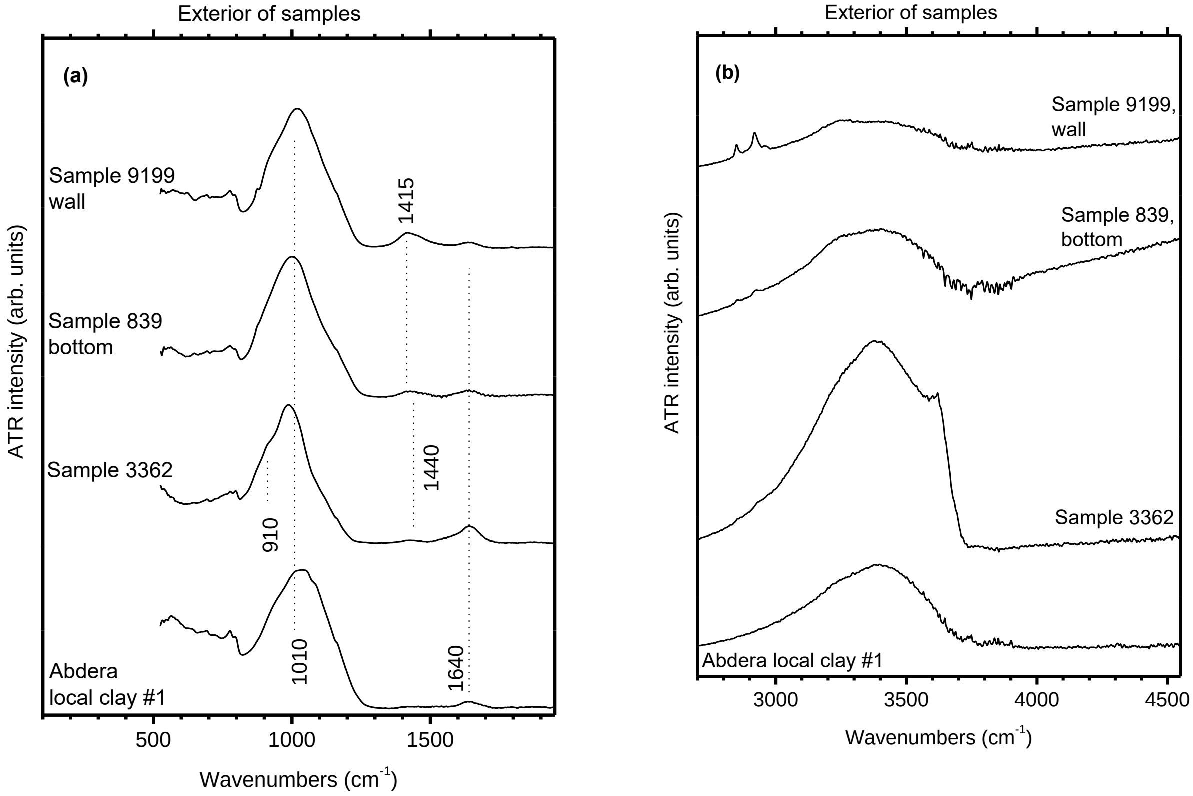

Figure 2. ATR spectra from the exterior of selected samples in the (a) low and (b) high frequency region.

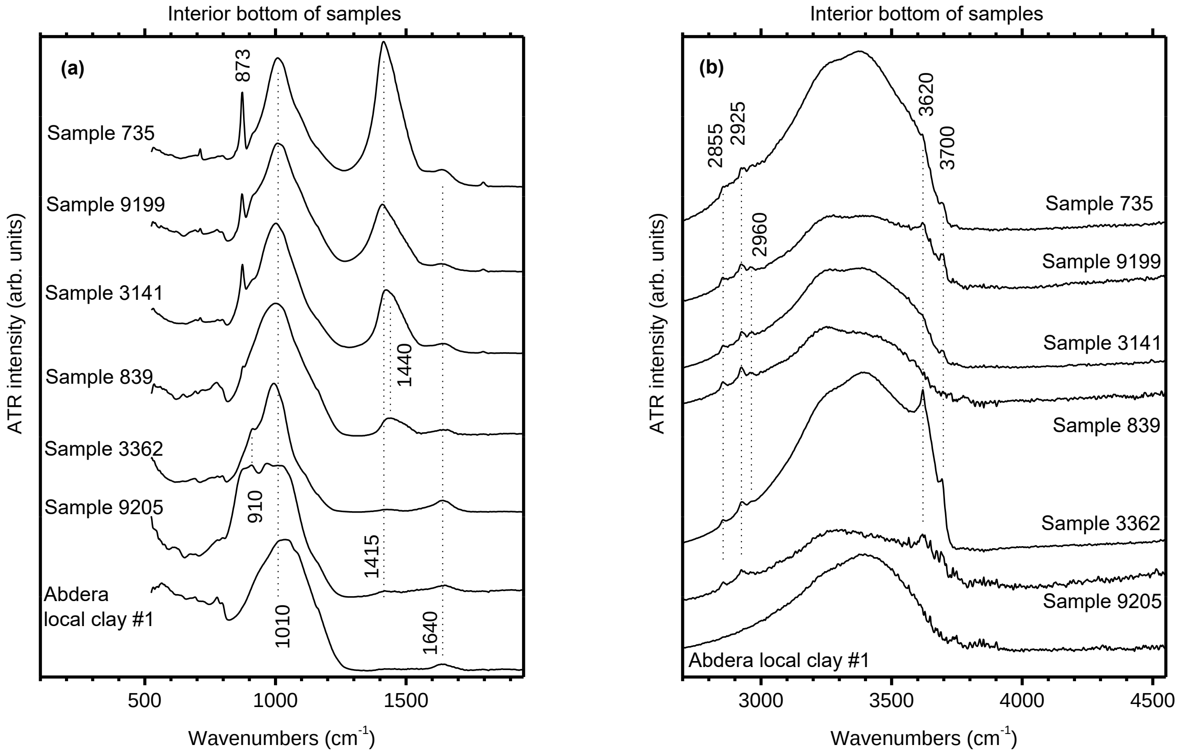

Figure 3. ATR spectra from the interior bottom of selected samples in the (a) low and (b) high frequency region.

4.3 Raman measurements

The presence of parasitic laser-induced luminescence in the Raman spectra forced us to attempt the use of six different laser lines to record acceptable spectra (457.9, 488.0, 514.5, 632.8, 785, 1064 nm). The first five excitation lines were used in a dispersive confocal Renishaw InVia Reflex Raman system (resolution 2 cm^{-1}) equipped with a microscope and a ×5 (N.A. = 0.12) and a ×50 long working distance (N.A. = 0.50) objective lenses. The 1064 nm laser line was used in a Bruker RFS 100 FT-Raman macro-system set to 4 cm^{-1} resolution with a fixed low magnification lens. In most cases, the 785 nm line turned out to be the one that gives the least parasitic luminescence allowing for the Raman signal to be recorded most effectively (i.e., with the best possible signal to noise ratio in a reasonable time frame).

In the low magnification lens spectra, the spatial resolution is of the order of 5-7 μm (depending linearly on the laser wavelength), while the sampling area of our laser beam is a circular disk of 300 μm diameter (1064 nm line) or a rectangle of 200×40 μm (785 nm line; a circular disk area is also available). Anatase titania is the only clearly seen phase (strongest peak at ca. 145 cm^{-1}) in this bulk characterization (Fig. 4). This is verified by spectra acquired with both the 785 nm and 1064 nm laser lines. The presence of anatase titania suggests terracotta firing temperatures below the anatase-rutile transition, i.e., 850 ± 100 °C (Wiescher et al., 2020).

The vast majority of the spectra from the low magnification lens from all samples, but also from the ×50 lens shows (Fig. 4): (a) a strong luminescence background together with (b) a recurring wavelike pattern with bands centered at ca. 220-230, 295-305, 365-375, 510-515 and 930 cm^{-1} – occasionally peaks at 145, 600 and 1050 cm^{-1} are also seen. Apart from these two common features, we observe an additional luminescence band (1200-1700 cm^{-1}) characteristic of specific samples. The absence of this broad band (seen with the 785 nm line), from the Raman spectra acquired with other laser lines is a strong indication that this is indeed a luminescence and not a Raman band. Raman spectra of specific crystalline or partly amorphized phases are observed when the ×50 lens is used.

Based on the spectra acquired from the local clay as well, we attribute the 220-230 and 295-305 cm^{-1} bands to amorphous hematite. The broad band centered at ca. 365-375 cm^{-1} is tentatively assigned to goethite (α-FeOOH). There is a difficulty in assigning the broad band at ca. 510-515 cm^{-1} as it is not correlated with the presence of titania and appears too strong to be attributed to hematite. It is conceivable that it may be a composite band from the contribution of the peaks of hematite (ca. 500 cm^{-1}) and goethite (ca. 530 cm^{-1}) combined with a photoluminescence overlap (see below in section 4.2.1). Most of these assignments are explained in Fig. 5 by comparison with Raman spectra of reference compounds.

Since we are interested in detecting organic substance remnants, we have to resort to microscopy with a higher magnification lens to pick out spectra from regions of the sample that would otherwise be too weak to detect in a "bulk" investigation. In this case the spatial resolution reaches 2-3 μm.

When the Raman microscope is used with higher magnification (Fig. 5), the three discernible phases are quartz (strongest peak at ca. 463 cm^{-1}), anatase titania and hematite (α-Fe_2O_3) – albite ($NaAlSi_3O_8$) was also detected in some spots of sample 839. The Raman cross-section of quartz and hematite are much lower than the one for titania (Efthimiopoulos et al., 2018) and become better visible when we focus the laser beam with the higher spatial resolution offered by a x50 lens through the microscope on a grain or area that is mainly comprised of the phase in question.

In general, the Raman spectra recorded with the 785 nm line show lower luminescence levels with respect to the Raman signal. On the other hand, the hematite spectrum with the lowest luminescence was acquired with the 633 nm line.

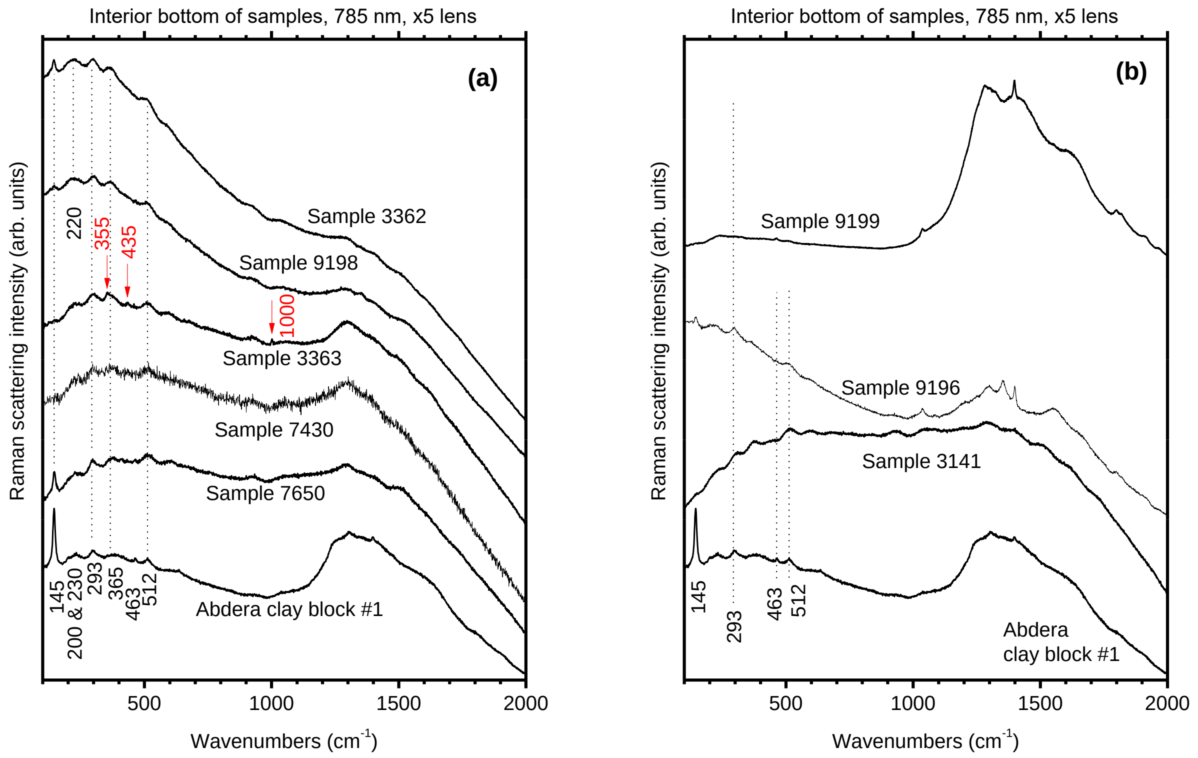

Figure 4. Raman spectra from the interior bottom of selected samples, acquired with the 785 nm laser line and a low magnification lens. Based on their similarities, the spectra have been grouped in (a) and (b).

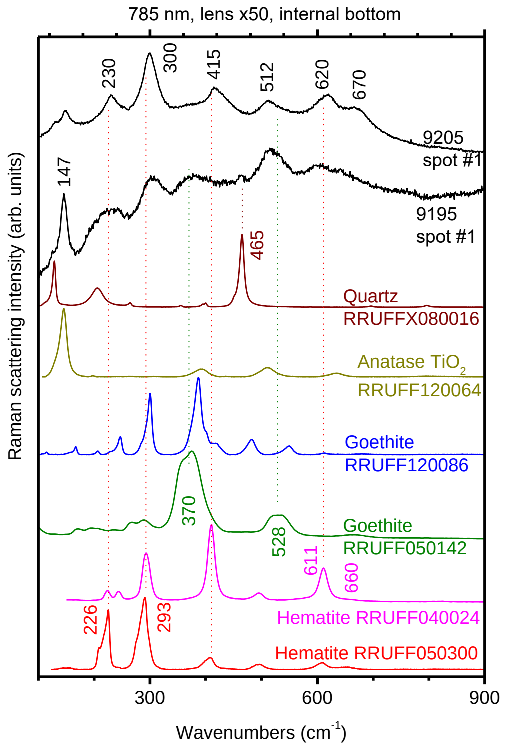

Figure 5. Raman spectra from the interior bottom of selected samples, acquired with the 785 nm laser line and a high magnification lens. Co-existence of hematite, goethite, anatase titania and quartz is observed.

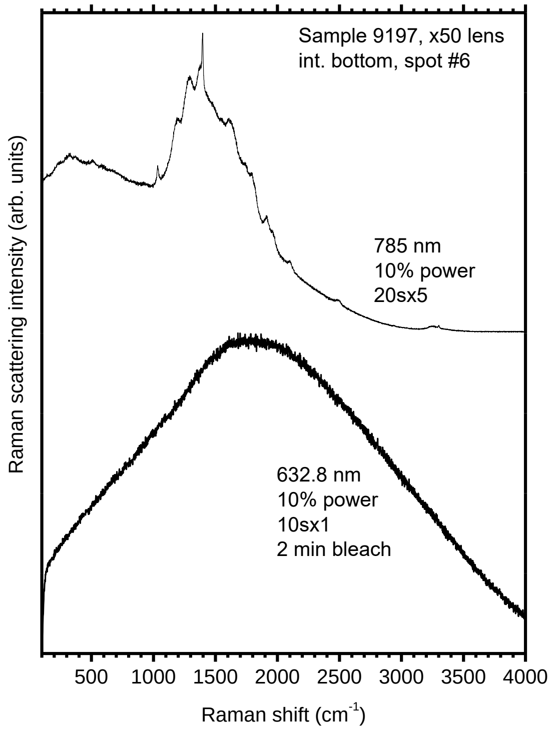

Figure 6. Raman spectra from the same interior bottom spot of sample 9197, acquired with two laser excitation lines.

4.3.1 Origin of part of the broad luminescence envelopes and of a group of narrow peaks observed in various samples with 785 nm laser excitation

Excitation with the 785 nm laser line leads to the observation of broad luminesce envelopes and a group of sharp peaks at ca. 1035, 1195, 1293, 1400, 1555, 1610, 1800, 1920, 1970, and 3300 cm^{-1}. The absence of the above-mentioned group of frequencies when another laser line is used for excitation (e.g., 632.8 nm), constitutes strong evidence that they are not Raman bands (Fig. 6) i.e., that they cannot be related to vibrational modes.

Erroneous identification of photoluminescence (PL) bands with Raman bands is likely especially for samples containing notable amounts of rare-earth (RE) elements with 4f electrons (see e.g. Lenz et al., 2015 and references therein). If such rare-earth ions are incorporated in crystalline materials, they may cause narrow-line emissions whose widths (a few cm^{-1}, at room temperature) are of the order of typical Raman bandwidths. The narrow rare-earth-related emissions may therefore easily be mistaken as Raman bands and vice versa. Crystal-field splitting of RE luminescence transitions depends on the local structural environments of the RE^{3+} cations (the first neighbors in these environments are usually oxygen octahedra or tetrahedra, involving varying degrees of strain). These structural environment/site variations may cause changes in multiplicity and exact positions of sublevel bands for particular emissions of a RE, depending on its host mineral. The detection of rare-earth centers in the Raman or PL spectra of natural/unknown samples can, in principle, evolve in a sensitive fingerprint probe of both the type of rare-earths and their corresponding crystal structure environments. Since variations of the line frequencies are seen between the PL spectra of the same natural mineral of different origin, the only way to identify the host crystal structure is after careful synthesis and characterization of reference host crystal structures.

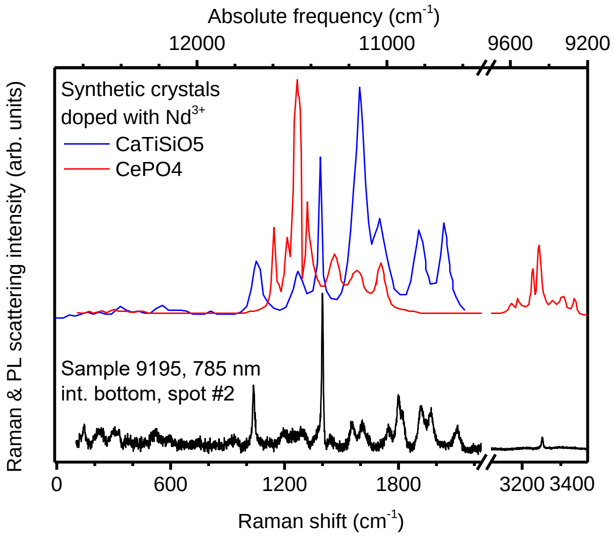

Figure 7. Comparison of Raman spectrum from spot#2 of sample 9195, after subtraction of the background scattering intensity with the Raman/PL spectra of synthetic crystals intentionally doped with Nd^{3+} ions (laser line 785 nm). The top axis is shown in absolute frequency units.

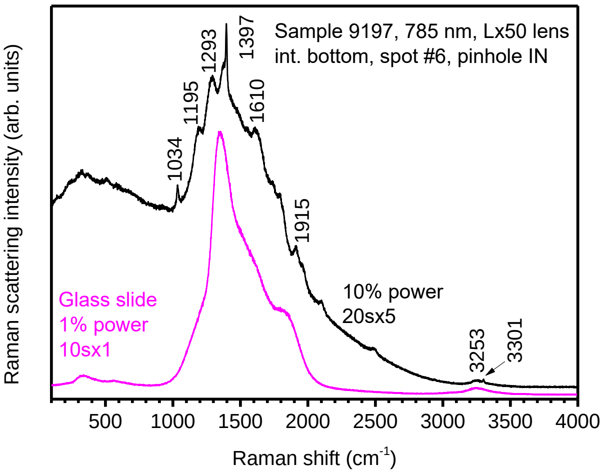

Figure 8. Comparison of the Raman spectrum from spot #6 of sample 9197 (acquired with the 785 nm laser line, see Fig. 5) with the Raman/PL spectrum of a typical soda-lime silicate glass slide (acquired with the same line). Some of the narrow PL lines are different than the ones in Fig. 7.

In our case, the energy of the 785 nm laser line (1.579 eV or absolute frequency of ~12,740 cm^{-1}) just happens to lie in the energy excitation range of the Nd^{3+} ion transitions $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (Lenz et al., 2015). To support our argument, we compare here the spectrum acquired from spot #2 of sample 9195 with the 785 nm line to the spectra acquired with synthetic $CePO_4$ and $CaTiSiO_5$ crystals intentionally doped with Nd^{3+} ions (3316 ppm Nd_2O_3 in $CePO_4$ and ca. 240 ppm Nd^{3+}in $CaTiSiO_5$, Lenz et al., 2015) (Fig. 7). For the frequency axis we use the absolute frequency values as well, so as to have a measure of the energy range involved. The two strongest bands at ca. 1035 and 1400 cm^{-1} are in very good agreement with the Nd^{3+} $^4F_{3/2} \rightarrow {}^4I_{9/2}$ PL in the $CaTiSiO_5$ crystal in terms of frequency and relative intensity between them; nevertheless, relative intensity variations depend strongly on the crystal orientation for backscattering instruments (as in our case) and are in general not a good indicator in comparisons (Lenz et al., 2013). Differences in frequency for other lines must be due to the different crystal-field environment of the Nd^{3+} in our sample, as compared with the titanosilicate or phosphate model crystals, but it is not unreasonable that the set of lines look more like the silicate model crystal; other possible candidate Nd^{3+} containing minerals that may be contributing to observed PL spectrum are albite ($NaAlSi_3O_8$) and wollastonite ($CaSiO_3$) (not shown); see Gaft et al., 2015. The peak linewidths from Lenz et al., 2015, are in general broader, probably because the grating groove spacing in that work was twice as wide (600 grooves/mm) compared to our instrument (1200 grooves/mm); in the case of synthetic crystals, line broadening due to substitutional disorder cannot be excluded but must be more limited as opposed to a natural sample. The ca. 3300 cm^{-1} peak appears to be the signature of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions and is not well resolved probably because of the low signal to noise ratio – this peak could be easily mistaken for a stretching band of either a structurally bound O-H or a triply bonded carbon -C≡H.

On the other hand, if the host material is amorphous instead of crystalline, one should expect these narrow transitions to become a broad envelope. A very good example of this is the "Raman" spectrum acquired from a soda-lime silicate glass slide using the 785 nm laser line, which contains Nd_2O_3 in the ppm range. The laser-induced PL is so strong that the Raman spectrum of the glass is practically invisible – this occurs only when the 785 nm line is used – see e.g. Kanidi et al., 2019. We suggest that part of the broad luminescence envelopes seen in the samples is of the same origin, namely laser-induced Nd^{3+} PL (Fig. 8). In fact, the similarity of the glass slide PL envelope in both shape and frequency with that of our sample in Fig. 8 is evidence that the host material from which it is emitted is a soda-lime-like silicate glass with a typical composition 13 Na_2O-10 CaO-6 MgO-70 SiO_2 (in mol%), with an additional total 1 mol% content of other oxides like Al_2O_3, K_2O, etc., including of course Nd_2O_3.

It is well known that the main substituting luminescence center in Si^{4+}-bearing minerals is Fe^{3+} in tetrahedral coordination. Crystalline and amorphous SiO_2 (quartz and silica, respectively) show one of their PL bands in the region 700-730 nm, which has been linked to the presence of Fe^{3+} (Gaft et al., 2015). This would agree with the observation of a maximum intensity at ca. 1700 cm^{-1} or 716 nm in our Raman/PL spectra acquired with the 632.8 nm line, is attributable to Fe^{3+} incorporated in the silicate phases (**Figure 6**).

4.3.2 Organic matter residue identification

On one occasion, the Raman spectrum acquired on a spot of the wall of sample 9205/spot#4 (laser line 632.8 nm, ×50 lens, see photo 1 at point [x,y]=[0,0]), provided evidence of organic matter (see the ca. 2940 cm^{-1} band in Fig. 9, attributed to C-H stretching vibrations), which bears common traits with the spectra of the candidate plants for "lykion". This pot dates in the late 1st.c. BC- early 1st c. AD and belongs to the type III.2 of Işin 2002 (Kallintzi 2016, 509, cat. no 8, MA 9205).

In Fig .9 we compare the Raman spectrum of sample 9205 (black line, after subtraction of the background scattering intensity) with the spectra of the selected plants; the latter being acquired with the 1064 nm laser line to avoid luminescence. Despite the fact that the detected organic substance must have probably suffered degradation, there are some similarities:

1. The C-H stretching band of aliphatic compounds. Clearly, the plants have wider and more asymmetric bands at ca. 2940 cm^{-1} indicating richer environments for the methylene (CH_2) and methyl (CH_3) groups, most probably containing an olefinic component (e.g., C=C bonds, see band or shoulder >3000 cm^{-1} for the goji berry seed and the three rhamnus family leaves spectra). The narrower and more symmetric band of the detected organic material in the sample 9205 could be a sign of the decimated aliphatic chain as a result of degradation over the centuries – mainly the methylene vibrations scattering intensity is visible, at the expense of the one pertaining to methyl.
2. The 1455 cm^{-1} band in our sample, attributable to C-H bending vibrations, has frequency very similar to the goji berry seed and to the leaves of rhamnus lycioides. The absence of the strong bands of the goji berry's red skin Raman spectrum (1150 and 1510 cm^{-1}) from sample 9205, tends to exclude this identification. Rhamnus sibthorpiana and berberis cretica should be also excluded, even though they bear a band similar to the 1455 cm^{-1} one, since they have stronger adjacent bands in the same frequency region.

The 1730 cm^{-1} band in our sample is absent or barely seen in some of the plant spectra; we assign it to the ester C=O band seen to develop in ozone-aged fats at 1745 cm^{-1} (Gamberini et al., 2011).

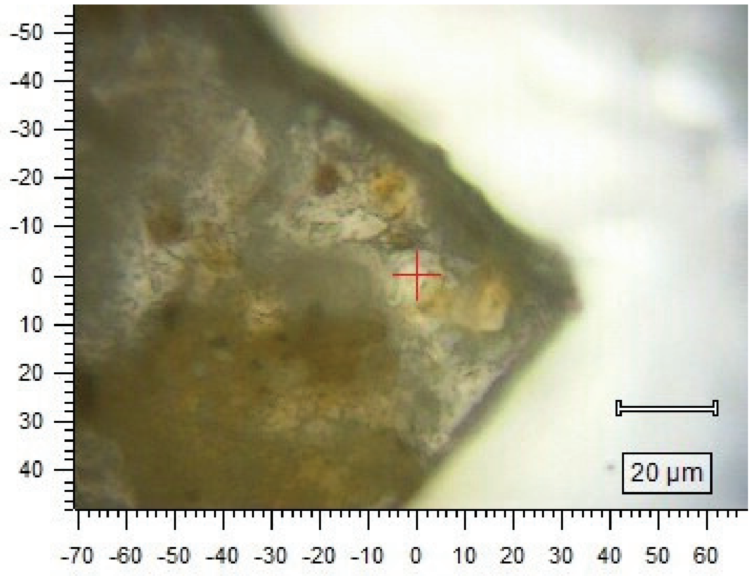

Photo 1. Sample 9205, ext. wall, spot #4. Microscope photograph (lens x50) of the sample region centered around point (x,y)=(0,0) (red cross position) from which the Raman spectrum of spot #4 was acquired. The 633 nm laser was focused as a ca. 2-3 µm diameter circular disc spot.

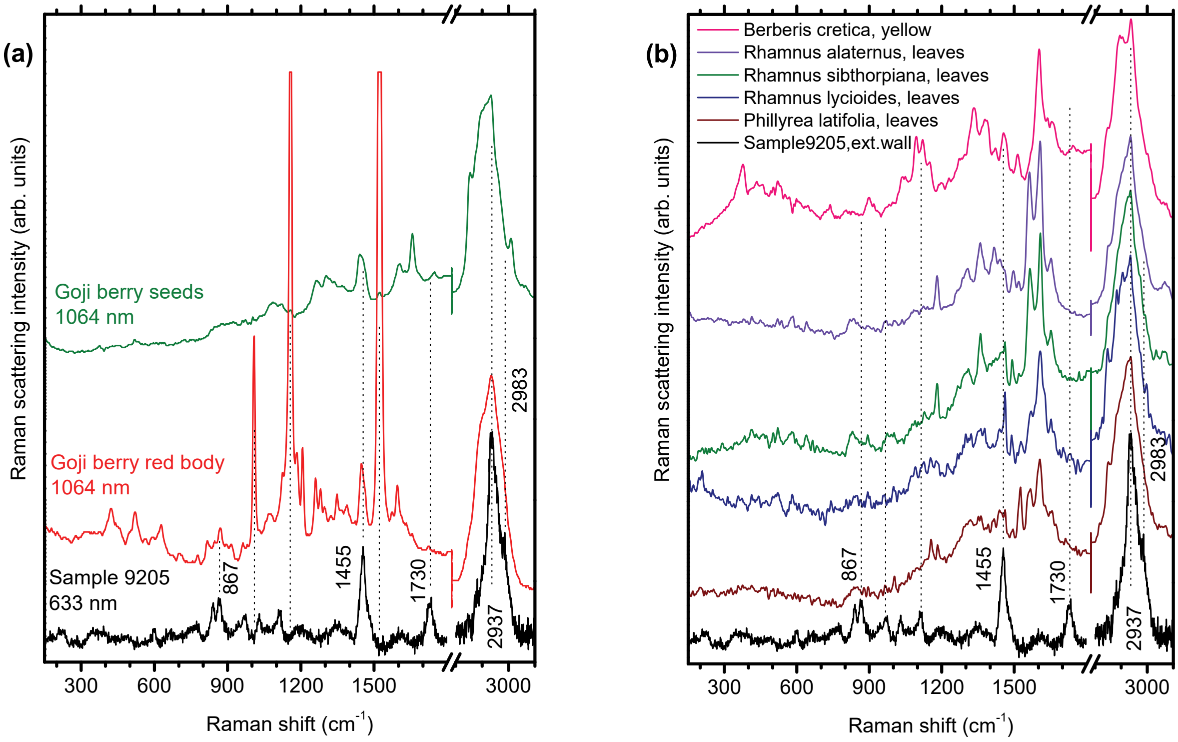

Figure 9. Comparison of the spectrum acquired from the spot shown in Photo 1 of sample 9205 (black line, after subtraction of the background scattering intensity) with the spectra of selected plants. (a) goji berry seed and red fruit body (the intense bands of the latter are shown saturated, as the spectra have been scaled with the band at ca. 2940 cm^{-1}), and (b) various other plant families. Note that the Raman spectrum of sample 9205 was excited with 633 nm laser line, while all other spectra were measured with 1064 nm excitation to avoid luminescence.

5. CONCLUDING REMARKS

The botanical identity of the *lykion* plant should be further investigated, but it has become clear that its most recent identification with goji berry (*lycium barbarum*) is questionable.

The spectroscopic analysis of the powder samples provided information on the technology of production of the vessels/containers of *lykion* as well as on their possible imported character. The inner subsurface of the vessels contains calcite $CaCO_3$ as a result of degradation. The main crystalline or partly amorphized phases detected are quartz, hematite, goethite and anatase titania in co-existence with a silicate-based glassy matrix. The parasitic luminescence observed in the Raman spectra, when the samples are excited with the 785 nm laser line, turns out to be laser-induced trivalent rare earth ion photoluminescence (basically Nd^{3+}) attributable to glassy and crystalline mineral phases. Thus, this method is proved to be a very useful fingerprint technique for the detection of these ions dispersed in relevant investigated materials. The identity of the crystalline photoluminescent phases is under investigation.

The concentration of the organic components is extremely low, but the detected remnant bears similarities with the spectra of the species *Rhamnus lycioides*.

This is work in progress in its preliminary stage. We intend to continue investigating this issue and we have already acquired study permits to measure stamped *lykion* vessels, which are our only concrete evidence regarding their content, and compare the results with the spectra from Abdera. The further analysis of our samples with other spectrometric (NMR) and chromatographic methods is also in our future plans.

AUTHOR CONTRIBUTIONS

The research project was conceptualized by Metaxia Papageorgiou who sought funding in collaboration with Vasiliki Boura. The methodology to be followed was discussed and approved unanimously. The primary investigation regarding the suitability of the assemblage from Abdera for spectroscopic analysis was conducted by Metaxia Papageorgiou and Vasiliki Boura, who also sought the relevant study permits. Sampling and Infrared analysis was conducted by Metaxia Papageorgiou, RAMAN measurements were acquired by Dimitrios Palles. Dr Palles collected, curated and interpreted the results of the spectroscopic analyses in collaboration with Dr. Kamitsos. The historical aspects of this paper were investigated by Metaxia Papageorgiou and Vasiliki Boura, however, the latter is credited with the exclusive treatment of the ancient scholarship and the review of *lykion's* botanical identity. The manuscript was prepared by the first three authors of the paper, and was reviewed and edited by the academic supervisors, Dr. Hariclia Brecoulaki and Dr. Efstratios Kamitsos, and by the director and the vice-director of the Xanthi Ephorate of Antiquities, Dr. Konstantina Kallintzi and Mrs Maria Chrysaphi. All authors have read and agreed to the published version of the manuscript.

ACKNOWLEDGEMENTS

This research is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning 2014-2020» in the context of the project "Lykion: A case study for medicines in Antiquity" (MIS 5048174). The authors would especially like to thank Dr. Theofanis Constantinidis, Associate Professor of Systematic Botany and Director of the Botanical Museum, Department of Biology, National and Kapodistrian University of Athens for the fruitful discussion on the relevant plant species that flourish in Greece and for providing certified plants from the museum's collection, which formed an integral part of this experiment. We would also like to thank the personnel of the Xanthi Ephorate of Antiquities for their support and technical cooperation.

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