ABSTRACT

Po-pu-re (porphyra) denotes the deep red/purple colour delivered from sea shells extraction and processing of five species and conversion to dye has been practice in ancient world, especially in the Mediterranean Sea. Archaeological excavations have shown that murex was used in Greece and in other areas, such as Egypt, Israel, Turkey, Italy, Spain and generally throughout the Mediterranean basin. The colour of murex was priceless and used in wall-paintings and textiles. Many fabrics have been found in Crete, Egypt and Israel. Considering the ancient texts, including those of Plutarch, Pliny, Aristotle, Herodotus and Xenokrates, it has been shown that its identification can be advanced by studying chemical production of purple-dye, while using spectroscopy and chemical analysis the basic chemistry, the dibromoindigotin (DBI), is identified. The present report reviews major murex producing workshops in the Mediterranean and archaeometrical analyses that identify this marine shell.

KEYWORDS: Po-pu-re, Porphyra, Murex, Bolinus brandaris, Hexaplex trunculus, Stramonita haemastoma, purple-dye production, Mediterranean, Textile, Workshops, Tyrian purple, Royal purple, Spectroscopy, Chromatography
INTRODUCTION

Po-pu-re, the vocalized word to denote purple, the Greek word πορφύρα (porphyra), which used by Mycenaeans and found Linear B tablets, for deep red to purple color, produced by marine shells murex species. Invertebrates are the largest animal group that exceeds one million species worldwide. Gastropods belong to the family of invertebrates. Specifically, is one of the five classes of the Phylum Mollusca. Their name gastropods are complex and comes from the ancient Greek word γάστρος = “abdomen” + πό-δαπ = “feet” (belly + feet) from the apparent picture of moving a part of their body, which, in reality, is fleshy leg. The first official recording and description of gastropods taxonomic designation is in 1795. The murex species: Bolinus brandaris, Hexaplex trunculus, Stramonia haemastoma belong to this category (Cooksey, 2001a) (Figure 1.1). Most murex species live in the sea, and have a gland that excretes a dye, the purple (Radwin and D’Attilio, 1986). Each kind of shell give us a percentage of colour, such us: red, blue, purple, yellow, etc (Table 1.1).

![Figure 1.1 Two representative schimatic drawings of Murex species (a, b) and a marine gastropod mollusc of rapaninae subfamily (c): a) Hexaplex trunculus, b) Bolinus brandaris, c) Stramonia haemastoma (drawing by A.K).]

Table 1.1 Percentage of colour in different kinds of shells as measured by HPLC peak areas at 288 nm, sample description and references. The archaeological samples analysis was made by improved HPLC, while samples where treated with DMSO at 80° C for 15’. IND: Blue colour INR: Red colour MBI: 6-Monobromoindigo 6’MBI: 6’-Monobromoindirubin 6MBIR: 6-Monobromoindirubin DBI: 6,6’ Dibromoindigo DBIR: 6,6’ Dibromoindirubin (based on Karapanagiotis et al, 2013).

<table>
<thead>
<tr>
<th>Region</th>
<th>Solvent</th>
<th>IND (blue)</th>
<th>INR (light purple)</th>
<th>MBI (purple)</th>
<th>6’MBIR (red)</th>
<th>6MBIR (light red)</th>
<th>DBI (Dark red)</th>
<th>DBIR (red)</th>
<th>Other</th>
<th>Sample</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexaplex trunculus</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Carthage</td>
<td>DMSO</td>
<td>62.6</td>
<td>1.2</td>
<td>31.9</td>
<td>0.2</td>
<td>0.3</td>
<td>3.7</td>
<td>0.1</td>
<td>Carthagian sample</td>
<td>Karapanagiotis et al., 2013</td>
<td></td>
</tr>
<tr>
<td>2 Croatia</td>
<td>DMSO</td>
<td>48.1</td>
<td>4.3</td>
<td>36.3</td>
<td>2.0</td>
<td>1.4</td>
<td>6.8</td>
<td>1.1</td>
<td>Croatian sample</td>
<td>Karapanagiotis et al., 2013</td>
<td></td>
</tr>
<tr>
<td>3 Tunisia</td>
<td>DMSO</td>
<td>34.9</td>
<td>0.4</td>
<td>49.4</td>
<td>0.3</td>
<td>0.3</td>
<td>14.3</td>
<td>0.4</td>
<td>Tunisian-red</td>
<td>Karapanagiotis et al., 2013</td>
<td></td>
</tr>
<tr>
<td>4 Tunisia</td>
<td>DMSO</td>
<td>53.5</td>
<td>1.5</td>
<td>39.0</td>
<td>0.3</td>
<td>0.7</td>
<td>4.8</td>
<td>0.2</td>
<td>Tunisian-blue</td>
<td>Karapanagiotis et al., 2013</td>
<td></td>
</tr>
<tr>
<td>5 Tarragona</td>
<td>Pyridine</td>
<td>56.0</td>
<td>0.0</td>
<td>37.0</td>
<td></td>
<td>7.0</td>
<td>0.0</td>
<td></td>
<td>Sample was stained cotton (not vat)</td>
<td>Wouters, 1992</td>
<td></td>
</tr>
<tr>
<td>6 Tarragona</td>
<td>Pyridine</td>
<td>53.0</td>
<td>14.0</td>
<td>33.0</td>
<td></td>
<td>0.0</td>
<td>0.0</td>
<td></td>
<td>Sample was dyed wool (vat)</td>
<td>Wouters, 1992</td>
<td></td>
</tr>
<tr>
<td>7 Akhziv</td>
<td>DMF</td>
<td>4.05</td>
<td>0.0</td>
<td>17.79</td>
<td></td>
<td>60.0</td>
<td>18.16</td>
<td></td>
<td>Data were collected at 600nm and converted to 288nm</td>
<td>Koren, 1995, 2008a</td>
<td></td>
</tr>
<tr>
<td>8 Saronikos</td>
<td>DMF</td>
<td>30.2</td>
<td>3.19</td>
<td>26.2</td>
<td>5.9</td>
<td>8.2</td>
<td>13.6</td>
<td>8.9</td>
<td></td>
<td>Karapanagiotis et.al, 2006, 2013</td>
<td></td>
</tr>
</tbody>
</table>

Mediterranean Archaeology and Archaeometry, Vol. 17, No 1, (2017), pp. 103-130
The colour of murex was priceless and symbolized the wealth. The purple fabric, with its indelible characteristic deep red color was equivalent to the value of silver. It was synonymous to the absolute luxury and opulence. In Roman time, there was a law forbidding ordinary to wear purple clothes (Rolfe, 1913).

Each shell gave only a drop of dye, since the 12,000 shells of Bolinus, could produce a few grams of purple able to dye a single fabric (Figure 1.2). The dye was not suitable only for clothes but also for wall-painting and even for cosmetic face pigment.

We do not know much about painting techniques and working methods of the painters. There was a tendency to keep secret the knowledge of profession. It was a profession taught by others with practical application probably changed a bit with the appearance of the first books. The dyeing techniques practically did not change until the late 19th century, when rapid changes in the textile industry demanded improvements in procedures paints.

![Figure 1.2 Parts of a Murex (drawing by A.K)](image)

![Figure 1.3 Painting of Heracles and murex by Peter Paul Rubens, Musée Bonnat, Bayonne (Börnchen, 2009)](image)
However, there are many reports about porphyra. Some of those that have survived during the centuries are mentioned in: Linear B, Homer, Aristotle, Herodotus, Aeschylus, Pindar, Simonides of Keos, Plato, Xenophon, Plutarch, Aelian, Pliny the Elder, Xenocrates, Oribasius.

According to tradition, the dog of Hercules (Fig. 1.3) bit a murex and its mouth was discolored red (Protopapas and Gatsos, 2003). Perhaps the same happened to people, since the shells were part of their diet. From the beginning purple it was supposed to be the noble colour and the symbol of Kings. According to mythology, when Perseus emerged from the water, his divine lineage was recognized by Zeus because he wore a purple mantle (Simonides 31:13D 371 P). Also, Theseus, when required by Minos to prove his divine origin, he sank into the sea and when he emerged he was wearing a purple garment, given by Amphitrite (Bacchylides, Lithyramvoi 17,112). Similarly, Jason had a purple robe given by Athena. Even Apollo presented wreathed with Parnassian laurel and his robe of Tyrian purple swept the ground (Bulfinch, 2009).

Figure 1.4 Tablet in Linear B indicating po-pu-re (Stieg-litz, 1994)

Linear B tablets (KNCH976) recorded the purple as (po-pu-re) (Chadwick, 1958; Piteros et al, 1982; Stieg-litz, 1994) and certify the earliest-Greek identity of the word, while excluding any relationship with the Eastern peoples, as the name of porphyra during the Phoenician times called “po-ni-ki-ja”(Cardon, 2007) (Figure 1.4).

However, from the shell dozens of Greek epithets are known, such as: πορφυρένιος (porfyrenios-purple), πορφυρίτης (porphyrite), Πορφυρογέννητος (Porphyrogennetus-prince born in the room of porfyra/purple), purple, πορφυρόχρωμος (porfuro-chromos-of purple colour), etc.

Figure 1.5 Hexaplex Trunculus from excavation of Antikythera, 2013, Hellenistic period (Permission by A.Tsaravopoulos)

Pliny (Historia NaturalisIX, 125-136) mentioned that it was mostly fished in the spring and for the fishing and use as a bait of bivalves. The wicker baskets are called “κύρτοι”(cyrtoi) from their convex shape, of pliable branches from sparto, which is a perennial broom and grows wild over much of the Mediterranean, from rushes or willow(Figure 1.5).

The 15th B.C. Minoans on Crete may have passed the art of processing murex to Phoenicians of the Levant. However, during the 17th century, Minoans and later Phoenicians made purple dye by extracting a liquid from glands of the murex. Each gland yielded only a drop or two of a yellowish substance which darkened when exposed to sun and air. Processing required a slow simmering over about two weeks usually in lead or tin pans, as other metals discolored the dye (Rystedt et al., 2010). At the same time mounds of crushed shells lie piled around ancient dye works, such as, at Tyre and Sidon, Syria, Ugarit and the Gulf coast of the Arabian Peninsula (Reese, 2010; Scott, 2006). The indelible dye of purple was so valuable that during classic period its value was equal to its weight in silver. Phoenicians developed a flourishing sea trade until the late fourth century BC, when the Phoenician cities in corporate into the Greek empire.

Many references are made in ancient sources. The Homeric epics often refer to aliporfyra (= marine porphyra). Homer uses this term to distinguish it from plant porphyra, which had markedly less value (Homer, Odyssey 6.53). Garments made for heroes such as Agamemnon with royal purple mantle, or Odysseus and Achilles, who appear to use purple covers for their tents. In the 8thc. B.C., Iliad and Odyssey reports of purple include: Andromache and Helen, for example, nip purple fabrics. Even Agamemnon, Odysseus and Telemachus were noted as having purple-dye fabric. Hector’s ashes were
placed in purple-dye fabric (Iliad: C 125 to 128, H 221, Q 796. Odyssey, S 115, S 351, 226 h).

Generally, the purple colour indicated prestige and status and therefore only kings and priests had it. Purple was even mentioned in Pindar and Simonides (15D, 371P), while in Aeschylus’ Agamemnon even purple carpets are noted. Extensive reference to purple is made by Plato, too. Also, Assyrians recorded two kinds of purple colours the Argamannu, which is the red colour and the Takiltu, which is the violet colour (in Plato Critias 120b and Timaeus 67c).

Plutarch (The Parallel Lives, 36) said that Alexander the Great, when he captured Susa in Iran, was impressed by the purple textile he found, originally produced at Hermione in Greece. Specifically he records:

“On making himself master of Susa, Alexander came into possession of forty thousand talents of coined money in the palace, and of untold furniture and wealth besides. Among this they say was found five thousand talents’ weight of purple from Hermione, which, although it had been stored there for a hundred and ninety years, still kept its colours fresh and lively. The reason for this, they say, is that honey was used in the purple dyes, and white olive oil in the white dyes; for these substances, after the like space of time, are seen to have a brilliancy that is pure and lustrous”.

Xenokrates (On abstinence from animal food, C’XXII) wrote that the best murex are the toughest ones. On the other hand, Oribasius (Oreivas.Aoy. D jf) argues that in order to obtain a sweeter taste they have to be boiled two or three times in clear water (Raeder, 1926).

The Roman historian Pliny the Elder, (Historia Naturalis IX, 124 - 142) left us one of the few references of the murex fishing method, in antiquity. He argues, therefore, that the ancient fishermen tied half-dead mussels and tossed them into the sea until murex attach to them. Then, the sailors quickly reel in the bait together with the murex.

The information recorded by ancient authors for approximately 2,700 years history of purple raises many questions. This is because the ancient writers who have dealt with the matter were not experts in textile dyes, about which there was an intended disclosure. The later writers who refer to purple quote earlier suppositions and oversimplifications. Today, archaeological excavations and surveys have given clues to many questions.

Vitruvius (Ten Books, VII, XIII) narrates about this:

“I would like to talk about the purple color, which goes far beyond all the colors which have been mentioned up to now and as to the accuracy and the amazing result. We have a shell from which the purple color can be obtained and which is excellent as well as anything on the nature in the eyes a careful observer, because it does not have the same shades in all parts, but these will vary depending on the course of the sun”.

Also, Aristotle mentioned that Aegean production and use of purple-dye was extensive in many regions such as Crete, Rhodes, Kos, Amorgos, Nisyros (which was the ancient name Porphyris), Chios and the west coast of Asia Minor, Troy, Peloponnesse, Cythera Laconia, Corinth and Hermione (Reese, 1980).

During the 17th century, Cyprus and later Tyre and Sidon in Phoenicia were famous centers of purple-dye production with the Phoenicians to dominate the Mediterranean, creating other centers in Egypt and Sicily (Orna, 2013).

Generally, purple was processed throughout the Mediterranean. Historical and archaeological evidences prove that Israel had had the art of purple and then Poulouzatoi (Philistines), who fled to Palestine and Syria in the 12th century BC during the decline of Late Bronze Age cultures in SE Mediterranean and the Middle East, when the Dorians invaded Crete, managed to acquire the knowledge of purple-dye production. Use of shell purple is met in later times in Byzantine period, e.g. Constantine’s surname, Porphyrogenitus, that is, born in the Purple Chamber of the Imperial Palace in Constantinople, as befitted legitimate children of reigning emperors. The indisputable relationship with Byzantium purple illustrated by the fact that this term appears in Byzantine hymnology, which praised the Mother of God (Troparion D):

“More exalted than the heavens, O immaculate Maid, rejoice, as the one who carried earth’s Foundation painlessly in your womb. Rejoice, O murex who dyed in your own virgin blood, the divine purple robe, worn by the King of angelic hosts.Glory”

It is known that the development of shell purple depends on:

- light
- temperature
- salinity
- availability of nutrients

(Lobban et al., 1985)

Today, however, the technique is known broadly that resembles that of the natural purple dye, since in antiquity were unique dye reduction, with the same precursor compound the indoxyl, which turns into indigotin (dye compound guinea) (Wouters and Verhecken, 1991) and 6,6'-dibromo indigotine,1 which is a dye compound of purple. The compound for murex is indoxyl. Indoxyl and free radicals give less electrons. This process causes dimerization, from which indigotine is produced. A simulated ex-

1For more information about 6,6'-dibromo indigotine see next chapter
Experiment for the production of shell dye has been made by Koren (2005a). The steps of this experiment includes, a) crushing the shell, b) reduced colour solution, c) resultant colour (Fig.1.6).

**Figure 1.6 Method of dyeing fabric and final grading of purple colour (Koren, 2005a)**

For the production of purple colour the shell was crushed to extract the living species, which is emulsified to an alkaline solution. The air oxidation of the dye makes changes from green to purple colour (Koren, 2005a). An early short review on Tyrian purple is made by Cooksey (2013).

2. EXCAVATED WORKSHOPS OF MUREX IN THE CENTRAL AND EASTERN MEDITERRANEAN

In the last two centuries, frequent archaeological excavations have been made in the Central and Eastern Mediterranean and in recent years in most of them production of purple-dye is revealed (Fig. 2.1, Table 2.1).

Below the discovery of purple dye shells is presented, either in inscriptions or in excavation per site as a brief summary highlighting major prints.

**Table 2.1: The workshops of purple dye in the Mediterranean**

<table>
<thead>
<tr>
<th>Workshop</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Agios Georgios, Athens</td>
<td>Lolos, 1990; Reese 2015b</td>
</tr>
<tr>
<td>2 Mitrou, Central Greece</td>
<td>Kramer-Hajos and O’Neill, 2008</td>
</tr>
<tr>
<td>3 Vouliada (Zalitsa), Central Greece</td>
<td>Jackson, 1917; Sideris, 2014</td>
</tr>
<tr>
<td>4 Corinthia, Central Greece</td>
<td>Ruscillo, 2005; Reese 2000, 2015b</td>
</tr>
<tr>
<td>5 Hermione, Argolid, Peloponnesse</td>
<td>Reinhold, 1970; Reese, 2010</td>
</tr>
<tr>
<td>6 Iklaina, Peloponnesse</td>
<td>Ruscillo, 2005</td>
</tr>
<tr>
<td>7 Paulopetri, Peloponnesse</td>
<td>Kardara, 1974</td>
</tr>
<tr>
<td>8 Kythera</td>
<td>Protopapas and Gatsos, 2003; Reese, 1987, 2015a</td>
</tr>
<tr>
<td>9 Yaros, Cyclades</td>
<td>Gounaris, 2005</td>
</tr>
<tr>
<td>10 Kythnos, Cyclades</td>
<td>Reese, 2000, 2015b</td>
</tr>
<tr>
<td>11 Delos, Cyclades</td>
<td>Reese, 2000, 2015b</td>
</tr>
<tr>
<td>12 Amorgos, Cyclades</td>
<td>Reese, 2000</td>
</tr>
<tr>
<td>13 Lesvos, western Aegean</td>
<td>Lowe, 2004; Reese 2000</td>
</tr>
<tr>
<td>14 Chios, western Aegean</td>
<td>Volonakis, 1990</td>
</tr>
<tr>
<td>15 Samos, western Aegean</td>
<td>Volonakis, 1990</td>
</tr>
<tr>
<td>16 Agathonisi, Dodecanese, Aegean</td>
<td>Volonakis, 1990</td>
</tr>
<tr>
<td>17 Kos, Dodecanese, Aegean</td>
<td>Volonakis, 1990</td>
</tr>
<tr>
<td>18 Nisyros, Dodecanese, Aegean</td>
<td>Reese, 2000</td>
</tr>
<tr>
<td>19 Chalkis, Dodecanese, Aegean</td>
<td>Lowe, 2004</td>
</tr>
<tr>
<td>20 Rhodes, Dodecanese, Aegean</td>
<td>Lowe, 2004</td>
</tr>
<tr>
<td>21 Khania, Crete</td>
<td>Shaw and Shaw, 2006; Reese, 1987, 2015a</td>
</tr>
<tr>
<td>22 Pefka, Crete</td>
<td>Apostolakou, 2009; Zimi and Tzachili, 2012; Betancourt et al., 2012</td>
</tr>
<tr>
<td>23 Mallia, Crete</td>
<td>Müller, 1991; Reese, 1987, 2015a</td>
</tr>
<tr>
<td>24 Papadiokampos, Crete</td>
<td>Sofianou and Brogan, 2010</td>
</tr>
<tr>
<td>26 Itanos, Crete</td>
<td>Carannante, 2006; Reese, 2015a</td>
</tr>
<tr>
<td>27 Koufonissi, island south of Crete</td>
<td>Papadakis, 1983; Ridout-Sharpe, 1998; Reese, 2015a</td>
</tr>
<tr>
<td>28 Christi, Crete</td>
<td>Apostolakou et al., 2010, 2012</td>
</tr>
<tr>
<td>29 Makrigialos, Crete</td>
<td>Shaw and Shaw, 2006; Reese, 1987, 2015a</td>
</tr>
<tr>
<td>30 Kormos, Crete</td>
<td>Shaw and Shaw, 2006; Ruscillo, 2006; Reese, 2000, 2015b</td>
</tr>
<tr>
<td>31 Monastiraki, Crete</td>
<td>Carannante, 2006; Reese, 2015a</td>
</tr>
<tr>
<td>32 Istanbul, Turkey</td>
<td>Çakır and Becks, 2009</td>
</tr>
<tr>
<td>33 Daskyleion, Turkey</td>
<td>Çakır and Becks, 2009; Reese, 2010</td>
</tr>
<tr>
<td>34 Troy, Turkey</td>
<td>Çakır and Becks, 2009; Reese, 2010</td>
</tr>
<tr>
<td>35 Pergamon, Turkey</td>
<td>Çakır and Becks, 2009</td>
</tr>
<tr>
<td>36 Ephesus, Turkey</td>
<td>Çakır and Becks, 2009</td>
</tr>
<tr>
<td>37 Miletus, Turkey</td>
<td>Çakır and Becks, 2009</td>
</tr>
<tr>
<td>38 Hierapolis, Turkey</td>
<td>Çakır and Becks, 2009</td>
</tr>
<tr>
<td>39 Hala Sultan Tekke, Cyprus</td>
<td>Belgirmo, 2004; Reese, 2010, 2015b</td>
</tr>
<tr>
<td>40 Minet el Beidha, Syria</td>
<td>Parri, 1932; Reese, 2010, 2015b</td>
</tr>
<tr>
<td>41 Byblos, Lebanon</td>
<td>Parri, 1932; Reese, 2015b</td>
</tr>
<tr>
<td>42 Saroepta, Lebanon</td>
<td>Parri, 1932; Pritchard, 1978; Reese, 2010, 2015b</td>
</tr>
<tr>
<td>No</td>
<td>City, Country</td>
</tr>
<tr>
<td>----</td>
<td>--------------</td>
</tr>
<tr>
<td>43</td>
<td>Sidon, Lebanon</td>
</tr>
<tr>
<td>44</td>
<td>Tyre, Lebanon</td>
</tr>
<tr>
<td>45</td>
<td>Tel Akko, Israel</td>
</tr>
<tr>
<td>46</td>
<td>Tel Mor, Israel</td>
</tr>
<tr>
<td>47</td>
<td>Tobruk, Libya</td>
</tr>
<tr>
<td>48</td>
<td>Sidi Khrishi, Bengazi, Libya</td>
</tr>
<tr>
<td>49</td>
<td>Leptis Magna, Libya</td>
</tr>
<tr>
<td>50</td>
<td>Sabratha, Libya</td>
</tr>
<tr>
<td>51</td>
<td>Menninx, Tunisia</td>
</tr>
<tr>
<td>52</td>
<td>Dar Essafi, Tunisia</td>
</tr>
<tr>
<td>53</td>
<td>Carthage, Tunisia</td>
</tr>
<tr>
<td>54</td>
<td>Agrigento, Sicily, Italy</td>
</tr>
<tr>
<td>55</td>
<td>Palermo, Sicily, Italy</td>
</tr>
<tr>
<td>56</td>
<td>Torre, Italy</td>
</tr>
<tr>
<td>57</td>
<td>Venice, Italy</td>
</tr>
<tr>
<td>58</td>
<td>Ancona, Italy</td>
</tr>
<tr>
<td>59</td>
<td>Monte Cinto Latrina, Italy</td>
</tr>
<tr>
<td>60</td>
<td>Aquilea, Italy</td>
</tr>
<tr>
<td>61</td>
<td>Coppa Nevigata-Apulia, Italy</td>
</tr>
<tr>
<td>62</td>
<td>Matya, Italy</td>
</tr>
<tr>
<td>63</td>
<td>Taranto, Italy</td>
</tr>
<tr>
<td>64</td>
<td>Otranto, Italy</td>
</tr>
</tbody>
</table>

Figure 2.1 Workshops of purple in the Mediterranean revealed by archaeological excavations

Thessaloniki (40.65°N, 22.9°E)

The term purple-dyer is attested in at least two inscriptions from Thessaloniki and Philippi. The inscribed stele from Thessaloniki, which is now in the Archaeological Museum of Istanbul (Mendel, 1914), bear a Hero - rider on top, and dates to the late 2nd century AD (Nigdelis, 2010). At the bottom of the column, the inscription is dedicated to a purple-dyer Menippos Severos by members of the battalion (IG, X.2.1, 291). The inscription reads as follows (Pilhofer, 1995) (Fig. 2.2).

"The Guild of purple-dyers whose workshops were on the eighteenth street dedicates it to the memory of Menippos Severos, son of Amicon, who came from Thyateira."

The inscription shows that purple-dyers had business relations in Roman Thessaloniki and that there was more than one workshop in the city, and that some people derive from Asia Minor.

The second inscription (697/M580) was from the city of Philippi, which was discovered in 1872. The inscription reads (Pilhofer, 1995):

"The city honored, among of purple-dyer, Antiochus, son of Lycus native of Thyateira as a local benefactor".
Figure 2.2 Drawing of an inscribed funerary stele from Thessaloniki, referring to Menippos the purple dyer from Thyateira, Istanbul Archaeological Museum. (Mendel, 1914).

In Macedonia, the evidence for the use of murex, for colouring fabrics and wall-paintings, have a long history from the Bronze Age to the Roman period. The evidence from excavations at Toumba Thessaloniki (Veropoulidou et al., 2008) and Aghios Mamas in Chalkidiki (Becker, 2001) of Bronze Age indicate small production of purple for the needs of the local community. This is supported by archaeological evidence dating from the Iron Age and includes crushed murex of Toumba Thessaloniki (Veropoulidou, 2011) and Methoni in Pieria (Veropoulidou, 2012).

From the Archaic to the Hellenistic period, fragments of murex have been found in Northern Greece. The evidence of purple as a symbol of the upper class is shown by the finds in the tomb of Vergina late 6th century (Faklaris, 1998), Aghios Mamas in Halkidiki (Moschonisiotou, 1989). Also, purple-dye workshop in Thessaloniki on the south side of the Roman Agora was revealed (Vitti, 1996). The workshop dates between the 2nd / 1st century BC and 1st century AD, (Karaberi and Christodoulidou, 1998). This workshop was part of a large complex next to the ceramic and metallurgical workshops, probably intended for dyeing.

Hermione (37°23'07"N, 23°14'50"E)

The region of Hermione in the Argolid was famous for purple-dye it was the most expensive dye of antiquity. In ancient times, Hermione was an important production center of purple-dye and textile. Many ancient authors such as Aristotle and Plutarch, noted that Hermione was a centre for purple-dye. The paint (“flower”, according to Aristotle (History of Animals, V15)) is found in shells, in which the gland was removed with suitable instantaneous breaking careful picking the shell and the living organism. For the dyeing of a cloak, a large amount of shells is required. The maintenance of painting could be done with the help of honey in sealed jars.

The fermentation of dye embossed lasted several days to complete the resulting white compound form soluble salt. As to the nature of the hair, as Plato says in the book of Politia D. “You know, I said, that dyers, when they want to dye wool for making the true sea-purple, begin by selecting their white colour first; this they prepare and dress with much care and efforts, in order that the white ground may take the purple hue in full perfection. Whatever is dyed in this manner becomes a fast colour, and no washing either with lye or without it can take away the bloom. But, when the ground has not been duly prepared, you will have noticed how poor is the look either of purple or of any other colour”.

Followed by exposure to the sun and the air, so as to cause oxidation and white compound be retranslated to 6,6 ‘-dibromoindigotin and give the purple colour. Followed by washing in a good brine bath, vinegar, etc., in order to remove the unpleasant smell and colour to acquire splend our and strength (Strabo, XVI 2,23).

It should be noted that murex-dye fabric had great resistance to washing and light. Experts noticed that the ancient painters were aware that mixing different types of shells (in "flower" of course) in certain proportions and proper way of preparing the reducing bath was what gave the variety of colours in purple and delicious tones and nuances. Moreover, the repetition of dunking in the same tub - bucket or different with other kind of shell was assumed. The shades of purple that had great appreciation was dark red, like clotted blood, known as the purple of Tyre, and that coloured amethyst, which was dyed were removed with suitable instantaneous breaking Animals

The ancient workshops of murex dyeing were located at the eastern edge of the modern city of Hermione, in Bisti (37°23'03"N, 23°15'24"E), which in antiquity was called "Poseidion." So, the bad smell from dyeing was blown out to sea. At the end of the 6th century BC a temple of Poseidon or Athena was built in the middle of the cape. The current location was a "square" great temple and probably the priests of the temple had the control and management of workshop. The research indicates that the people of workshop took the porphyra and followed the same process for the production of the purple colour.
In the 5th century B.C., walls were built around Hermione and had as a binder broken shells instead of gravel. Also, 18% of the binder was broken shells, which means that more than 250 tones were used in building the ancient wall at least 10 million shells. Also with shells built areas through the side of the wall and the use of broken shells as a binder also continued later.

The reports indicate that the dyeing workshops must have been at the side of the modern windmill. They should begin to work at least the 6th century BC and continued until the 6th century AD. During the 1000-plus years of operation in Hermione hundreds of millions of shells were used.

The extraction of the dye from the shells was in the workshop of porpfura, where is the central workshop. Piles of broken shells indicate the position of the workshop. The on-the-spot examination in the region give the impression that workshop should be located at the eastern end of the cape.

The workshops paint needed rain water and thus storage cisterns. In Bisti, there are several, most female figures carved in the rock. Also, the facilities were necessary to present chemical containers, such as caustic soda or potash, soaps, etc. Standard dyed yarn as samples and mixing utensils, scales etc. was considered self-evident. The existence of these, justify the findings and quirky utensils found at the Rauphi at Isthmia, where excavations were made in large amounts of dyes.

The number of shells collected in Bisti reached several thousand a day, which gave 10-20 kg murex purple-dye (Elsner and Spanier, 1985). Therefore, should be specific repository. Surveillance was obvious and rigorous, and economic significance for the city great. This explains the peak of the city by building the walls, temples, etc. The management of such great wealth required people who knew the internal and external markets, since the bulk of the dye was exported. If operated about 1000 years with an average use of 10,000 shells per day, then during this operation three billion shells were processed!

Returning to the text of Plutarch for purple of Hermione found by Alexander at Susa, it is not clear if it was found 5000 fabric dyed with murex, which had been stored before 190 years, using local fresh honey. Also, he noted oil used to create white purple which is incomprehensible if it is cloth (Jameson et al., 1994). Plutarch, who lived in the 1st century AD, certainly reads somewhere this information about events that took place four centuries earlier, and probably did not realize the problem of purple dye being white. In chemical terms, however, it seems that in Susa it was found purple-dye rather than fabrics.

It is known that concentrated alkaline solutions, create a sensation resembling of oil. Therefore, this is probably the white oil, as Plutarch said. If the coating weight was 5000 talents, it is 130,000 kg. This means that at that time in Hermione processing for export was over 100 million shells. Whether workshops capable for dealing per day a few thousand shells, it makes apparent that the coatings must have been worked intensively for 50 years or so.

The Persian emperor Darius I (522-486 BC) reaches its greatest prosperity and glory with the center of vast state Susa, until overwhelming of Alexander the Great in 330 BC by Darius III. The workshops of Hermione gave the purple-dyeing to the Persians for at least two centuries and reaping huge revenues and giving great prosperity to the city by building walls, temples etc. Cyrus the Great was one of the biggest personalities and he was under control of all the workshops of purple-dyeing in Phoenicia. After the annexation of Asia Minor in the 6th century BC all the facilities of purple dyeing used purple imported from a hostile country and especially from Hermione.

On-site collection of shells, chiefly found in Hermione and removing purple-glands, found that their hands painted a purple and violetcolor, close to amethyst. Similar color was a simple dyeing process directly from the "flower" in white cotton fabric. On the other hand, shells of Tyre, which found in the sea of Hermione, but in a small percentage, excretes red color.

Experts believe that the color complexion was impressive. This was the main reason for its production during reign of Cyrus and Darius. Today there is no recollection of the famous Hermione purple-dyers only the piles of broken shells, scattered around the Cape of ancient workshop, witnessing the ancient grandeur and glory of the city.

**Chania (35° 30' 40" N, 24° 1' 45"E)**

In 2002, during a rescue excavation at Kydonia region (35°30'52"N, 24°00'48"E) remains of the Hellenistic and Roman periods came to light.

In the eastern section of the plot, murex processing installation was found. The remains of the installation comprise of two circular ovens built of rough stones. They are 1.82 and 1.45m in diameter and their sides are preserved to a height of 0.60-0.70m. There is a large round stone in the middle of its oven presumably for the deposition of vessels in which murex shells boiled. A layer of ash and intense traces of burning were located in front of the ovens. The third oven was destroyed by a modern pit (Tsingou, 2009).
Rhodes (36°11′42″N, 27°56′49″E)

The ancient Rhodes stated between the positions of the Aegean producing murex-dye. Indications for treatment of murex on the island have been since prehistoric times. Porphyra, which was found strewn on the floor substrate of the Late Bronze IA settlement in Trianta is a good testimony to similar activity of the inhabitants of this region.

The presence of crushed murex in thickness up to 0.50 m in excavations of the city of Rhodes found in the early 1970s testifies to the presence of a workshop of purple-dyeing. Workshops are located in several places in the city. Foundries within the area of the Temple of Diagoridon road (36°26′27″N, 28°12′54.5″E), workshop glass beads in the southern part of the city, but also in artisanal zones near the edges of the city, such as ceramic workshops in the large port on the side northeastern fortifications, all inside the fortified walls.

The Hellenistic city of Rhodes was not the only place on the island which developed crafts. There are two other metallurgical workshops in Ialyssos, and potteries making amphorae in the area of Ialyssos and Charaki and other areas on the island.

In southern fortifications of Rhodes there has been identified litharge plant (Kakavogiannis, 1984). In the same area outside the walls, a part of murex workshop has been found. A large amount of shells, which is visible today, has been found in landscaped archaeological site and dated to the early 3rd century BC.

Characteristic is the image of historical stratigraphy in eastern cheek on the southern part of the murex workshop, the east exterior wall of the southern area (Fig. 2.3). Stratigraphy features seven layers. The presence of two successive layers of murex and the combustion layer below this is indicative of the activity on site. The layer II, under a surface of gray colour soil (layer I), was mainly ash and carbon, located at the southern end of which is inserted a thin layer of murex (layer III). It was a thicker (layer IV) with murex. The next layer V contained soil with carbon, while the latter layer murex grazed her on brown soil.

In accordance with the data of the excavation, it should be noted that the area took place all the work on the production dye, but the next stage of the dye. The complex, located outside the city, covered all the basic tasks for the production of murex dye.

![Figure 2.3 Stratigraphy in eastern section east of the southern area (Kakavogiannis, 1984)](image1)

Very close to the shambles of the defense system of Hellenistic Rhodes and out of town, just south of wall (built after the earthquake of 227 BC) workshops were found in 1979 for processing murex dyes. The location of the workshop on the outskirts of the city, in the space between the wall of the city and necropolis meet the demands of the time for such an establishment. One of the main characteristics of workshop was the distance from residential areas, because of the bad smell, which exposed during the dyeing process (Kakavogiannis, 1984).

![Figure 2.4 Hexaples found in Psaropoula area of Rhodes](image2)

The crushing shells was the wider open space with the remains of the rampart. In the southern area with temperatures of south tanks made probably stages of boiling for the production of pigment. In this case, should have been space outdoor. The found eleven coins over and near the steps of the laboratory of Rhodes is a possible indication of trade era of porphyra (Fig. 2.4).

Agathonisi (37.46°, 26.96°)

The archaeological site Kastraki in the Island includes a fortress in the inaccessible area in the northern part of the island on a rocky hillside at height of 34m above sea level. Kastraki preserves impressive fortification walls, projecting between dense shrubby vegetation and enclose the west, north and south side of the rocky hill. Southwest saved this rectangular and carvings of ancient dockyards, whose relics are below the sea level. These building materials related to fortification, probably the port of the ancient city of Tragaia. The construction of the fort in the northern part of the island is not unexpected, since that the position is of strategic importance to the marine control strait between Miletus and Samos and channel from Kos to Samos. During the Hellenistic
period Miletus in order to protect the territorial integrity of the marine area of the Aegean Sea from the thriving piracy Cretans and goblets resorted necessarily the equipment and military installation Guard at Miletus islands as Lipsi, Arki, the Pharmakonisi, Leros and Patmos. The archaeological site identified during the surface surveys of 2001 - 2005 yields many movable finds mostly sherds of Hellenistic and Early Roman periods and household items such as sanders, grinders, and mortars (Triantafyllidis, 2015).

Unexpected was the discovery near the southeastern edge of the southern fortification wall section workshop facilities which are likely related to the production of pigments and dyes, dating from late Hellenistic and Early times (1st century BC-1st century AD). The associated tanks seem to be connected through the system of overflow and inside them there are numerous marine shells, some of which were found in a stone trough in the southwestern corner of the tank. Though there were no masses of purple dye, however from the field of tanks and around this coming from sections pigments such as ocher, yellow, red and white.

Antikyra, Phokis
A plethora of murex trunculus and brandaris is found in Antikyra area (Pelatia and Boulis sites) in classical to Roman times. Ancient historian-traveller Pausanias (X, 37, 3) reports on this (see, Sideris, 2014). In 2016 season in Kastrouli late Helladic settlement from Tomb A and the commingled layer of bones, soil and small finds comes also a very tiny seashell fragment of a gastropod mollusk, which, on the basis of its physical characteristics, it has been tentatively identified with murex *Hexaplex trunculus*. This edible marine gastropod, which is common in the entire Mediterranean, is abundant in the Corinthian gulf and was used in Antiquity also for the production of a blue-purple dye, documented in the ancient sources for Boulis, a site in the easternmost edge of the Gulf of Antikyra (Sideris 2014). Its presence in the secondary burial is rather unusual (Sideris et al 2017).

3. WORKSHOP OF PURPLE IN THE MEDITERRANEAN

TURKEY

Troy (39°57′27″N 26°14′20″E)
Initial excavations of Schliemann in the 1880s and all the recent excavations at Troy have demonstrated the use of *Hexaples* for the production of purple dye (Figure 3.1). These data have been collected by Çakırlar and Becks (2009) and Reese (2015b).

Figure 3.1 The nine layers of Troy (Tobin, 2011)

Uluburun (Kaş) wreck (36°7′43″N 29°41′9″E)
The shipwreck in the region of Kaş (Uluburun) (Fig. 3.2) produced a large quantity of murex. The Uluburun operculae were a by-product a shell purple-dye industry (Reese, 2010, 2015b).

Figure 3.2 Uluburun (Welter-Schultes, 2008)

EGYPT

Bates Island (Marsa Matruh, White, 1987) (31°21′13″N, 27°14′16″E)
In Late Bronze Age and Roman small offshore island near the border with Libya, produced 2,352 murex. In Bates’ Island (Marsa Matruh) identified two types of Murex dyed in Coptic textiles (Pfister, 1951; Walton, 1985; Reese, 2002, 2010). A purple painted Egyptian woolen cloak of the 3rd century AD is derived from Bolinus (Wouters, 1992). The second fabric for 3rd/4th century AD in Philadelphia was derived from Hexaples (Michel et.al, 1992b).

The two Coptic textiles in Flemish collections have been analyzed: the first fabric, imported from Persia or Mesopotamia the 8th-9th century AD (Wouters, 1993) [using Bolinus] and the second, an Egyptian production of the 5th or 6th century AD (Wouters, 1993) [possibly using Hexaples].

LEBANON

From Beirut, there is no shell evidence, only a Greek inscription of the 5th-6th century AD. honour-
ing a dyer of purple (Reese, 2010). In Lebanon the production points of shell purple are located at Sidon (Parri, 1932; Reese, 2010, 2015b), Sarepta (Parri, 1932; Reese, 2010, 2015b) and Tyre (Astour, 1965; Reese, 2010, 2015b).

Sidon (33°33’49”N, 35°22’07”E)

Figure 3.4 Crushed Hexaples found in Sidon (de Saulcy, 1864)

In early 1863 de Saulcy found a huge amount of broken Hexaples (de Saulcy, 1864). Shortly afterwards, in 1864, nearby, the French physician Gaillardot discovered broken Hexaples and Bolinus in very good condition (Gaillardot, 1865, 1873).

An article of 1874 (Anonymous, 1874), based on publications of de Saulcy and Gaillardot, erroneously reported separately in Bolinus and Stramonita. This mislead writers like Born (1937) and Ziderman (1887, 1990). Lortet (1883) reported that in the region of Sidon found large quantities of broken Hexaples hundred feet long and several feet thick. A portion of this large set found was recorded as 120 meters long and 7.8 meters high (Forbes, 1956).

Also, Cooke (1909) visited the area. Huge number of Hexaples was also observed during the excavations 1914-1920 (Cardon, 2003). Jensens claimed that the crafts of Sidon used mainly Hexaples and the same kind found in old walls of the space, the south gate, and south of the area (Jensen 1963; Jensen and Jensen 1965; Reese, 2010) (Figure 3.4).

Tyre (33°16’20”N, 35°12’11”E)

Hexaples were found in 1793 and 1811 by Lord Valentin. While in 1839-1840 along the coast, the Irishman Wilde (1839, 1844) found round depressions of broken Hexaples.

Chehab (1965) identified a Roman crushed murex through the craft district of the city and a Byzantine workshop. Jidejian (1969) report that the shell is from Tyre and dates from the 1st century A.D.

Therefore, it is worth noting that the Bolinus depicted on the coins of Tyre from 112 AD and later (Jackson, 1916; Reese, 2010). There is written evidence for the imperial purple production during the reign of Diocletian (Eusebius, Ecclesiastical History, VII, 32), and in 383 AD production became a state monopoly (Codex Justinianus IV. 40.1).

SYRIA

Minet el-Beidha (35°36’03”N, 35°47’05”E)

Piles of murex found in the area of Minet el-Beidha (Figure 3.5), and the port of Ras Shamra, dating to the 15th to 13th century BC (Schaeffer 1929, 1951). Local production of purple fabric are mentioned in Ugaritic texts in the first half of the 14th century BC and confirmed by excavation at Ras Shamra in 1933 and 1937 (Thureau-Dangin, 1934; Schaeffer, 1951; Reinhold, 1970; Reese, 2010).

Tell Rifa’at (36°28’23”N, 37°05’47”E)

Figure 3.6 Crushed Hexaples found at Tell Rifa’at (Biggs, 1967)

In the Orontes River in the hinterland of Syria, over 100 km from the Mediterranean coast, a large pile of shells Hexaples (Figure 3.6) was found, which was crushed in an Hellenistic house (Biggs, 1967; Reese, 2010).
ISRAEL

According to archeological elements, the areas of Israel such as Tell Akko, Tell Abu Hawam, Tell Keisan, Tel Shiqmona, Tel Megadim, Tel Dor, Yavneh Yam, Tell Mikhmoret, Tel Mevorakh, Tel Mor, Apollonia Arsuf, were workshops of purple-dye (Fig.3.7).

During the Archaic period (800 BC – 480 BC) many areas involved in dyeing fabrics (Koren, 2005b) in purple color or the processing shell or processing minerals. Below analyzed the areas where identified species of Murex after archaeological excavations (Fig. 3.7).

Tell Akko

In 1980 in northern Israel, large quantities of shells were found. The three species found in layers of purple excavation and furnaces, that demonstrate the use and production of purple (Dothan, 1981; Raban 1983; Karmon and Spanier, 1987). Crushed shells in thick layers dating from the 13th to the 12th century BC (Karmon and Spanier, 1987; Reese, 2010) were found and in nearby buildings quite a large number of broken and intact shells (including the three species of shells) were found and dated to the Persian and Hellenistic periods (Karmon and Spanier 1987, 1988).

Tell Abu Hawam

This area is located north of Mount Carmel 1.5 miles from the sea. In 2001, the excavation revealed large quantities of broken shells of the species Hexaples. The 155 shells produce 0.5 liters of pigment. An estimate of the minimum volume of 40,000 liters is estimated for breaking 12,400 shells (Baruch et al, 2005; Reese, 2010).

Tell Keisan (Puech, 1980)

This site is currently about seven kilometers from the coast. Samples of purple color found inside a large bowl of Iron Age I date (11th century BC) and examined, proved to be shell purple. In the same area, they found small amounts of Hexaples and Bolinus (Reese, 2010).

Tel Shiqmona

Large quantities of shell species Hexaples and Bolinus found in Tel Shiqmona in fieldwork (Karmon and Spanier, 1987, 1988). Broken shells of three species found outside the archaeological field, about half a mile south and crafts indicate that could be used for the production of purple dye (Karmon and Spanier 1987, 1988). Also, a number of sherds of Iron Age II (9th-8th century) contained purple spots, indicating the specie of Murex (Karmon and Spanier 1987; Cardon, 2003; Reese, 2010).

Tel Megadim

Excavations in 1967-1969 by M. Broshi on the coast found numerous Bolinus and Hexaples from the Persian layers (5th century BC). The 1968 excavation unearthed 56 Bolinus and two Hexaples (Reese, 2010).

Tel Dor

In Tel Dor in the laboratory area there was a thick layer of crushed thousands Hexaples. Among others, two in Hellenistic period (layer IV) and some whole

Figure 3.7 Areas of Israel, Tell Akko, Tell Abu Hawam, Tell Keisan, Tel Shiqmona, Tel Megadim, Tel Dor, Yavneh Yam, Tell Mikhmoret, Tel Mevorakh, Tel Mor, Apollonia Arsuf (Google Earth).
shells as well. (Karmon and Spanier, 1987; Stern, 1994; Reese, 2010).

Yavneh Yam
This coastal area is full of many broken Hexaples, Bolinus shells from the Hellenistic and Roman period (Reese, 2010).

Tell Mikhailmore
From the excavations of 1982-1984, Stiglitz wrote, "We found many shells kind murex. I believe it is from the Byzantine era. The shells were mixed in Persian, Hellenistic and Byzantine period" (Porath et al., 1993; Reese 2010).

Tel Mevorakh
This region showed numerous shells, including the Hexaplex, and a sea-shell of the 4th to 3rd-century BC (Stern, 1978; Reese 2010).

Tel Mor
There are many samples of murex from the Canaanite period, according to Raban (1981) and Reese (2007, 2010). They refer to an old report of Dothan (1960) that date the material, but it is more likely that the shells for purple-dye purposes are dated to the Hellenistic period.

Apollonia Arsuf
At this site there were found shells dating from the Persian and Hellenistic period (Karmon, 1999; Reese 2010).

TUNISIA
Carthage (36°51′29″N 10°19′51″E)
Although there have been many excavations in Carthage, only those made from 1982 to 1989 show a large percentage of murex (Reese, 2015b). There has been found a total of 2084 shells of which 1666 or 80% were used for the production of purple color. British, Danish and German excavations confirm the number of shells used for purple-dye production. The other 20% was used for consumption (Zaouali, 1994).

4. METHODS, SAMPLES AND CASE STUDIES

4.1 Murex shell molecular analysis
Several analytical methods have been applied to identify and study the chromophore components of murex shells that produce tyrann purple, such as 3D fluorescence spectrometry (Shimoyama and Noda, 1994), NMR (nuclear magnetic resonance) spectrometry (Clark and Cooksey, 1997, 1999; Voss, 2000; Voss and Schramm, 2000; Cooksey, 2001a, 2001b; Cooksey and Withnall, 2001; Hoffman et al., 2010), MS (mass spectrometry) (McGovern and Michel, 1990; McGovern et al., 1992a; Withnall et al., 1993; Gibbs et al., 1995; Clark et al., 1996; Clark and Cooksey, 1997; Voss and Schramm, 2000; Benkendorff et al., 2001; Cooksey, 2001a, 2001b; Cooksey and Withnall, 2001; Andreotti et al., 2004; Papanastasiou, 2005; Surowiec et al., 2012), Raman spectrometry (Withnall et al., 1993; Tatsch and Schrader, 1995; Clark and Cooksey, 1999; Cooksey, 2001a, 2001b; Ajiki et al., 2012), IR (infrared) spectrometry (Baker, 1974; McGovern and Michel, 1985; Voss and Gerlach, 1989; Tatsch and Schrader, 1995; Clark and Cooksey, 1997, 1999; Cooksey, 2001a, 2001b), PIXE (particle induced x-ray emission) and ESCA (electron spectroscopy for chemical analysis) (McGovern and Michel, 1984, 1985), Visible Spectrophotometry (Saltzman, 1978, 1986, 1992; Shen et al., 1991; Withnall et al., 1993; Serrano-Andrés and Roos, 1997; Daniels, 1989; Koren, 1993; Miliani et al., 1998; Cooksey, 2001b; Nowik et al., 2011), TLC (thin-layer chromatography) (Cooksey, 1995; Cooksey and Withnall, 2001; Hiyoshi and Fujise, 1992), GC (gas chromatography) (Benkendorff et al., 2001), and HPLC (high-performance liquid chromatography) (Wouters and Verhecken, 1991; Wouters, 1992; Koren, 1994a, 1995, 2006; Clark and Cooksey, 1997; Cooksey, 2001a; Cooksey and Withnall, 2001; Withnall et al., 2003; Karapanagiotis et al., 2006; Nowik et al., 2011; Mantzouris and Karapanagiotis, 2014; Vasileiadou et al., 2016).

Murex shells produce three main colour components: the isatinoids group, comprised of three chromophores, isatin (IS), 4-bromoisatin (4BIS), 6-bromoisatin (6BIS), which generates the yellow colour; the indigoids group, comprised of three chromophores, indigo (IND), 6-monobromoindigo (MBI), 6,6-Dibromoindigo (DBI) which generates blue and purple colours and the indirubinoids group, comprised of four chromophores, indirubin (INR), 6-monobromoindirubin (6MBIR), 6'-monobromoindirubin (6MBIR), 6,6-dibromoindirubin (DBIR), which generates that red colour (Koren, 2006).

4.2 Case Studies
The basic dating method used is radiocarbon and the analysis is made by various chromatography techniques. Methods used in earlier times and/or rare use of methods include: Thin Layer Chromatography (TLC), Liquid Chromatography with Atmospheric Pressure Chemical Ionization-Mass Spectroscopy (LC-APCI-MS), Nuclear Magnetic Resonance Spectroscopy (NMR), Mass Spectrometry (MS), Proton-Induced X-ray Emission (PIXE), Ultraviolet/Visible spectroscopy (UV/Vis), Electron Spectroscopic Chemical Analysis (ESCA), Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICRMS) and Microchemical tests (MCT). Modern
spectroscopy applied includes: High Pulsed Liquid Chromatography (HPLC), High Performance Liquid Chromatography Photodiode Array Detector (HPLC-PDA), High Performance Liquid Chromatography-Diode Array Detector (HPLC-DAD), X-Ray Florescence XRF, Environmental Scanning Electron Microscopy coupled with X-Ray microanalysis (ESEM-EDX), Infrared Spectroscopy (IR), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy (Raman).

A useful bibliography on papers regarding tyrian purple is given online (http://www.chriscooksey.demon.co.uk/tyrian/cjcbiblio.html)

Table 4.1 Samples of murex dye or pigment analyzed per region and technique applied (Karapanagiotis et al, 2013 enriched).

<table>
<thead>
<tr>
<th>a/a</th>
<th>Location</th>
<th>Date</th>
<th>Object/Samples</th>
<th>Technique</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Trianda, Rhodes, Greece</td>
<td>17th c. BC (or earlier)</td>
<td>Pigment</td>
<td>HPLC-DAD, Raman, FTIR</td>
<td>Karapanagiotis et al 2011, 2013</td>
</tr>
<tr>
<td>2</td>
<td>Akrotiri, Thera, Greece</td>
<td>17th c. BC (or earlier)</td>
<td>Lump of pigment and wall paintings</td>
<td>XRD, XRF, HPLC-DAD, LC-APCI-MS, RAMAN, FTIR</td>
<td>Karapanagiotis et al, 2011, 2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Karapanagiotis et al., in press.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Karapanagiotis, 2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sotiroupolou and Karapanagiotis, 2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>van Elslande, et al., 2008</td>
</tr>
<tr>
<td>3</td>
<td>Kerameikos, Athens, Greece</td>
<td>430-400 BC</td>
<td>textile</td>
<td>ESEM-EDX, RAMAN</td>
<td>Margariti et al 2013</td>
</tr>
<tr>
<td>4</td>
<td>Cave of Koroneia, Central Greece</td>
<td>6th-2nd c. BC</td>
<td>Astragalos made of sheep knucklebone</td>
<td>ESEM-EDX</td>
<td>Colombini et al., 2004</td>
</tr>
<tr>
<td>5</td>
<td>Chania, Crete, Greece</td>
<td>ca 300 BC</td>
<td>Hellenistic figurines</td>
<td>FTIR, XRF</td>
<td>Maravelaki-Kalaitzaki and Kallihrakas-Kontos, 2003</td>
</tr>
<tr>
<td>6</td>
<td>Tomb of Phillip II, Vergina, Macedonia, Greece</td>
<td>336 BC</td>
<td>Casket fabric</td>
<td>FTIR, MCT</td>
<td>Hofen de Graaff, 2004</td>
</tr>
<tr>
<td>7</td>
<td>Tomb III at Agios Anthanasiou, Macedonia, Greece</td>
<td>Last quarter of the 4th c. BC</td>
<td>Wall painting</td>
<td>XRF, HPLC-DAD</td>
<td>Karydas, 2006; Andreotti, et al., 2006</td>
</tr>
<tr>
<td>8</td>
<td>Tomb of the palmettes, Mieza, Macedonia, Greece</td>
<td>First half of the 3rd c. BC</td>
<td>Wall paintings</td>
<td>HPLC-DAD</td>
<td>Andreotti, et al., 2006</td>
</tr>
<tr>
<td>9</td>
<td>Strozzacaponi, Perugia, Italy</td>
<td>2nd -1st centuries BCE</td>
<td>textile</td>
<td>HPLC-DAD</td>
<td>Gleba and Vanden Berghe, 2014</td>
</tr>
<tr>
<td>10</td>
<td>Daskyleion, Turkey</td>
<td>5th c. BC</td>
<td>Painted surface of a kline, textile fragment</td>
<td>SEM-EDX, FTIR, HPLC</td>
<td>Papliaka et al., 2015</td>
</tr>
<tr>
<td>12</td>
<td>Tel Shiqmona, Israel</td>
<td>9th /8th c. BC</td>
<td>Sherd</td>
<td>IR</td>
<td>Karmon, and Spanier, 1988</td>
</tr>
<tr>
<td>14</td>
<td>Tel Keisan, Israel</td>
<td>11th c. BC</td>
<td>Vessel</td>
<td>MCT</td>
<td>Karmon, and Spanier, 1987</td>
</tr>
<tr>
<td>15</td>
<td>Tel Kabri, Israel</td>
<td>7th c. BC</td>
<td>Pigment potsherd</td>
<td>HPLC-DAD</td>
<td>Koren, 1995</td>
</tr>
<tr>
<td>16</td>
<td>Bible Lands Museum, Jerusalem, Israel</td>
<td>486/485 BC</td>
<td>Outer surface of Darius I stone jar</td>
<td>HPLC-DAD</td>
<td>Koren, 2008a</td>
</tr>
<tr>
<td>17</td>
<td>Royal tomb complex within the palace Qatna, Tell Mishrife, Syria</td>
<td>Late Bronze Age</td>
<td>Several sediment samples of decayed fabrics, fossilised woollen textiles</td>
<td>FTIR, HPLC-DAD, NMR</td>
<td>James et al., 2007, 2009</td>
</tr>
</tbody>
</table>

5. ANALYTICAL METHODS

Radiocarbon dating

Suitable for dating samples usually consist of organic materials found in archaeological sites, such as charcoal, wood, seeds, shells, cloth and other plant residues, and human and animal bones (Damon,
1989). It has not been used often in murex. But a characteristic application is by van Strydonck et al, (2012) from Balearic Islands, Spain.

**Spectro UV-VIS and RAMAN**

Early spectrum analysis for murex recognition started with spectrophotometry UV-VIS spectra, (Koren, 1993), while recently it has been overwhelmed by Raman Spectroscopy which is widely used to solve various problems of chemical, associated with the structure, kinetics, identification, quantitative analysis of various compounds, and in murex in particular (fig. 4.1). Raman has the advantage over uv/vis of suppressing of fluorescence radiation in textiles. For example, analysis with micro - spectroscopy Raman identified the main component dye, 6,6'-dibromoindigotine, and part of the inorganic pigment was rich in CaCO3 (as calcite and aragonite)(Chryssikopoulou et al., 2001; Withnall et al., 1992).

**Fig. 4.1 Raman spectra of the excavated textile (red line) and modern fibre (black line) (Margariti et al., 2013)**

**XRF**

The technique of fluorescent X-ray analysis method is a sample based on the X-ray fluorescence and exploits the fact that the energies of the photons emitted by an excited atom is characteristic for the type of atom and may lead to determination of the chemical substance. In murex, high bromine content that implies 6,6'-dibromoindigotine.

An earlier use of PIXE has been reported in literature (Table 4.1).

**XRD**

Analysis of the samples by X-ray diffraction (XRD) provides the mineralogical context of the analysed solid material. The X-ray spectroscopy describes the interaction of radiation with matter based on diffraction of monochromatic X-ray radiation with a certain wavelength from respective crystal lattice. Aragonite has been detected in this case. In fact, the content of purple that is bromine (6,6'-dibromoindigotine) and is associated with the presence of aragonite (CaCO3) from the crashed shell and its content, is an indicator of Murex shell from which the pigment derives from (e.g. in Akrotiri by Aloupi et al. 2000).

**HPLC (-PDA and -DAD)**

Chromatographic spectrosopies were conducted in parallel to the painted surface samples and in samples of a substance to form fine purplish powder (Figure 4.3). Samples were discovered in the area of Akrotiri, the assay results confirm the similar nature of all samples (Karapanagiotis et al., in press). Characteristic absorption peaks of a standard tyrian purple sample are presented in Fig. 4.2 (Koren, 2008b). Earlier use of TLC has been reported (Table 4.1).

It was found of interest to perform a cluster analysis of different percentages of colors of murex from various origins that may be identified by similar preparation techniques and origin and type of murex
(see Table 1, Section 1 and Karapanatios et al., 2013) (Fig. 4.3). Here the clusters differentiate type and preparation of murex as appear for T1, T2, T3, T4, T5, T10, T12, separate little locus for T7, T9, for B1, B2, B5, H3 (Spain, Greece, Israel), then B3, H1, H2 (Greece, Spain), then a larger group of AK1, Tri, AK3, AK2, Dar1, Ra, the the sole B4 and H4 (Italy, Greece) and outliers T11, T6, T8 expected as derived from far away sites (France, Greece, Eastern Spain), while the Akrotiri, Trianda at Rhodes and Darius stone are similar. Though of different murex species the preparation produced same pigment i.e chemical compounds.

Figure 4.2 HPLC-PDA analysis of standard tyrian purple dyes visualized at 400nm for the isatinoids (top: isatin (IS), 4-bromoisatin (4BIS), and 6-bromoisatin (6BIS)) and at 594nm for the indigoids and the indirubinoids (bottom: indigo (IND), indirubin (INR), 6-monobromoindigo (MBI), 6-monobromoindirubin (6MBIR), 6,6'-dibromoindigo (DBI), 6'-monobromoindirubin (6'MBIR), and 6,6'-dibromoindirubin (DBIR)) (Koren, 2008b)

Figure 4.3 Cluster analysis of samples from Table 1 from Chapter 1. T: Hexaplex Trunculus: T1(Carthage, Tunis), T2(Croatia), T3(Tunis), T4(Tunis), T5(Tarragona), T6(Tarragona), T7(Akhziv, Israel/Jordan), T8(Saronikos, Greece), T9(Akhziv), T10(Spain), T11(France) T12(Hermione, Greece), B: Bolinus Brandaris: B1(Tarragona, Spain), B2(Tarragona), B3(Saronikos), B4(Fiumicino), B5(Thera), H: Stramonita Haemastoma: H1(Tarragona), H2(Tarragona), H3(Israel), H4(Hermione), and the archaeological samples Ak1, Ak2, Ak3 (Akrotiri, Thera), Ra(Raos, Thera), Tri(Trianta, Rhodes) and Dar1(Darius stone jar). (Data based on data by Koren, 2008a; Karapanagiotis et al 2013; Mantzouris and Karapanagiotis, 2014).
FTIR

FTIR spectrometers (Fourier Transform Infrared Spectrometer) are widely used in organic synthesis, polymer science, petrochemical engineering, pharmaceutical industry and food analysis. In addition, since FTIR spectrometers can be hyphenated to chromatography, the mechanism of chemical reactions and the detection of unstable substances can be investigated with such instruments. The measurement of the degree of absorption helps to identify minerals and chemical elements, in the case of Tyrian purple presence of bromine (6,6' -dibromoindigotine) (Fig. 4.4 Karapanagiotis et al., in press).

![FTIR spectrum](image)

**Fig. 4.4 (Lower) FTIR spectrum of a pigment sample from Akrotiri, Thera (Late Bronze Age), from the fresco painting “Mistress of Animals and Saffron Gatherer” (Xesté 3, room 3a, First floor, Northwall), containing the purple paint details and the reference substance (upper) 6,6'-dibromoindigotine. Bands attributed to 6,6'-dibromoindigotine, aragonite (and partially to calcite) as well as the consolidant used by the restorers can be identified (Karapanagiotis et al., in press).**

Optical Microscope

Optical microscopy was applied to a textile excavated in Kerameikos, Athens, Greece (fig. 4.5) (Margariti et al., 2013). There was identified a decoration with purple colored wefts.

SEM-EDX

SEM microscopy is a non-destructive technique which will allow us to investigate the structure and the decay of sensitive samples without any additional alterations, such as fibers. In combination with the EDX method and the SEM can provide us with a qualitative and quantitative data analysis. This method allows a fast and non-destructive chemical analysis with spatial resolution in the micrometer regime. The detection of bromine will reveal the presence of murex (Fig. 4.6).

![Optical Microscope image](image)

**Figure 4.5 Image from Optical Microscope on a fragment of textile from the excavation site in Kerameikos, Athens, Greece (430-400BC). Identification of the decoration with purple wefts is apparent (Margariti et al., 2013).**
6. METHODS OF PRODUCTION AND THE CHEMISTRY OF TYRIAN PURPLE

Ways of production of Tyrian purple has been reviewed by Wolk and Frimer, (2010); including significant works such as Cooksey, (2001a) and Imming et al., (2001). Initial attempts in using alkali chemical reagents at dibromoindigotin (DBI) for obtaining corresponding color has been made by Michel and McGovern (1990) shown in brief steps below:

\[
\begin{align*}
\text{DBI} + \text{NaOH} + 90^\circ C + 1\text{h} & \quad \text{Deep Purple} \\
\text{DBI} + \text{K}_2\text{CO}_3 + 90^\circ C + 2\text{h} & \quad \text{Purple} \\
\text{DBI} + \text{K}_2\text{CO}_3 + 90^\circ C + 1\text{h} & \quad \text{Light Purple}
\end{align*}
\]

In experiments performed with different solutions in urine Ph that give the same colors is as below:

\[
\begin{align*}
\text{DBI with pH 9} + 50-60^\circ C + 1\text{h} & \quad \text{Light Violet} \\
\text{DBI with pH 8.6-8.8} + 60-70, \text{or 90}^\circ C + 1\text{h} & \quad \text{Light Violet}
\end{align*}
\]

In another experiment for blue, brown and pink:

\[
\begin{align*}
\text{Deionized water} + \text{IND} + \text{CaO} + \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} + 45^\circ C + 6\text{days} & \quad \text{Light Blue} \\
\text{DBI} + \text{Deionized water} + \text{CaO} + \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} + 45^\circ C + 6\text{days} & \quad \text{Pink} \\
\text{Deionized water} + \text{CaO} + \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} + 45^\circ C + 6\text{days} & \quad \text{Light brown}
\end{align*}
\]

A follow up has been reviewed by Ziderman et al., (2004); Son et al., (2004); Cooksey and Sinclair, (2005); Koren, (2012); Lavinda et al., (2013); Ramig et al., (2015), among others.

Overall, the murex has been given special attention throughout the last 5,000 years at least in Mediterranean region, but the World as well, and reconstructing trade routes along the orient and occident, from China to Europe, are of particular interest. In fact, among the more unlikely ‘matchmaking’ arranged by human ingenuity is the one between the Chinese domesticated silk moth, *Bombyx mori*, and the Mediterranean marine snails, *murex*, of the Muricidae family. The sea snails produce a pigment that, when brought together with silk, led to the world’s longest-lasting fashion statement, while in China and elsewhere used it as traditional medicine (Benkendorff et al., 2015).

7. CONCLUSION

Purple is a pigment, which is created by the sea-shell family gastropods. In antiquity, the essence of the animal was used to paint the people of nobility their clothes, so it was considered a “royal” color. Indeed, several ancient sources record the sea-shell of murex while its use of purple is recorded in Linear B tablets, the Homeric epics, by Aristotle, etc. The purple dye tested for the first time in Minoan Crete from the 17th century BC, and since used mainly in the SE Mediterranean. The workshops that were processing the shell to get purple, covered almost the entire Mediterranean mainly the eastern part. The technique of dye was made in several stages with complex processes.
The hues of the dyed fabrics vary from blue-green to blue for indigo, blue to violet for 6-bromindoindigo, and violet blue to purple for 6,6' -dibromoindigo, as determined by reflectance measurements. Many of the dyed fabrics change color markedly with application of gentle heat.

Purple is evocative in its preparation, engages in the colors of the rainbow and raises the royal purple through centuries of given gloss. With all these elements, purple retains almost magical properties and has been used throughout the World as dye and edible for medical purposes. The magnificence of silk and woolen veil, the simple brilliance of parchments and frescos through this color of an inaccessible sophistication compared to modern synthetic dyes, as well as, its multi-color knowledge with the overall elegance, is worthy of attention in our cultural space.

A plethora of scientific methods have been applied to identify this organic pigment in ancient materials. Spectroscopic, chromatographic, microscopic techniques are often used with success and have recognized the chemical substance.

ACKNOWLEDGEMENTS

We thank Assoc. Prof. I. Karapanagiotis and an anonymous referee for useful comments. This is part of a major project of Eastern Mediterranean - China Cultural Contacts led by Ioannis Liritzis as PI of Chinese National Social Science Fund’s “Great Site and Capital Civilization’s Research of He Luo (Yellow river and Luo river) and Three Generations (Xia, Shang and Zhou Dynasties)” Phased Results (Project Approval: 13 & ZD100).

REFERENCES

Aristotle, History of Animals, V15
Bacchylides, Lithyramvou 17,112


Diocletian, Eusebius, *Ecclesiastical History*. VII, 32

Diocletian, *Codex Justinianus IV*. 40.1


Mediterranean Archaeology and Archaeometry, Vol. 17, No 1, (2017), pp. 103-130

Homer’s *Iliad*: C 125 to 128, The 221, Z 796. (http://classics.mit.edu/Homer/iliad.html)

Homer’s *Odyssey*: S 115, S 351, h 226 (http://classics.mit.edu/Homer/odyssey.html)


McGovern, P.E., Michel, R.H. (1984) Royal purple and the pre-Phoenician dye industry of Lebanon, MASCA J., 3(3), 67-70

McGovern, P.E., Michel, R.H. (1990) Royal Purple dye: the chemical reconstruction of the ancient Mediterra-


Michel, R.H., McGovern, P.E (1990), The Chemical processing of Royal Purple Dye: Ancient Descriptions as

Michel, R.H., Lazar J., McGovern, P.E., (1992a) The chemical composition of the indigoid dyes derived from

Miliani, C., Romani, A., Favaro, G.A. (1998) Spectrophotometric and fluorimetric study of somean-


Nowik, W., Marcinowska, R., Kusyk, K., Cardon, D., Trojanowicz, M. (2011) High performance liquid chro-

Papiaka, E.Z., Konstanta, A., Karapanagiotis, I., Karadag, R. Akyol, AA


Nigdelis, P. (2010) Voluntary Associations in Roman Thessalonike: In Search of Identity and Support in a


Papanastasiou, M. (2005) FTIR imaging and HPLC reveal ancient painting and dyeing techniques of molluskan


Plato, Politia D, Critias 120b, Timaeus 67c

Pliny, Historia Naturalis, IX

Plutarch, The Parallel Lives, 36


Protopapas, S., Gatsos, V. (2003) The famous ancient purple of Hermione and its technology, Archaeolo-


Reese, D.S. (2010) Shells from Sarepta (Lebanon) and East Mediterranean Purple-dye Production, Mediterranean Archaeology and Archaeometry 10, no. 1, 113-41


Mediterranean Archaeology and Archaeometry, Vol. 17, No 1, (2017), pp. 103-130


Simonides 31 (13D 371 P)


Strabo, XVI 2,23


Thureau-Dangin, F. (1934) Un comptoir de laine pourpre à Ugarit d’après une tablette de Ras-Shamra. Syria 15, 137-146.

Tobin, J. (2011) From Troy to Constantinople: Cities and Societies of Ancient Turkey, Recorded Books, LLC.


Vitruvius (Ten Books, VII, XIII)


Xenokrates, *On abstinence from animal food*, C’XXII


