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Glass and other vitreous materials through history

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Early vitreous materials include homogeneous glass, glassy faience, faience and glazed stones. These materials evolved slowly into more specialized substances such as enamels, engobes, lustres, or even modern metallic glass. The nature and properties of vitreous materials are summarized briefly, with an eye to the historical evolution of glass production in the Mediterranean world. Focus is on the evolution of European, Egyptian, and Near East materials. Notes on Chinese and Indian glass are reported for comparison. The most common techniques of mineralogical and chemical characterization of vitreous materials are described, highlighting the information derived for the purposes of archaeometric analysis and conservation.

1. Introduction: chemistry, mineralogy and texture of vitreous materials

Glass is a solid material that does not have long-range order in the atomic arrangement, as opposed to crystalline solids having ordered atomic configurations on a lattice (Doremus, 1994; Shelby, 2005). It has been shown experimentally (Huang *et al.*, 2012) that amorphous solids can be described adequately by the model proposed by Zachariasen, the so-called random network theory (Zachariasen, 1932). Because of the contribution of configurational entropy, glass has a higher Gibbs free energy than a solid with the same composition. To decrease its free energy, glass tends inevitably to transform into the related crystalline form with time: the process is called devitrification. However, the kinetics of transformation at ambient temperature is very slow, so that the glass appears thermodynamically stable over the human life time. Glass can also be considered to be a metastable undercooled liquid, that is a liquid that has solidified below its melting temperature but did not have enough time to order (*i.e.* crystallize) because of the slow diffusion kinetics of the atoms. There is no critical temperature for the melt–solid transformation such as is present for crystalline solids, rather there is a temperature region (defined as Tg or the glass transition temperature)

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where the thermodynamic variables (volume, enthalpy and entropy) change continuously without showing sharp discontinuities. Ancient glasses were invariably produced by high-temperature melting technology, whereas nowadays there are several ways of producing glass materials at low temperature, such as vapour deposition, sol–gel processing of solutions, or neutron irradiation of crystalline solids.

From the point of view of composition, there are few oxides of 3- or 4-coordinated cations that can form a continuous network of oxygen-sharing polyhedra and produce glassy materials: they are B_2O_3, SiO_2, GeO_2, P_2O_5. The cation–oxygen bonds in good glass networks should have nearly 50% of covalent bond character. B, Si, Ge and P are the cations that form oxides satisfying these conditions, and therefore they are all natural 'network formers' although throughout history only silica-based glasses are found. Virtually, glass science is the mineralogy, chemistry and physics of silica. Natural glasses are formed at high temperature by rapid quenching of a silica-rich melt. There are three main geological processes which form glass: rapid cooling of a lava flow (obsidian, pumice), jet cooling of ejecta from a meteoritic impact (tektites) and quenching of the molten layer at the site of the shock impact (impactite, desert glass). All three types of natural glass have been used by humans to make implements or decorations (Fig. 1).

Because it is virtually impossible with old pyrotechnologies to reach the melting point of quartz (1610ºC) or the high equilibrium temperature of the polymorphs of silica (trydimite 1703ºC, cristobalite 1723ºC), in order to produce silica glass with ancient technologies, the melting point had to be lowered substantially. This was achieved by adding elements with a very low electronegative character that form highly ionic bonds with oxygen, commonly alkali elements (Na, K) or Pb. These elements are called network modifiers (or fluxants). However, silica glass that contains only alkali

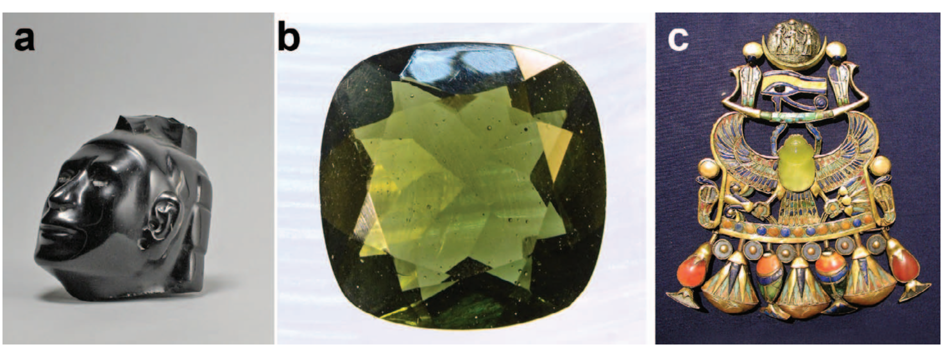


Figure 1. (a) Head of the Central Mexican god Xochipilli-Macuilxochitl made of black obsidian. Late Aztec sculptural tradition dated to the 15^{th}–early 16^{th} century AD; (b) a modern gem in moldavite, that is an olive green tectite found in southern Germany and the Czech Republic, formed about 15 million years ago; (c) Tutankhamen's pectoral ornament decorated with precious stones (such as carnelian, lapis lazuli, turquoise). The yellow central scarab is carved from desert glass, Egypt 18^{th} Dynasty. [Figure credits: (a) Metropolitan Museum of Art (MET) website, public domain; (b) retrieved from wikipedia public domain; (c) retrieved from www.egyptarchive.co.uk, Copyrighted free use].

cations is easily degraded, and it must be stabilized by cations with a greater ionic strength, most commonly alkaline earths (Mg, Ca), or stabilizers. Some other elements with intermediate electronegative character between the network formers and the network modifiers are called intermediates (Al, Ti, Zr). They can never act as network formers, though they can substitute Si in the tetrahedral sites of existing networks.

Finally, the only other intentional components present in the formulation of ancient glass are the colourants: commonly oxides of the transition elements (V, Cr, Mn, Fe, Co, Ni, Cu); and the decolourants: Sb, Mn (Bamford, 1977; Gliozzo, 2017). If the colourants are added in small amounts they are dispersed and diluted in the glass network, so that the material is coloured, transparent and homogeneous. However, if they are added in substantial amounts they may form specific crystalline compounds and modify the optical properties of the glass. For example, Cu-coloured glass is blue, but it may turn red if cuprite crystals or copper metal are formed (Fig. 2). Such glass is commonly called aventurine glass.

Bulk glass is thus composed of amorphous matter, although it may contain variable amounts of crystal phases. Crystals in glass may originate from three main processes (Artioli *et al.*, 2008): (1) the incomplete melting of the starting raw materials employed as network formers, commonly quartz sand or quartzite rocks; (2) deliberate addition as opacifying agents; and (3) nucleation and crystal growth from the molten glass during cooling. The latter process depends heavily on the chemical composition of the system, the solubility properties of the components employed, and the kinetics of cooling.

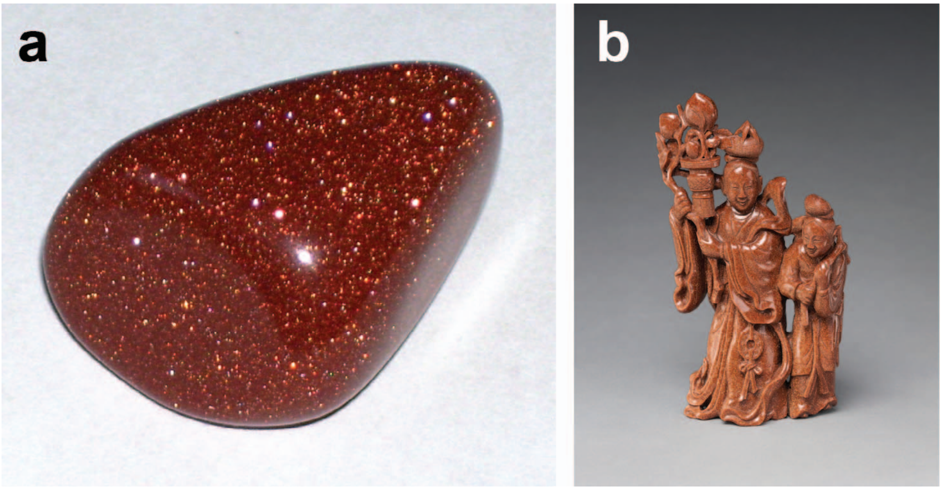


Figure 2. (a) A mass of goldstone, or aventurine glass from the Italian *avventurina*. The name derives from the term *avventura* that means 'adventure' or 'chance' (due to the difficulty in obtaining the right red colour); (b) small (17.8 cm in height) statue in aventurine glass from Qing dynasty (1644–1911 AD), China, 18th century. [(a) Retrieved from commons.wikimedia.org/w/index.php?curid=2419956, under CC BY-SA 3.0; (b) retrieved from the MET website www.metmuseum.org/art/collection/search/43374, public domain].

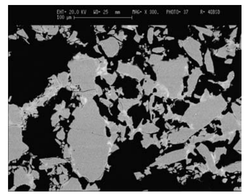
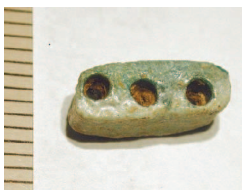
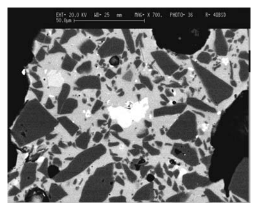
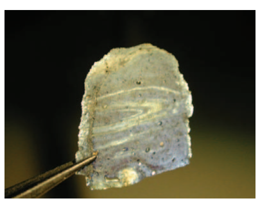
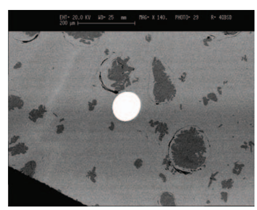
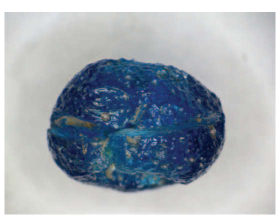
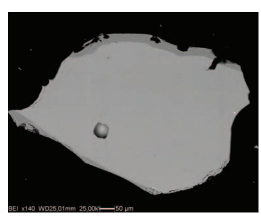
Based on the final proportions between the glass matrix and the crystalline phases, and the composition, size and distribution of the crystal phases, the glass may be transparent, translucent, or opaque.

The general term 'vitreous materials' refers to a wide range of materials that besides true glass includes glazed lithics, specific synthetic pigments such as Egyptian blue and Egyptian green, enamels, frits, faience and glassy faience. 'Frit' is a processed material that is commonly manufactured as an intermediate during the production of glass and faience: it is obtained by the partial melting and/or sintering of the raw materials, and it must undergo further grinding and furnace (or crucible) heating to yield the final product (Tite and Shortland, 2008).

Egyptian blue and Egyptian green are synthetic pigments that will be described in detail below. They are considered to be among the earliest man-made pigments and they are actually mixtures of specific mineral phases (cuprorivaite, wollastonite, cristobalite, *etc*.) and a minor amount of amorphous glass. The Cu-containing cuprorivaite causes the blue colour in Egyptian blue, whereas the Cu,Fe-containing glass causes the green tinge in Egyptian green (Jaksch *et al*., 1983; Pagès-Camagna and Colinart, 2003; Tite *et al*., 2008g). When coloured glass is produced specifically for application onto a metallic substrate it is called 'enamel'. This is generally achieved by grinding the glass to a fine powder that is then fused to the metallic substrate by high-temperature firing.

Faience is defined as a glazed non-clay ceramic material (Nicholson, 1998; Nicholson and Peltenburg, 2000) having a body (or core) composed of quartz sand that may contain small quantities of interparticle glass. The body is covered by a coloured glaze and a layer comprising a mix of glass and crystalline phases, the 'interaction layer' (IAL) is present between the glaze and the core. The thickness of the IAL and the small amount and distribution of glass in the core are related to the glazing method used in the faience production (Tite and Bimson, 1986; Tite, 1987; Tite *et al*., 2008a). The structure and the texture of faience are completely different from those of glassy faience, the latter being a vitreous material often confused with faience or with opaque glass. Glassy faience, named by Lucas also as 'faience Variant E' (Lucas and Harris, 1962), is a homogeneous material that may be considered as a hybrid of faience and glass (Tite *et al*., 2008a), with roughly equal proportions of amorphous and crystalline phases. Lucas described glassy-faience objects from Egypt lacking a surface glaze layer; nevertheless some objects show a glassy faience texture but also a distinct blue glaze on the surface. Several ornaments produced in Italy during the early phases of the middle Bronze Age present such features (Angelini *et al*., 2002; Tite *et al*., 2008b). These Italian materials do not fit properly with the 'faience Variant E' class as described by Lucas. Considering the measured proportion between the glass matrix and the crystalline phases, however, and taking into account that the assumed production technique is necessarily different from those used for the production of faience present in the same area, the material is also described as glassy faience (Angelini *et al*., 2002; Bellintani *et al*., 2006a). The characteristic inner textures of objects made of faience, glassy faience and glass are reported in Table 1.

Table 1. Typical examples of faience, glassy faience and glass textures from Bronze Age Italian vitreous materials.

Object type	Image	Micro-texture (SEM-BSE images)	Proportion of amorphous glass *
Faience: biconical bead (Lavagnone – BS)			0.03
Glassy faience: bead spacer (Prato di Frabulino – VT)			0.44
Opaque glass: slice of raw glass scrap (Frattesina – RO)			0.88
Transparent glass: flattened globular bead (Alba – CN)			1.00

* The proportion is reported as [(volume of glass)/(volume of glass + volume of crystalline phases)].

The terms ‘paste’, ‘glass paste’ or ‘glassy paste’ are often used in a colloquial and non-rigorous way, and do not relate to the texture, the nature or the composition of the vitreous materials. In order to avoid ambiguity and misunderstanding, these terms should not be used even when the identification of the proper type of vitreous materials is difficult or in the presence of weathering and leaching of the glass phase.

Based on the archaeological and historical evidence, the time of appearance, diffusion and the extent and duration of use of the different types of vitreous materials (faience, glass, pigments, *etc*.) is characteristic of different geographical and cultural contexts. Vitreous objects and evidence of glass-production technology, therefore, may be regarded as excellent indicators of cultural and technological diffusion, exchanges and trades.

Iconic illustrations of such processes are, for example, the introduction of 'trade beads' produced in Europe, the Islamic world and India into Africa in exchange for goods and slaves (Fage, 1962; Alpern, 1995; Lankton and Dussubieux, 2006; Robertshaw *et al*., 2010; Wood, 2011), or the introduction of glass by traders and explorers to indigenous people in North America (Hancock *et al*., 1996; Sempowski *et al*., 2001). Of course investigation of the cultural, social and personal use of the glass objects may also transcend the simple materiality of the objects themselves, providing insights into the intangible values of heritage materials (Yentsch, 1995).

A brief overview and some of the main features of physicochemical and textural variations of glass in time will be attempted below.

2. Composition of vitreous materials through time in the Mediterranean and Indian worlds

Ancient glass is generally classified into compositional groups, based mostly on the relative amount of fluxant (Na, K, Pb) and stabilizing elements (Mg, Ca). The observed chemical-compositional groups correspond roughly to chronologically and/or geographically distinct glass productions, and reflect the use of different components in the glass formulation and production technology. Sayre and Smith (1961) distinguished several compositional groups, based on the chemical and archaeological evidence available at the time. Their observations are still largely valid (Henderson, 2001, 2013a,b), although subsequent analytical data allowed refinement of the distribution and evolution of early vitreous materials (Rehren and Freestone, 2015). Table 2 reports the main compositional groups of ancient glass. Modern ordinary soda-lime silica glass is very similar to standard Roman glass.

2.1. Bronze Age

Glazed stones are the earliest vitreous materials invented by ancient artisans. They may be classified in two categories: 'glazed steatite' and 'glazed quartz', the latter including quartzite, chert and crystalline quartz.

Small objects made of glazed quartz were produced in Egypt (Fig. 3a) and the Near East from about 4000 BC, as suggested by Beck (1935). However, due to the large uncertainty in dating the materials it is not known if glazed quartz predated glazed steatite production (Tite *et al*., 2008c). Glazed quartz has been reported from Nubia (nowadays North Sudan) since the A-group period, about 3100 BC, and production is suggested to occur in Kerma in the flowering period of the Kerma Culture (corresponding approximately to the late Second Intermediate Period of Egypt)

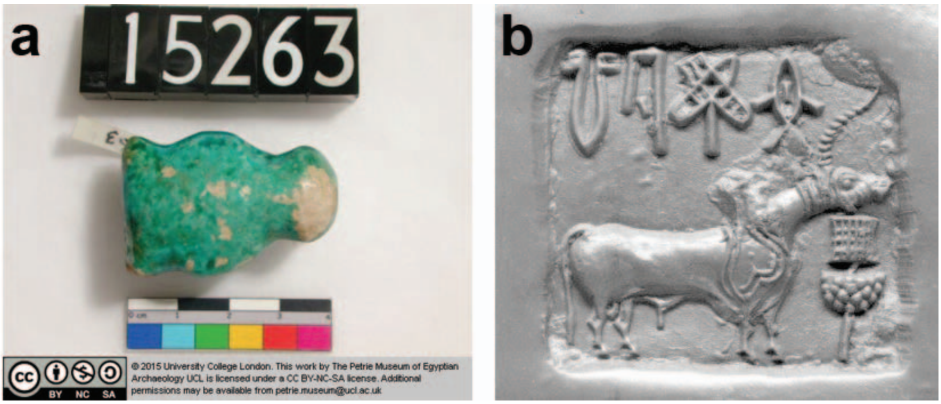


Figure 3. (a) An Egyptian blue bucranium amulet in glazed quartz, dated to the Early Dynastic Period; (b) stamp seal in burnt steatite, Harappan culture, Indus Valley (~2600–1900 BC) [(a) The Petrie Museum of Egyptian Archaeology UCL website; (b) from the MET website].

based on the archaeological objects, even if no direct evidence of furnace or workshop has been found (Lacovara, 1998). To date, no chemical analyses of glazed quartz are known, therefore the raw materials used and the production technology are still hypothetical.

Early glazed steatite production, mainly of small beads, is dated to about the end of the 5th millennium BC, and was in use in Egypt, the Near East and the Indus Valley (Tite *et al*., 2008c). Steatite is formally a soft compact rock composed mainly of talc (hardness of talc is 1 on the Mohs scale) and minor amounts of other minerals, such as chlorite, mica, tremolite, quartz and magnetite. In the archaeological literature, steatite is frequently termed ‘soapstone’, whereas formally soapstone should be characterized by larger contents of chlorite, serpentine and sometimes dark mica. However, both rocks are characterized by a low hardness (<3–4) and may be cut and engraved easily. Because of their soft state, they are still used widely today to carve ornaments, decorations and tourist souvenirs. In the early stages of glass/glaze development, steatite and soapstone were, therefore, ideal to carve and shape the core of small objects that was subsequently stabilized by glazing.

In fact after the shaping of the objects the hardness could be increased up to 5–7 by heating at >900ºC (Rapp, 2009). The talc undergoes high-temperature decomposition reactions and it is transformed into enstatite and cristobalite (Nakahira and Kato, 1963; Wesolowski, 1984; Zhang *et al*., 2006):

$$Mg_3Si_4O_{10}(OH)_2 \text{ talc} \leftrightarrow 3\ MgSiO_3 \text{ enstatite} + SiO_2 \text{ cristobalite} + H_2O$$

Small ornaments made of heated steatite were used widely since prehistory in numerous archaeological cultures in North America, Europe and Africa (Rapp, 2009), although the early use of glazed steatite was limited to three regions: Egypt, the Near East and the Indus Valley. On the surface of a steatite body a glazing slurry was applied

Table 2. Major compositional groups of archaeological and historic silica-based glass. Modified from Artioli (2010, table 3.12). The significant chemical signatures distinctive of the group are in bold.

Glass type	Chemical signature (oxide wt.%)					Note	Alkali source
	Na_2O	K_2O	MgO	CaO	Other		
HMG	8–20	**0–3**	**2–10**	3–10		**High-Mg glass** – Near East (1500–800 BC)	plant ash
LMHK	0–8	**4–18**	**0–1**	0–4		**Low-Mg High-K glass** – Europe (Final Bronze Age), China-Thailand (400 BC–200 AD)	plant ash
LMG (SLS)	13–20	**0–1**	**0–1**	5–10	0–1 Fe_2O_3 0–2 MnO	**Low-Mg glass** – Near East (after 800 BC) and standard Roman-type **soda-lime silica** glass (50–300 AD)	natron salts
HIMT	16–20	**0–1**	1–2	5-9	**1–3** Fe_2O_3 **1–3** MnO **0–1** TiO_2	**High-Fe-Mn-Ti glass** – Mediterranean area and Northwestern provinces (300–500 AD)	natron salts
LEG	10–15	**0–1**	0–1	8–12	**1-3** Al_2O_3	**Levantine-type** – Near East, Mediterranean area, Northwestern provinces (500–800 AD)	natron salts
HSB	15–21	**0–1**	0–1	4–6	**0–2** Sb_2O_3	**High-Sb glass** - Near East, Mediterranean area (100–300 AD)	natron salts
HKEG	0–14	**2–14**	0–5	6–20		**High-K Medieval glass** – Europe (stained window glass)	plant ash
HLLA	2–4	3–6	2–5	**16–25**		**High-lime Low-alkali glass** - Britain (17^{th}–18^{th} cent AD)	plant ash

HLEG	0–1	**3–10**	1–3	4–16	**20–65** PbO	**High-Pb Medieval glass** – Europe	plant ash
HMEIG	10–18	1–3	**3–7**	6–12	**0–1** MnO	**High-Mg Early Islamic** glass (840–1000 AD)	natron/ plant-ash
HBHA	17–21	4–5	1–5	2–6	**0.1–0.2** B **8–12** Al_2O_3	High-B High-Al Byzantine Western Anatolia	mineral flux
HLIG	8–10	0–2	0–1	4–5	**30–65** PbO	**High-Pb Islamic glass** (1000–1400 AD)	natron/ plant ash
HLHB	2–9	0–4	0–1	0–3	**18-44** PbO **6-22** BaO	**High-Pb High-Ba glass** – China (Han Dynasty 206 BC-221 AD)	witherite
HSHA	15–20	0–5	0–3	0–6	**10–15** Al_2O_3	**High-Na High-Al glass** Asia (China, Korea, Southeast Asia)	mineral flux
HAG	2–12	**4–16**	1–2	2–6	**2–4** Al_2O_3	**High-Al glass** – India (1st millennium AD) – maybe several groups	plant ash
HLHA	0–7	3–8	0–1	**11–31**	**11–18** Al_2O_3	**High-Ca High-Al glass** – West Africa (9th–13th cent AD)	plant ash
FDV	12–15	2–4	1–3	4–10		**Venetian** “cristallo” and **Dutch** “façon de Venise” (16th–17th cent AD)	soda-rich ash

before the heating process in order to obtain a glaze with the preferred colour covering the object. The slurry always contains some kind of fluxing agent, with different overall composition specifically depending on the geographical area. The thermally stimulated reaction between the glaze and the talc core may form specific mineral phases, mostly forsteritic olivine (Mg_2SiO_4) or enstatitic pyroxene ($MgSiO_3$), though the local concentration of alkali may stimulate the crystallization of unusual phases of the osumilite–milarite group of minerals (Artioli *et al.*, 2013). The morphology and distribution of the crystals in the internal part of the glaze is indicative of the glazing process that could be either direct application or cementation (Tite and Bimson, 1989).

In Mesopotamia the early known glazed steatite is dated to 5500−4000 BC, and was found in Arpachiya, Niniveh and Tepe Gawra. Production continued to be in use in the Early Dynastic period (3000−2350 BC) and later, as testified by the finds of some seals in Ur and Kish (Beck, 1934; Moorey, 1994; Tite *et al.*, 2008c). The steatite generally is white, displaying at best a poorly glazed surface layer, therefore these materials were named by Beck (1934) and Morey (1994) as 'burnt steatite'. However, the strongly weathered state of the finds does not allow exclusion of the presence of an original fully glazed layer that is now totally lost (Tite *et al.*, 2008c). To date, no analyses of Mesopotamian burnt steatite are known, adding to the uncertain interpretation of these materials and their production technique. In the Levant, ~200 white beads dated to the 5th millennium BC were found in the Chalcolithic burial cave of Peqi'in (northern Israel). X-ray diffraction (XRD) and scanning electron microscopy-energy dispersive spectrometry (SEM-EDS) analyses performed on some of the beads (Bar-Yosef Mayer *et al.*, 2004) confirmed that they are made of glazed steatite. Traces of Cu are present suggesting an original blue colour of the glaze, although no information about the fluxing agents or other chemical species are reported. Based on the dimensions and the orientation of the enstatite crystals, the authors suggested that the beads were produced by a sort of 'steatite faience' process, *i.e.* a faience production made with crushed steatite instead of sand or quartz. To date, steatite faience is known from pre-Indus and Indus civilizations (Tite *et al.*, 2008c), but it has not been found in the Egyptian and Mesopotamian world. Moreover, Bar-Yosef Mayer *et al.* (2004) do not report SEM or optical microscopy (OM) images of sections of the beads, so the question of the fabrication technique of such materials requires further investigation.

Steatite faience is rare, and is known mainly from South Asia: in Mehrgarh (pre-Indus period) and in Nausharo (Indus period). The steatite faience from Mehrgarh seems to be produced by the efflorescence or the application method and the amorphous phase has a composition similar to that observed in glazed steatite (discussed below). From Nausharo analytical data are available only for one sample, and its peculiar composition suggests a different origin (Barthélemy de Saizieu and Bouquillon, 1997, 2001; Tite *et al.*, 2008c).

Glazed steatite is found largely in the Indus Valley during the Chalcolithic (about 4500−3500 BC) and the Indus period (2500−2000 BC), and its use disappears from 1900 BC onwards (Barthélemy de Saizieu and Bouquillon, 2001). The glaze has a greater Al content than local sands (a similar Al content is known also for later Indian glass − see below). The ratio of the monovalent alkali contents suggests that *ghar* (a local type of plant ash) is used as flux or, more rarely, *reh* a mix of efflorescent salts, is suggested as flux (Tite *et al*., 2008c). An important production centre of glazed steatite, other stone beads and faience, is Harappa, where excavation provided a large number of materials and finds related to production activities (Kenoyer, 1994, 1997; Miller, 1999) (Fig. 3b).

Egyptian glazed steatite was widely diffuse both in terms of geographical distribution and time range (Fig. 4). Referring to the standard Egyptian chronology as reported in the Cambridge Ancient History volume, the earliest glazed Egyptian steatite is dated to the late 5th millennium BC (Predynastic Period) and it was found in graves at Qau-Badari (Badarian Culture). It comprises mainly small coloured beads that continued to be produced in the Naqada I and II phases of the Predynastic Period (~4000−3000 BC). From the Early Dynastic (3000−2570 BC) to the Middle Kingdom (1991−1750 BC) not only beads, but also amulets and scarabs were produced. Since the New Kingdom (1540−1070 BC) and until the early Late Period (747−332 BC) the production of glazed steatite continued: amulet scarab, seals, small and large decorative objects were produced commonly, whereas the manufacture of beads was rare (Vandiver, 1983). Tite and Bimson (1989) analysed a few Badarian beads and decorative object of the New Kingdom finding that different recipes and glazing methods were used. The glaze of the Badarian beads shows large Mg, Na and Cu contents, suggesting that a mix of natron and copper minerals is used to prepare the slurry and create a blue glaze. Forsterite crystals are present in the glaze with a preferred dimensional distribution: the smaller are close to the surface and the larger are formed in the area of interaction with the talc core: this suggests to the author the probable use of the cementation process.

The glazed steatite of the New Kingdom is characterized by a glaze with large Na and K and small Mg and Al contents; therefore the likely use of powdered quartz or pure sand mixed with soda plant ash (or sometimes mixed alkali plant ash) can be assumed. The glaze is coloured by Cu, although found in smaller concentrations than in the Badarian glazed steatite (Tite and Bimson, 1989; Tite *et al.*, 2008c).

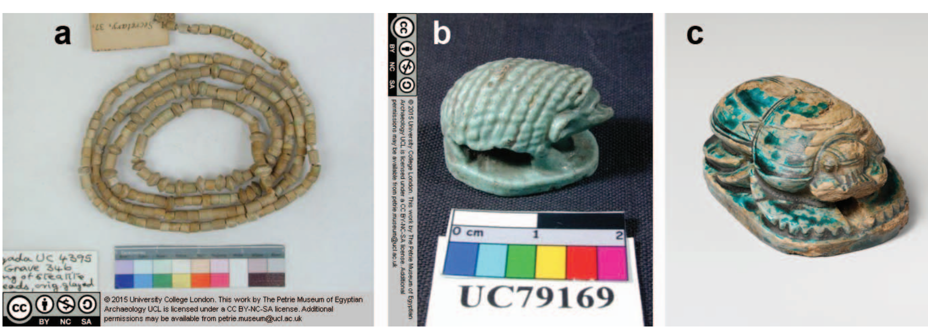


Figure 4. (a) Glazed steatite beads from Naqada Tomb-346, Egypt (Naqada II, ~3500 −3200 BC). The whitish colour is due to the loss of glaze; (b) blue-green glazed steatite scaraboid in form of hedgehog (18th Dynasty, 1540−1295 BC); (c) commemorative scarab of Amenhotep III recording a Lion Hunt. Glazed steatite, 18th Dynasty, from Thebes. [(a) and (c) from The Petrie Museum of Egyptian Archaeology UCL website; (b) from the MET website].

An important and widely found vitreous material is faience. Faience first appeared at the end of the 5th millennium BC in the Near East and then in Egypt (Nicholson, 1998; Nicholson and Peltenburg, 2000; Tite *et al.*, 2008d). In the Caucasian regions, faience has been known since the middle–end of the 3rd millennium BC (Shortland *et al.*, 2007a) and seems to predate the presence of the earliest faience in Europe in the BzA1, about 2200−1900 BC (Bellintani *et al.*, 2006b). In the Aegean world, early faience is known from the Middle Chalcolitic cemetery in Cyprus (3200−2900 BC), at approximately the same time at which they appeared in Crete. Some time later it is present in Rhodes and mainland Greece (Tite *et al.*, 2008e). In the Indus Valley there is an independent development of a faience industry that takes place and prospers during the entire Indus Civilizations (from the beginning of the 3rd millennium BC to the early 2nd millennium BC). Some of these faience productions and the early known or possible production centres will be discussed in detail.

In the Near East, the oldest known faience materials are dated to the "final phase of the Ubadi period (5500−4000 BC)" (Tite *et al.*, 2008f). Throughout this time, beads and vessels were produced in blue-green Cu-coloured faience. During the 3rd millennium BC (Early Dynastic and Akkadian periods), a number of different object types were produced, such as amulets, seals, moulded vessels and others. The same types of objects were still manufactured in Mesopotamia during the first half of the 2nd millennium BC, although new colours and decorations were introduced. Black-brown decorations obtained from Fe-Mn ores are specifically to be noted. In the same period, faience was introduced in the Levant, probably from Egypt, although the possibility of local production is not to be excluded (Tite *et al.*, 2008f). The second half of the 2nd millennium BC was a time of significant changes in the production of vitreous materials thanks to technical developments in the glass industry. Nevertheless, faience continued to be produced, largely in the Near East, and new colours such as yellow (due to Pb antimonate) and different hues of green obtained by mixing Cu and Pb antimonate were used. Glazed pottery products were created now and their production increased progressively during the 1st millennium BC. Small objects and faience vessels continued to be produced during the 1st millennium BC up to the Sassanian Period (637 AD) (Tite *et al.*, 2008f). Despite the importance of the Near East faience production, archaeometric investigations have been extremely scarce. Information about the colouring agents and opacifiers is available based on the analyses of ~300 objects (Kaczmarczyk, 2007) using non-invasive analysis. Chemical data for the amorphous phase are available only for a few objects from Tell Taya, dated to 2200 BC (Tite *et al.*, 2008f) (Fig. 5a). The data suggest that sand was used for the production of faience, but due to the weathering of the glass phase it is difficult to evaluate the fluxant used. Large K contents suggest the use of mixed alkali plant ash, but K may also be derived from feldspar present in the sand, therefore the use of soda plant ash is also possible (Tite *et al.*, 2008f).

More data are available for Egyptian production thanks to the large number of excavations and archaeometric studies. For the manufacture of the body a paste composed of sand or ground quartz mixed with water and flux was prepared (flux is

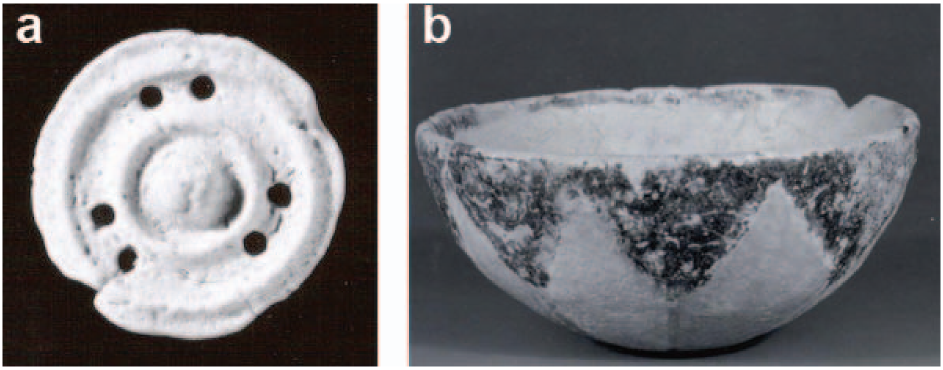


Figure 5. (a) Early Bronze Age faience ornament from Tell Taya, Mesopotamia, *ca*. late 3rd millennium BC. The white colour is typical of the strong weathering of these faience; (b) faience bowl from Mesopotamia, 16th–12th centuries BC [Images from the MET website].

added only if the glaze is obtained by efflorescence). The body of the faience could be shaped in different ways: manual modelling, moulding, core forming, rod forming, using different techniques of inlay and by less common methods (Vandiver, 1982; Nicholson, 1998; Nicholson and Peltenburg, 2000). Three main glazing techniques are known:

(1) direct application: a vitrifying slurry is prepared with water, flux, lime, colouring agent (generally Cu) and eventually ground quartz or sand and it is applied to the surface before firing;

(2) efflorescence: the vitrifying slurry is mixed in the body paste before the shaping phase, then the faience is dried in air (when the alkali salts effloresce on the surface) and fired;

(3) cementation: the shaped nucleus is immersed in a powder of lime, flux and colouring agent, and then fired.

The glazing techniques have been discussed in detail in the literature and experimental replicas have been performed to investigate the correlation between the resulting microstructure of the faience and the production techniques (Vandiver, 1982; Tite and Bimson, 1989; Nicholson, 1998; Nicholson and Peltenburg, 2000; Shortland and Tite, 2005; Tite *et al.*, 2008d). The modelling and glazing techniques changed over time, as did the variety of objects produced and the colours used. The main changes (Vandiver, 1982; Nicholson, 1998; Patch, 1998; Nicholson and Peltenburg, 2000; Tite *et al.*, 2008d) are summarized here.

Early Egyptian faience, mainly beads and amulets, is known from Badarian burials in the 4th millennium BC, but it is not clear whether they were an independent local invention or the knowledge of faience production derived from the Near East. Predynastic faience is generally coloured by copper and it seems that all three glazing techniques were actually in use (Fig. 6a). During the Early Dynastic period the same type of faience was produced, and vessels, tiles and statuettes (dog, bird, baboon, *etc*.) were manufactured. The variety of faience items produced during the Old Kingdom and

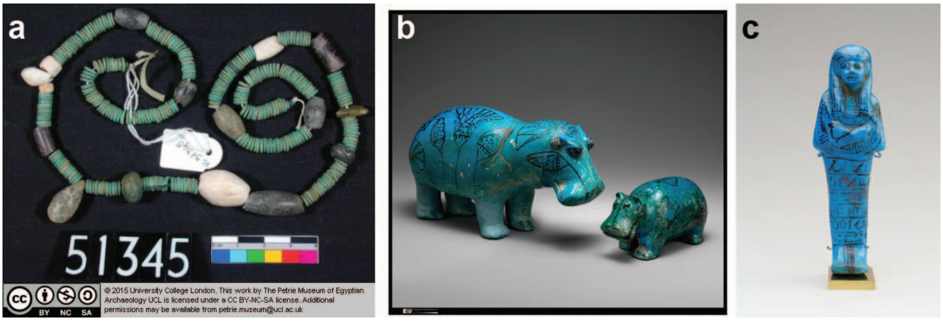


Figure 6. (a) Faience beads dated to the Predynastic Period, from Diospolis Parva (Egypt); (b) faience hippo from Meir (Egypt), Tomb B3, Khashaba excavations, 1910. Dated to the Middle Kingdom, 12th Dynasty, reign of Senwosret I–Senwosret II (*ca*. 1961–1878 BC); (c) Shabti of Paser, the Vizier of Seti I and Ramesses II. Dated to *ca*. 1294–1213 BC, 19th Dynasty, New Kingdom; [(a) from The Petrie Museum of Egyptian Archaeology UCL website; (b,c) from the MET website].

the First Intermediate Period is even wider, and includes plaques, game pieces and boat models, though the main products are beads and especially tiles. A massive amount of high-quality blue faience tiles was found in Djoser's step Pyramid in Saqqara (3rd Dynasty) and in the Reneferef's Pyramid in Abusir (5th Dynasty). In this phase new colours were used: black-brown decorations obtained by the use of Mn-Fe pigments and white objects resulting from faience prepared without colouring agents. By the 12th Dynasty the variety of faience objects increased again and small statues of all scales were produced. In the Middle Kingdom and the Second Intermediate Period a wider range of faience objects was created, including jewellery, vessels and animal figurines such as hippos, apes, cats and hedgehogs (Fig. 6b). Composite objects were prepared by joining different faience pieces using quartz-paste slurry. The apogee of faience production may be considered the New Kingdom and in particular the 18th Dynasty. At this time a multitude of object types was created: shabtis, sistra, furniture models, game boards, statuettes, plaques, bowls, canopic jars, boxes and others. The most colourful faience was produced thanks to the discovery of new colourants: Co for deep dark blue; Pb antimonate for yellow and in combination with Cu for green; iron oxide for red. As noted for coeval Near East faience, the development in this chronological phase of an evolved glass industry had a positive influence on faience production. The link between faience and glass production is supported by the simultaneous presence of both types of product in the same site, such as in Amarna and Quantir (Table 3 and references therein). During the Third Intermediate Period the same types of faience objects continued to be produced, especially shabtis, beads, amulets and chalices. The colour palette was limited: cobalt blue disappeared and Pb antimonate was scarcely used.

The earliest production centre of faience excavated in Egypt is Abydos. The site dates from the middle of the Old Kingdom to the early Middle Kingdom. Remains of circular features and bricks are associated with the probable presence of a kiln (Nicholson, 1998; Nicholson and Peltenburg, 2000). Evidence for the existence of a faience workshop in Lisht comes from the reading of an epigraphic note on a sarcophagus reporting the existence of an "overseer of faience workers" (dated to the 13th Dynasty, 1750–1640 BC). Moreover, excavation campaigns of the Metropolitan Museum of Art at the beginning of the 19th century unearthed the remains of a kiln (Nicholson, 1998; Nicholson and Peltenburg, 2000). However, at the Lisht site, glass finds and waste connected to glass production are present: glass slags, cullets, crucibles and glass fragments of objects were found, together with faience beads and pendants, half-finished glass and faience objects. The site of Lisht has been established since the 12th Dynasty (1985–1956 BC), however the finds connected to the vitreous material production do not have precise archaeological context and, based on the typologies of finished objects, the glass-related activity at the site may span from 1295 BC to 1070 BC (Keller, 1983). Possible faience production has also been suggested in Kerma (north Sudan) due to the presence of quartzite pebbles and other remains related to faience production. No kiln or furnace has been identified (Reisner, 1923; Nicholson, 1998; Lacovara, 1998; Nicholson and Peltenburg, 2000). Confirmed evidence of faience production is known from the excavations of the New Kingdom sites in Malqata, Amarna and Qantir. The excavations at Malqata in the palace of Amenhotep III (18th Dynasty, 1390–1352 BC) yield scraps of faience, finished objects and ceramic moulds, some of them with the faience paste still pressed in the mould (Nicholson, 1998; Nicholson and Peltenburg, 2000). At the same site, the presence of a crucible with dark blue glass and glass rods may be indicative of the production of glass. Unfortunately, some of the rods are now lost and the production of glass at the site is still debated (a summary in Pusch and Rehren, 2007). In the site of Amarna the excavation started in the end of the 18th century with the works of Petrie (1894), and modern campaigns are progressing thanks to the numerous activities of Nicholson and others (Amarna Project website: www.amarnaproject.com/pages/publications/excavation.shtml). Remains of kilns and materials related to the production of faience, glass and Egyptian blue have been found (Nicholson, 1998, 2007; Nicholson and Peltenburg, 2000). During the excavation at Qantir, an incredible number of faience moulds and also Egyptian blue cakes, tiles and faience objects were discovered. For this reason the production of faience is suggested, although the kiln has not been found (Hamza, 1930; Nicholson and Peltenburg, 2000). The production of glass at Qantir is attested by the presence of firing crucibles, raw glass remains and glass objects (Pusch and Rehren, 2007). Considering the presence of finished objects in vitreous materials from Kom Medinet Ghurab, the possible production of faience and/or glass in the site has been suggested, but to date no evidence has been found of a firing structure or remains related to the production process (Nicholson, 1998; Nicholson and Peltenburg, 2000; Pusch and Rehren, 2007). In Memphis, excavation by Petrie discovered one of the most important sites for the production of faience in Greek-Roman time (Petrie, 1909, 1911). Six kilns were identified, probably related to the production of faience and Egyptian blue: lumps of the pigment were actually found in the site. The presence of glazed pottery also suggests that this material could have been produced at Memphis. A furnace dated to the Roman period was discovered in excavation at the area of Kóm Helul, in Memphis (Nicholson, 2002, 2013). In Naukratis, a Greek settlement dated to

Table 3. Main archaeological sites showing evidence of working or production activity of faience, Egyptian blue or glass in Bronze Age Egypt and Near East.

Area	Site	Age	Materials /activity	Presence of kiln	Selected references
Egypt	Abydos	Middle Old Kingdom – early Middle Kingdom	Faience production	Trace and possible remains of a kiln	Nicholson (1998); Nicholson and Peltenburg (2000)
Egypt	Lisht	Faience: Middle Kingdom (13th Dyn. 1750–1640 BC), Glass: 20th Dyn (1985–1956 BC)	Faience production Glass working and production	Remains of a kiln	Keller (1983); Nicholson (1998); Nicholson and Peltenburg (2000); Mass *et al.* (2002); Shortland and Eremin (2006); Shortland *et al.* (2007b); Smirniou *et al.* (2018)
North Sudan	Kerma	Middle Kingdom (1991–1640 BC)	Faience production	No conclusive evidence	Reisner (1923); Nicholson (1998); Lacovara (1998); Nicholson and Peltenburg (2000)
Egypt	Malqata (Thebes)	New Kingdom, Amenhotep III (18th Dyn., 1390–1352 BC)	Faience production. Glass working-Glass production?	No remains	Nicholson (1998); Nicholson and Peltenburg (2000); Mass *et al.* (2002); Shortland and Eremin (2006); Shortland *et al.* (2007b); Degryse *et al.* (2010)
Egypt	Amarna	New Kingdom, Akhenaten (18th Dyn., 1352–1336 BC)	Faience, Egyptian blue and glass production	Several structures are present	Petrie, (1894); Brill (1999); Nicholson (1998); Nicholson and Peltenburg (2000); Shortland (2000); Nicholson (2007); Henderson *et al.* (2010); Shortland and Eremin (2006); Shortland *et al.* (2007b); Degryse *et al.* (2010); Smirniou and Rehren (2011)

Egypt	Qantir	New Kingdom (1540–1070 BC)	Faience, Egyptian blue and glass production	No remains	Hamza (1930); Rehren (1997); Rehren and Pusch (2005); Pusch and Rehren (2007)
Egypt	Kom Medinet Ghurab	New Kingdom, Amenhotep III (1390–1352 BC) – Ramesess II (1279–1213 BC)	Faience production? Glass production?	No remains	Nicholson (1998); Nicholson and Peltenburg (2000); Pusch and Rehren (2007)
Egypt	Memphis	Greek – Roman	Faience and Egyptian blue production	Several kilns	Petrie (1909, 1911); Nicholson (2002, 2013)
Egypt	Naukratis	Greek – Roman	Faience production?	No remains	Petrie and Gardner (1886); Nicholson (1998)
Egypt	Buto	Greek – Roman	Faience production?	Base of the furnace	Nicholson (1998); Shortland and Tite (2005)
Syria	Tell Brak	15^{th} – 14^{th} century BC	Glass working Glass production?	No evidence	Oates *et al.* (1997); Brill (1999); Shortland and Eremin (2006); Shortland *et al.* (2007b); Degryse *et al.* (2010); Henderson (2010, 2013b)
Turkey	Alalakh, Tell Atchana	Late Bronze Age I (*ca.* 1500–1450 BC) – Late Bronze Age II (1400–1300/1200 BC)	Glass production and working	A kiln	Barag (1970, 1985); Bimson and Freestone (1985); Henderson (2013b); Dardeniz (2018)

the Late Period, Petrie reported the presence of a scarab factory possibly related to faience production (Petrie and Gardner, 1886). However, recent information about the materials and the work of Petrie is lacking, so that the production of faience at the site is unconfirmed (Nicholson, 1998).

Chemical analyses of a very large number of Egyptian faience pieces were performed by Kaczmarczyk and Hedges (1983) in non-invasive mode by X-ray fluorescence (XRF). The data are useful mainly for identifying the type of colouring agent and opacifier (discussed above). Chemical data measured on sections of the beads by SEM are reported by Shortland (2000); Tite and Shortland (2003); Shortland and Tite (2005); and Tite *et al.* (2007). The results were well summarized and discussed by Tite *et al.* (2008d). The analyses show that the flux used in faience production from the Middle Kingdom to the New Kingdom (18th Dynasty) is soda-rich plant ash, that was replaced by natron from the beginning of the 3rd Intermediate Period onwards. Concerning the source of silica, the level of Al and other elements, suggests that in the majority of cases quartz sand was used. In a small number of objects from Amarna, ground quartz pebbles were preferred. The Co ores used to colour the faience come from the Western Desert of Egypt, specifically from the Kharga and Dakhla Oases, where cobaltiferous alum ores are present. The origin of the Co ores may be identified in the glass and glaze by the high Al and Mn levels and by the presence of traces of Ni and Zn. All these elements are characteristic of the Co-ores from the Western Egyptian Desert. In contrast, an Eastern source of Co from Iran seems to be associated to a trace of As (Tite *et al.*, 2008d; Henderson, 2013b).

The technology of faience spread from the Near East and Egypt to the Mediterranean world around the end of the 3rd millennium BC or the beginning of the 2nd millennium BC. In the northern Caucasus, faience beads appear probably earlier than in Europe: cylindrical and tubular faience beads, white or coloured, are present at the end of the Catacomb Culture (~2600−2200 BC) and in the Lola Culture (~2000−1900 BC). A small set of Caucasian pearls has been analysed by wavelength dispersive spectroscopy (WDS) (Shortland *et al.*, 2007a). The results show a variable composition: some faience is soda-rich, some potash-rich and some has a peculiar composition. Cu is present as a colouring metal, whereas Co and Sb were not identified. Based on their chemistry, some of these beads are similar to Egyptian analogues, whereas others are probably made locally because of the peculiar composition (Shortland *et al.*, 2007a). Because of such early occurrences, it is suggested that the spread of the faience technique to Europe may have occurred through the Caucasus.

In Central Europe, small cylindrical, biconical, annular and segmented beads have been present since the very start of the Early Bronze Age (Bz A1), ~2200−1900 BC (Bellintani *et al.*, 2006b). During the beginning of 2nd millennium BC faience was present in the Carpathian basin (Angelini *et al.*, 2006), Switzerland (Henderson, 1993; Angelini and Olmeda, 2018), Poland (Robinson *et al.*, 2004), Holland, France (Gratuze *et al.*, 1998, 2013; Gratuze and Janssens, 2004; Gratuze and Billaud, 2014), northern Italy (Angelini *et al.*, 2006; Bellintani *et al.*, 2006b) and Great Britain (Aspinal *et al.*, 1972; Sheridan *et al.*, 2005). The general shape of the beads is similar, but local typological variations are present suggesting the existence of different production centres. The early analyses of European faience were done by neutron activation analysis, a non-invasive technique producing bulk chemical data. In this case the comparison between the composition of faience from different sites is problematic because the amorphous and crystalline part are analysed together. Nevertheless, Harding and Warren (1973) were able to distinguish some compositional ranges of trace metals that allowed the discrimination of British faience (with high Sn) from the Carpathian (with higher Co and Sb). The chemical SEM/EDS and WDS data available for faience found in central and western Europe have been collected and compared in Tite *et al.* (2008b). A mixed alkali flux was used in the production of all the analysed European faience, suggesting a rather different formulation from those used in Egypt and the Near East. The large Al content in the amorphous phase and mineralogical studies (when available) suggest the use of sand as the source of silica. Generally, the beads are copper-blue coloured. The analyses of minor and trace elements suggest the existence of many different production centres in Europe, but to date no hard archaeological evidence has been discovered.

The diffusion of faience throughout Europe decreased later, and virtually stopped at the end of the Early Bronze Age. A small group of ornaments in glassy faience that are considered a local production dated to the early phases of the Middle Bronze Age 1–2 (~1700/1650–1450 BC) have been found in northern and central Italy. They are characterized by the 'typical' European low magnesia/high potash (LMHK) composition (Table 2) produced using mixed alkali as flux. These glassy faience items are mainly conical buttons (Fig. 7c), a typology known only in the area (Angelini *et al.*, 2005; Bellintani *et al.*, 2006a,b). Both chemical and typological variations within this class of materials, and other glassy faience spread in the same area suggest that possibly two different production centres were active (Angelini, 2014).

Egyptian blue is another type of vitreous material sometimes confused with faience or glassy faience. Egyptian blue is a synthetic pigment composed mainly of cuprorivaite ($CaCuSi_4O_{10}$) that is responsible for the typical blue colour. The cuprorivaite crystals are invariably associated with unreacted or partially transformed quartz, cristobalite, wollastonite and an alkali-rich glass phase depending on the

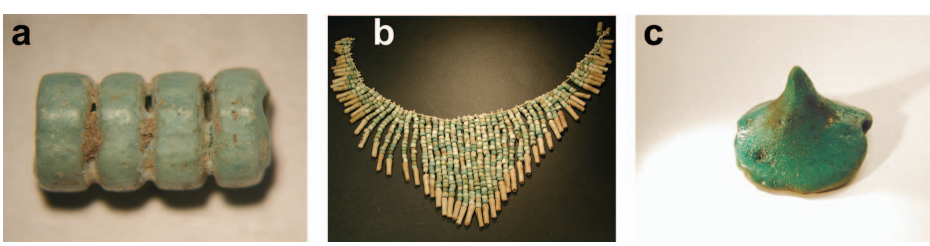


Figure. 7. (a) Segmented faience beads from the pile dwelling of Lavagnone (northern Italy), dated to the Early Bronze Age IA–IC (2100–1800 BC); (b) a faience collar from the cemetery of Nižná Myšl'a, Slovakia (about 1800–1600 BC); (c) glassy faience conical button from Mercurago, Middle Bronze Age 1–2 (~1700/1650–1450 BC).

production process. To obtain Egyptian blue, ground quartz, lime, copper compounds and small quantities of alkali were mixed and fired at a temperature in the range 850–1000ºC (Tite *et al.*, 2008g). The dimensions of the crystals and the amount of the amorphous phase seem to be related to the different blue hues of the pigments (Tite *et al.*, 1984, 2008g; Henderson, 2013b).

Egyptian green (or green frit) is a pigment similar to Egyptian blue. It is synthetized using the same raw materials, although mixed in different proportions and fired under different condition with respect to the production of Egyptian blue. In particular, lime must exceed the Cu content in the production of Egyptian green, which is composed of large amounts of wollastonite and Cu-coloured glass, with residues of unreacted quartz (Tite *et al.*, 2008g).

Both Egyptian green and Egyptian blue were used mainly as pigments; however, Egyptian blue was also used in massive form in the production of small objects (Fig. 8). Egyptian blue was first produced in the early 3rd millennium BC in the Near East and in Egypt. The most ancient evidence of Egyptian blue in Egypt is from the painting of a tomb of the 1st Dynasty in Saqqara (~2900 BC), but its use became widespread only with the 4th Dynasty (2570–2450 BC). Egyptian green was used mainly in Egypt and had a very limited diffusion outside. The beginning of the use of Egyptian green is debated in the literature and spans from the First Intermediate Period to 18th Dynasty depending on the author (Tite *et al.*, 2008g). In the Near East, small beads from the Ur cemetery dated to the Early Dynastic III (~2600–2305 BC) are the oldest witnesses of

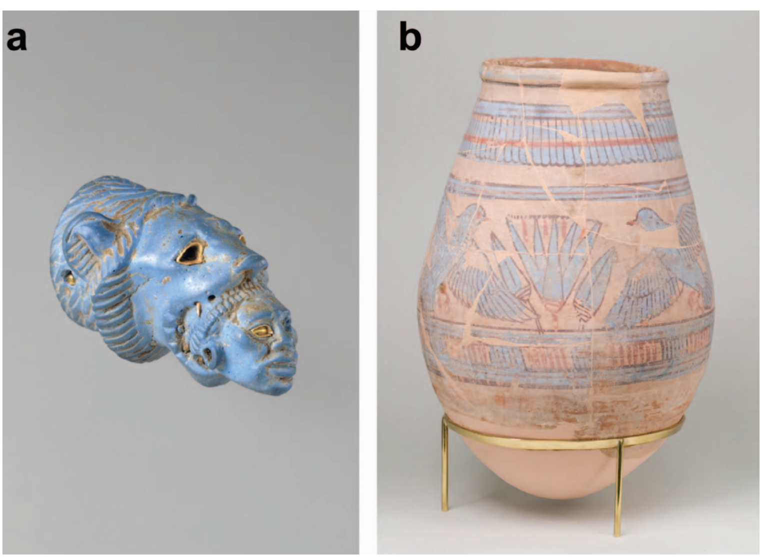


Figure 8. (a) Handle depicting a lion subduing a Nubian head, dated to the 19th Dynasty, reign of Ramesses II (*ca*. 1279–1213 BC). Egyptian blue, said to be from Eastern Delta, Qantir (Piramesse), Egypt; (b) jar painted with Egyptian blue from Malqata, New Kingdom, 18th Dynasty, reign of Amenhotep III (*ca*. 1390–1353 BC). [Images from the MET website].

the use of Egyptian blue. In the Near East therefore Egyptian blue was at the beginning employed for the production of objects and only later on as a pigment. Small ornaments in Egyptian blue are present in numerous sites around the middle of the 2nd millennium BC, such as Ugarit (Syria) and Nuzi and Tell Brak (Iran). The use of Egyptian blue for the production of small items continued in Niniveh and Nimrud at the beginning of the 1st millennium BC, and throughout the Achaemenid period (540−330 BC) in Iraq and Iran (Moorey, 1994; Tite *et al.*, 2008g). By the 2nd millennium BC the use of Egyptian blue spread in the Mediterranean area: small ornaments were found in Knossos (19th century BC) and in Middle Minoan–Late Minoan tombs in Crete (~1700−1200 BC). In Mycenaean Greece, Egyptian blue appeared only later, around 1400−1200 BC, but examples of Egyptian blue in wall paintings are known in Crete and in mainland Greece (Tite *et al.*, 2008g). Egyptian blue is of course well known in the Roman world, where it was traded as small balls and largely used as pigment. It was used extensively in the Pompeii frescos, where lumps of this pigment were found in a villa that was under restoration at the time of the Vesuvian eruption (Varone and Beart, 1996). Production centres of Egyptian blue are known in Egypt and were discussed before (see also Table 3).

The most ancient known glasses from the Near East and Syria are dated to the middle of the 3rd millennium BC, or later (Moorey, 1994). Based on linguistic analyses of cuneiform texts reporting instruction for glass production and the colouring process, Oppenheim (1970) suggested that glass was invented in northern Syria. In the Near East, some of the very early finds are: a pale-yellow bead dated to the early 3rd millennium BC from Tell Judeideh (Syria); a glass head pin from Nuzi (Iraq), ~2350−2150 BC; a chipped glass rod from Tell Asmar, pale blue-green in colour and dated to the 23rd century BC; a block of blue glass found in Eridu (Iraq) and dated approximately to 2300 BC. The analyses of the sample from Eridu show that the glass is coloured by Co and produced with plant ash flux and sand (Garner, 1956; Henderson, 2013b). After this early start glass production remained more or less inactive for ~1000 years, and the really important development in the production of glass started, both in the Near East and in Egypt, around 1500 BC. In the Mesopotamian area, new techniques of glass working were implemented, *e.g.* at the end of the 16th−15th century BC glass vessels were first made. Glass vessels have been found in the Near East in: Tell Brak (Syria), Chagar Bazar (Syria), where a polychrome vase of the 15th−14th century BC and a mosaic vessel of the 1350−1000 BC were found; Ashur and Niniveh (Assiria); Alalakh (Turkey); Nuzi, Assur, Tell el-Rimah (Mesopotamia, Iraq). Mosaic vessels were probably invented by Mesopotamian glass workers because they have a peculiar design typical of this area and age (~15th−13th century BC). Mosaic vessels are known from: Rimah, Aqar Qüf (Mesopotamia) and Marlik (Iran; Henderson, 2013b), although vessels are not the only glass objects found in these sites. Considering the presence of raw glass and other evidence that may be related to glass production, several sites need to be highlighted:

(1) Tell Brak (north Mesopotamia, Syria): glass vessels, mosaic glass vessels, polychrome beads, core-moulded glass bottles, ingots and fragments of

ingots mainly of pale blue glass. The finds are dated between the 15th century (vessels and beads) and the 14th century BC (ingots) (Oates *et al*., 1997; Henderson, 2013b).

(2) Alalakh, Tell Atchana (Turkey): decorated plaques and vessels dated from the late 16th to the 13th century BC. The vessels include bottles, bowls and goblets, generally blue with white, opaque yellow and brown translucent decoration. Three pieces of raw glass, dated to the 15th century BC are also present (Barag, 1970; Henderson, 2013b). Two ingots are red glass coloured by cuprite crystals and covered with a green layer of weathered glass (Bimson and Freestone, 1985; Barag, 1985). In recent excavations numerous glass, faience objects, possible remains of crucibles and a kiln were discovered, proving the production activity at the site (Dardeniz, 2018). The workshop area is dated to Late Bronze Age I (~1500−1450 BC) - Late Bronze Age II (~1400−1300/1200 BC). Chemical and isotopic investigations show that the glass objects were made using plant ash glass, with a peculiar chemical fingerprint. Two objects were used for isotopic analysis; the results are different: the blue glass data plot in the isotopic field together with those from Tell Brak (Degryse *et al*., 2010; Henderson *et al.*, 2010) and may be a signal characteristic of the Alalakh glass; the amber glass is close to a small group of glasses from Nuzi (Degryse *et al.*, 2010). As suggested also by Dardeniz (2018), more data are necessary for a better understanding of glass production and trade in the area.

(3) Assur (Iraq): many vessels were found at the site during old excavations, but the majority are still unpublished (Henderson, 2013b). Considering the typology of the vessels the context may be dated to the 15th−14th centuries BC (Barag, 1970) or to the 13th century BC (Moorey, 1994), depending on the author. A cullet of probable raw glass is also present. Particularly significant is the presence of numerous mosaic glasses. Due to the type of items discovered and to their large number, a local glass workshop or even a larger glass production has been suggested (Moorey, 1994).

(4) Ugarit, Ras Shamra (Syria): from the excavations of the site ~20,000 objects were discovered, mainly faience and glass, but also Egyptian blue and glazed pottery. A large variety of vessels, beads, pendants and other items was unearthed. Moreover, the presence of raw glass and ingots suggests that a production or working centre is present at the site (Matoïan, 2000; Henderson, 2013b). The site is dated to the 14th−12th centuries BC.

(5) Tell el-Rimah (Iraq): the excavations discovered a large quantity of vessels (also made of mosaic glass) that may be stratigraphically dated to 1350−1250 BC. Frit and faience manufactures were also found (Oates, 1968; Henderson, 2013b).

(6) Tell Ashar-Terqa (Iraq): at the site a large ingot of blue colour was found, ~5 kg in weight (Matoïan and Bouquillon, 2000; Henderson, 2013b).

(7) Nuzi (Iraq): an incredible quantity of glass was found in the site: beads, amulets, moulded objects, vessels, plaques and also chunks and chips of raw glass. The materials may be dated to ~1450–1350 BC (Barag, 1970; Henderson, 2013b).

Other sites (*e.g*. Ur and Nippur, Iraq and Tchoga Zanbil, Iran) have been suggested to have glass working centres, but with very little archaeological evidence. Other than at Alalakh, no remains of kilns have been found at these sites, so even if in some cases the glass working activity is confirmed, no archaeological evidence of glass production has been found. Glass has been found commonly at numerous Syrian-Palestinian sites and among them there are also Mesopotamian glass objects (Henderson, 2013b).

Another invention of Mesopotamian glass production is the core-forming vessel, that is the making of vessels by winding molten glass around a sand core supported by a rod. After forming, the object is removed from the rod and annealed. After annealing, the core is removed by scraping. The most ancient products of this kind were found in the late 16th–15th centuries BC and are soda-lime-silica glass fluxed with plant ash (Henderson *et al*., 2010).

Chemical investigations of Near East glasses are available for several sites, the main set of data is related to: Nuzi, Tell Brak, Alalak, Nippur (Brill, 1999; Shortland and Eremin, 2006; Shortland *et al*., 2007b; Henderson *et al*., 2010; Degryse *et al*., 2010; Walton *et al*., 2012; Dardeniz, 2018). Brill (1999) also performed chemical analyses of the major and minor element contents of glass dated to Bronze Age and Iron Age from: Tell Al-Rimah, Tchoga Zanbil, Nimrud, Hasanlu, Marlik and Persepolis. The general composition of the glass from all these sites is similar, all the glasses are prepared using plant ash. The variation in minor elements and trace elements helps in the identification of similarities and differences. It is important to note that coeval Egyptian (Fig. 9) and Greek glass were also produced using plant ash, and the general composition is similar.

Chemical analyses of Egyptian glass are available for numerous samples from Amarna, Malkata, Lisht and Qantir (Rehren, 1997; Shortland, 2000; Mass *et al*., 2002;

Figure 9. (a) Bowl in transparent blue glass from Egypt, New Kingdom, 19th–20th Dynasty (*ca*. 1295–1070 BC); (b) opaque glass bottles in the form of pomegranates, Egypt, New Kingdom, 19th–20th Dynasty (*ca*. 1295–1070 BC). [Images from the MET website].

Rehren and Pusch, 2005; Pusch and Rehren, 2007; Shortland and Eremin, 2006; Shortland *et al.*, 2007b; Jackson and Nicholson, 2007; Henderson *et al.*, 2010; Degryse *et al.*, 2010; Smirniou and Rehren, 2011, 2013). The production of glass in Quantir (Rehren and Pusch, 2005; Pusch and Rehren, 2007), Amarna (Smirniou and Rehren, 2011; Shortland and Eremin, 2006; Shortland *et al.* 2007b) and Lisht (Smirniou *et al.*, 2018) has been discussed and supported by in depth analysis of major-, minor- and trace-element contents. It is generally accepted that these sites are not simply workshops, but also important glass production centres. On a similar basis, it has been demonstrated recently that trace elements are able to distinguish Egyptian glass from Mesopotamian, mainly by the variations of Ti, Cr, Zr and La (Shortland *et al.*, 2007b; Walton *et al.*, 2012; Smirniou and Rehren, 2013; Dardeniz, 2018; Smirniou *et al.*, 2018). Also the colouring agents have been studied in detail, as for example the Co source in the blue coloured glass from Nippur is clearly different from the one used in the Egyptian Co-coloured glass (Walton *et al.*, 2012).

The early glass in Egypt appeared during the reign of Thutmose III (1479–1425 BC) (Lilyquist and Brill, 1993). The origin of the invention of glass is not certain, even if the presence of early glass in Mesopotamia, as discussed above, suggests that it originated in that area, or in northern Syria as proposed by Oppenheim (1970). Thutmose probably imported glass into Egypt for the first time at the beginning of his reign (Shortland, 2009). The identification of early glass production or working sites in Egypt is difficult. Confirmed glass working sites have been identified in Malqata, Amarna, Lisht and Quantir (Table 3), but recently primary glass production has been proposed for Amarna, Qatir and Lish (see above). In order to confirm whether glass production in Egypt and Mesopotamia was different, isotopic analyses were performed on samples from Tel Brak and Nuzi (Mesopotamia) and from Amarna and Malkata (Egypt) (Degryse *et al.*, 2010; Henderson *et al.*, 2010). The results show that the Egyptian glasses have a signal which is clearly different form those of the Near Eastern materials. The use of diverse raw material is responsible for this difference. Moreover the Mesopotamian data seem to group in three classes, suggesting the existence of several production centres. Based on trace-element analysis, a recent study demonstrated that two coloured rods from Amarna are actually made with Mesopotamian glass (Varberg *et al.*, 2016). Notably, these data seem to prove for the first time that even in an important Egyptian production centre such as Amarna, glass derived from trade with distant countries may be present and worked together with local products.

Glass was introduced in the Aegean during the 15th century BC and may be found both in Minoan Crete and in Mycenaean territories. Around 1450 BC the Mycenaean products dominate over those from Minoan Crete and their vitreous material products spread in the Aegean Sea and in mainland Greece. Both faience and glass are used, often associated with gold. Even if glass vessels are known, the vitreous materials were mainly used for jewellery. Blue glass is used to create beads and pendants with peculiar typologies. Decorated relief beads (Fig. 10) are crafted by moulding the glass and sometimes covering the bead with gold foil. During the three centuries of life of the Mycenaean culture, beads and plaques continued to be manufactured, not only in glass

Figure 10. (a) Ornamental moulded plaques in blue glass, Late Helladic III (*ca*. 1370–1200 BC); (b) ivy-leaf-shaped ornament made with moulded glass. Late Helladic III (*ca*. 1370–1200 BC). [Images from the MET website].

and faience, but also in Egyptian blue and cobalt blue glassy faience (Panagiotaki *et al*., 2004; Tite *et al*., 2005). Due to the specific typologies of the items, the existence of local glass working centres is clear. But the possibility of the presence of local glass production has been debated in the literature for a long time, especially after the discovery of the Uluburun shipwreck. The shipwreck is located off the coast of Turkey (near Kas) and in its cargo incredible quantities of metal and glass were found, both as ingots and objects. Among the glass there were 175 ingots of different colours (mainly blue) and a Canaanite jar full of beads (Pulak, 1998). The early analyses performed on the glass ingots from Uluburun show a similarity with some Egyptian and generally also with other Mycenaean and Mesopotamian glasses (Brill, 1999). The final answer to the origin of the Uluburun glasses comes from recent works that analyse major and trace elements of the ingots (Jackson and Nicholson, 2010; Smirniou and Rehren, 2013). Comparison of Egyptian and Mesopotamian data has proved clearly the Egyptian origin of both Cu-coloured and Co-coloured glass. In a similar way Walton *et al.* (2009) analysed 11 Mycenaean beads (seven from unknown origin and four from Tiryns). The results show that six Co and Cu coloured beads are from Egypt, whereas the other five Cu-coloured ones are from Mesopotamia. In order to investigate the origin of the glass, isotopic analyses were also used. Henderson *et al.* (2010) proved the Egyptian origin of nine beads dated to the 13th and the 12th centuries BC from Tebe, Elateia and Atlanti-Spartia (Greece). Only one of the ornaments analysed originated from Mesopotamia: a bead from a cemetery in Athens with a “Nuzi” typology and dated to the 15th century BC (Henderson *et al*., 2010). The Egyptian origin has been identified also for 11 Co-coloured beads from the Mycenaean tholos tomb of Kazanaki in eastern Thessaly (Smirniou *et al*., 2012). Even though only a few Mycenaean glasses have been analysed to date , it is possible to draw a general picture: Cu-coloured glass seems to be imported both from Egypt and Mesopotamia, whereas the Co-coloured glass comes only from Egypt. The local production of glass in the Aegean and in Greece in the Bronze Age has still to be proven.

Early ‘true glass’ appears in south and central Italy in the Middle Bronze Age 1–2 (~1650–1450 BC) and are small beads obtained using plant ash as flux (HMG – high magnesia glass). They are mainly beads with simple typology (such as annular and globular beads) and arrive more or less at the same time as the arrival of glass in the Aegean and Greek world. It is not possible to say if the beads arrive by direct contact with the Egypt or the Levantine world or thanks to middle-men, such as Mycenaean or Aegean traders (Angelini *et al.*, 2005; Bellintani *et al.*, 2006b; Angelini, 2011; Artioli and Angelini, 2013). At the same age in northern Italy, particular LMHK glassy faience that is probably of local production is present (see above). In any case, it was only with the end of the Middle Bronze Age and the Recent Bronze Age (1450–1200 BC) that HMG glasses are became widespread throughout the whole Italian peninsula (Fig. 11a,b). They consist mainly of beads of blue glass, sometimes with white decoration and the general composition is comparable with all the coeval plant-ash glass from Egypt and Mesopotamia (Angelini *et al.*, 2005; Bellintani *et al.*, 2006b; Angelini, 2011; Artioli and Angelini, 2013). At the moment no trace-element analyses are available for these materials. The range of shape of the glass beads is now wider and many typologies are similar to those of Mycenaean and Levantine. Beside glass, glassy faience and some faience with typical Mycenaean, Egyptian and Levantine typologies are also present (Bellintani *et al.*, 2006b; Bellintani, 2011). The glassy faience of this age shows a variable composition: it has an amorphous phase with HMG glass, or a peculiar composition with low K, Ca and Mg, and some show a chemistry very similar to Mycenaean coeval glassy faience (Angelini *et al.*, 2005; Tite *et al.*, 2005). So, considering both the shape and composition, the glassy faience seems to prove contact with the Mycenaean world.

During the Bronze Age in central and northern Europe a large number of glass beads made with plant ash as flux (HMG glass) have been identified. As far as we know from archaeometric analyses, they are spread throughout France (Guilaine *et al.*, 1991; Gratuze *et al.*, 1998, 2013; Plouin *et a*l., 2012), in Denmark (Varberg *et al.*, 2015, 2016); Poland (Purowski *et al.*, 2014, 2018), Germany (Hartmann *et al.*, 1997; Varberg *et al.*, 2016; Mildner *et al.*, 2010, 2014, 2018) and Romania (Varberg *et al.*, 2015). The majority of the HMG glasses are dated between the 14th and the 13th century BC, but their appearance and disappearance seem to vary within the various regions. In Italy they are present only until the end of the 13th century BC, then are substituted completely by the LMHK glass (mixed alkali glass), a typical recipe of Final Bronze Age Europe (Bellintani *et al.*, 2006b; Angelini, 2011; Artioli and Angelini, 2013). Considering the analysed beads, Bronze Age HMG glass is reported from Denmark in1400–1100 BC (Varberg *et al.*, 2015, 2016), in Romania in the 14th–12th century BC (Varberg *et al.*, 2016), in Germany in 1500–1050 BC (Mildner *et al.*, 2014). In Poland early HMG beads are reported in the BzB (roughly 1600–1500 BC), but the majority are present in the BzC-HaA1 (~1500–1025 BC) (Purowski *et al.*, 2018). In France HMG glass is described from Ancient Bronze Age/Middle Bronze Age to the Bronze Final IIb-IIIa (~1600–1000 BC) (Guilaine *et al.*, 1991; Gratuze *et al.*, 1998; Plouin *et al.*, 2012), This seems to be the wider chronological range identified for this glass in a region.

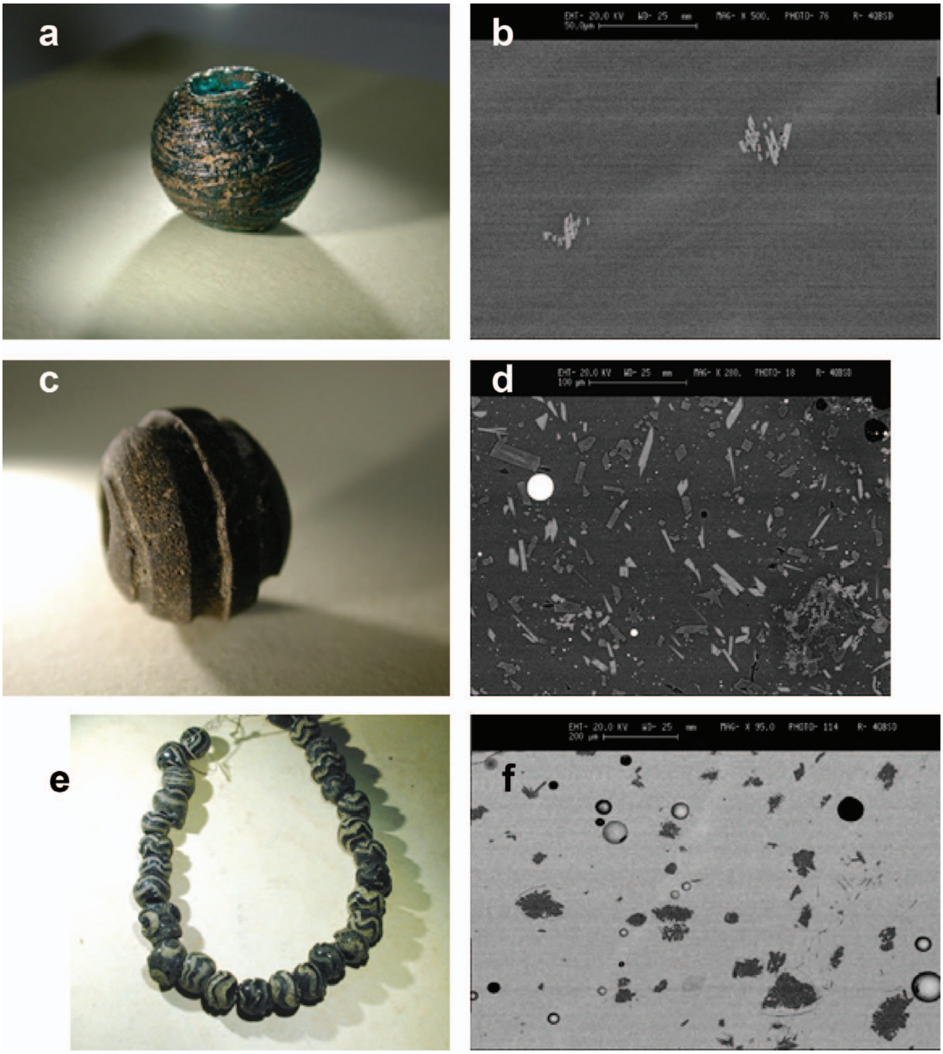


Figure 11. Examples of glass beads from Italy consisting of glass with the typical compositions present in the Middle and Final Bronze Age: (a) HMG blue bead dated to the 13^{th} century BC, Franzine (VR); (b) SEM-BSE image of an HMG glass with the typical homogenous texture. Here in white a few devitrification crystals of Na-Ca silicate; (c) HMBG brown glass bead: a composition present only in northern Italy (age and origin as in a); (d) SEM-BSE image of an HMBG glass with devitrification crystals of diopside (pale grey), zoned augite (dark grey) and Cu sulfides (white); (e) LMHK beads with Co-blue body and white decorations from Bismantova (RE) – Final Bronze Age; (f) typical texture of LMHK glass rich in SiO_2 inclusions that may be quartz, trydimite or cristobalite (see Section 5).

In order to define a clear picture of the early use of HMG in Europe, their diffusion *via* possible trade routes, and especially to understand when HMG was replaced by LMHK glass, it will be important in the future to link the analytical data with a more detailed archaeological characterization of the finds in all regions. From what we know at the present time, it seems that in central and northern Europe HMG glass was in use for a longer time than in Italy and that there is a coexistence of HMG and LMHK glass for a greater range of time than in southern Europe. In Italy HMG glass was rapidly replaced by LMHK glass at the beginning of the 12^{th} century BC. This was probably related to the existence in northeast Italy of working/production centres of LMHK, as discussed below.

Recently, trace element analysis has provided interesting new information about the possible origin of the European HMG glass. According to Varberg *et al.* (2015, 2016), the majority of the Danish, Romanian and German beads that they analysed are from Mesopotamia. Co-blue glasses have been identified both from Mesopotamia and in minor amounts from Egypt. Those authors also identified specific compositions that may be interpreted as a mix of Mesopotamian and Egyptian glasses. The HMG from Poland has been considered to originate in Mesopotamia too, except for one Co-coloured glass that is considered to be from Egypt (Purowski *et al.*, 2018). From these data, Mesopotamia seem to be the principal supplier of HMG glass to Europe, apart from the Co-coloured glass that may be somehow derived from Egypt. A different interpretation has been proposed by Mildner *et al*. (2010, 2014, 2018) both for their data and for the previously published data from Denmark. It has been noted that some samples from Germany have different Ti, Zr, La, Cr and Nd contents with respect to Egyptian and Mesopotamian glass. This group of glasses has a different and unknown origin. Many of the other glasses have contents of these elements that show a trend comparable with the Mesopotamian one, but with generally higher concentration of the elements. Also the quantities of P and B seem to differentiate the European HMG from the Near Eastern and Egyptian ones. Mildner *et al.* (2018) observed the presence of several HMG compositional groups, possibly associated with different production centres. Based on the analysis of later glass from Turkey, they suggested a probable location of some of these productions in Anatolia.

If raw imported glass was worked in Europe or if we take into account the possible recycling of the glass, it is clear that some elements may be derived from the interaction of the melt with the crucible and this may change the trace-element pattern of the original glass. Besides the Mycenaean contexts, the only known evidence of remains connected to the process of working HMG glass in Europe is from the Anzola *terramara* (northern Italy) and is dated to the 13^{th} century BC. It consists of a pottery tray with an encrustation of a layer of HMG glass that has been analysed recently (Cupit *et al*., 2018). Indirect evidence of possible glass production comes from a small group of brown beads spread throughout central and northern Italy (Fig. 11c,d). These beads are HMG glasses but with higher contents of Al, Fe and Ca than the blue ones. Moreover they are characterized by the presence of numerous spherical segregations of copper sulfides and devitrification crystals of diopside and augite. Similar types of beads with comparable chemical and textural features are unknown outside this area; therefore, up to now, they have been considered to have been produced somewhere in the area

(Angelini *et al.*, 2005; Angelini, 2011; Artioli and Angelini, 2013). Interestingly, such beads are also found in the beginning of the 12th century BC, a time when in Italy the production of another type of glass starts: the mixed alkali glass (LMHK, Fig. 11e,f).

In the Final Bronze Age, LMHK glass was widespread in Europe, used mainly for the productions of beads. Archaeometric investigation shows its presence in Italy (among other locations: Brill, 1992; Santopadre and Verità, 2000; Towle *et al.*, 2001; Angelini *et al.*, 2002, 2004, 2010; Conte *et al.*, 2019), France (Guilaine *et al.*, 1991; Gratuze *et al.* 1998, 2013; Gratuze and Billaud, 2014; Séguier *et al.*, 2010; Plouin *et al.*, 2012), Bohemia (Venclová *et al.*, 2011), Switzerland (Henderson, 1993; Angelini and Olmeda, 2018), Germany (Hartmann *et al.*, 1997; Lorenz, 2006; Mildner *et al.*, 2014, 2018), Poland (Purowski *et al.*, 2018), Greece (Nikita and Henderson, 2006), Ireland (Henderson, 1988) and also England (Paynter, 2014). The typologies of the beads are similar throughout the whole of Europe: annular, globular or barrel-shaped blue body, sometimes decorated with white points, a spiral or eyes (Bellintani *et al.*, 2006b; Nikita and Henderson, 2006; Bellintani and Stefan, 2009; Venclová *et al.*, 2011; Gratuze and Billaud, 2014; Purowski *et al.*, 2018). The blue colour is obtained from Cu and/or Co and the Co is found with associated traces of Ni and As. All the researchers that have analysed LMHK glass agree that the source of Co is different from those used in the Egyptian or Mesopotamian glasses, but possible provenance is still unknown. Despite the large diffusion of LMHK glass there are only a few sites with evidence of working and possible production activities and all are located in northeastern Italy, in the Veneto region. Among these, Frattesina is the most investigated and best known site. Analyses of glass from Frattesina have been done by several researchers (Brill, 1992; Santopadre and Verità, 2000; Towle *et al.*, 2001; Angelini *et al.*, 2004, 2010; Henderson *et al.*, 2015). Less known are other sites where scraps of coloured glass and glass wastes have been found: Mariconda di Melara (Italy), Montagnana (Italy) and Fondo Paviani (Italy). Moreover, in Frattesina and Mariconda, fragments of crucibles or ceramic trays with a glass layer on the surface are present. Considering also the large amount of glass finds, the LMHK glass in Frattesina and Mariconda was probably produced and not just worked (Towle *et al.*, 2001; Bellintani *et al.*, 2006b; Bellintani 2011; Angelini *et al.*, 2004, 2010; Artioli and Angelini, 2013; Angelini, 2019). Actually, in these two settlements the bead typologies (Bellintani and Stefan, 2009) and the variety of glass colour are wider than in the rest of Europe. In particular beads with red surface or with red decorations that are not spread in the rest of Europe were found (only a few exceptions are known; Angelini and Olmeda, 2018; Angelini, 2019). In the glass from Frattesina different techniques seem to have been used in order to obtain the same colour, *e.g.* based on the chemical and mineralogical features two types of white and two types of red glass have been identified (Angelini *et al.*, 2004, 2010; Angelini, 2019).

Beside the LMHK glass, potash glass is present in small quantities in Frattesina and in other sites in Italy, but also in numerous sites in France, Germany, Bohemia and England (Towle *et al.*, 2001; Angelini *et al.*, 2004, 2010; Séguier *et al.*, 2010; Venclová *et al.*, 2011; Plouin *et al.*, 2012; Gratuze and Billaud, 2014; Mildner *et al.*, 2014, 2018; Conte *et al.*, 2019). The type of flux used in this glass is not known nor is their origin clear.

Isotopic analyses have been done on a few LMHK and one potash glass from Frattesina (Henderson *et al*., 2015). The two type of glass present diverse isotopic ratios suggesting the use of different sands in their production. Henderson *et al*. suggest that one source is compatible with local sand and the second one is possibly located in central Italy. Actually, there is no evidence of glass production in central Italy and the finds of LMHK glass in the area are scarce. As also noted by those authors, there are too few data for a definitive answer. The database of mineralogical, chemical and isotopic data of fluvial sand also needs to be improved for proper comparison with the archaeometric data.

2.2. Iron Age

Since the beginning of the Iron Age glass production was characterized by the change in the flux used: plant ash was replaced by a soda mineral source: natron. Natron is an evaporitic rock with variable composition, consisting mainly of: (1) sodium carbonate and bicarbonate essentially in the form of trona ($Na_2CO_3.NaHCO_3.2H_2O$) or natron ($Na_2CO_3.10H_2O$), and with lesser amounts of nahcolite ($NaHCO_3$) or thermonatrite ($Na_2CO_3{\cdot}H_2O$); (2) mixed Na carbonate and sulfate, *e.g*. burkeite ($Na_6CO_3.2SO_4$); (3) Na sulfate as thenardite (Na_2SO_4) and mirabilite ($Na_2SO_4{\cdot}10H_2O$); (4) and Na chloride, halite (NaCl). Potassium may also be present as a substitute for Na. The composition of natron may vary depending on the geographical origin, the season of collection, and the weather and changes in hydrography through time (Shortland 2004; Shortland *et al*., 2006, 2011). The best natron for the production of glass has to be rich in carbonate and bicarbonate and poor in chloride and sulfate. It is important therefore to know not only the origin of the natron (related to the composition), but also how the deposits were exploited. It has been suggested that some treatment of the "raw" natron was probably applied also in order to increase the carbonate content and reduce the sulfate content (Shortland *et al.*, 2011). Experimental and analytical work confirms the exploitation in antiquity of Wadi Natrum (northwest of Cairo) and al-Barnuj (Western Nile Delta), both in Egypt. These, and especially Wadi Natrum are considered the major sources of natron in pre-Roman times onwards (Shortland *et al*., 2006). The exploitation of Wadi Natrun in Roman times is testified by the remains of large glass-making factories located close to some lakes, established in the area before the 1st century BC (Nenna, 2003, 2007). Nevertheless other areas are reported in the historical literature as sources of natron (in particular in the *Natural History*, *book XXXI*, by Pliny the Elder): a salt lake near al-Jabbul (northern Syria); Lake Van in Armenia; and Lake Pikrolimni in Macedonia (Shortland, 2004; Shortland *et al*., 2006). These lakes are known to have been exploited in different historic times, but no reliable information is available for ancient times. Recent analyses of evaporite samples from Lake Pikrolimni (Macedonia) show its compatibility with its use in glass production (Dotsika *et al*., 2009). This has to be considered in the study of Hellenistic glass production.

Natron has been used in the production of vitreous material since the 4th millennium BC. In the Badarian Culture, blue glazed steatite was produced by a mixture of natron and Cu applied to the steatite body (Tite *et al*., 2008c). Then the use of natron in the vitreous production seems to have been ignored up to the beginning of the 1st millennium BC when natron glass appeared.

Natron glass is also known as LMG (Low Magnesium Glass) for its small Mg content compared to plant ash glass (Table 2). Compositionally, LMG shows high levels of Na, low K and trace of Cl and S, chemical characteristics derived from the use of natron. LMG glass is present in Egypt, Near East, Europe and generally in the entire Mediterranean area. In the Near East, especially in Mesopotamia, the traditional plant ash glass continued to be produced in the Iron Age (Shortland *et al.*, 2006; Henderson, 2013b).

The early known natron glass dates from the 10th–9th centuries BC, but it is only from 800 BC that it is systematically produced in large quantities. The most ancient confirmed date for LMG glass is a core-formed vessel from the tomb of Nesikhons, in Egypt dated to the 10th century BC (Schlick-Nolte and Werthmann, 2003). LMG Co-coloured glasses come from 8th–9th century BC Nimrud and prove the early use of natron in the Near East, even if plant ash glass is also present at the site (Reade *et al.*, 2005). Early natron glasses from Nimrud and Egypt show such a small amount of lime that their stability and durability are seriously compromised. Ca and Mg stabilize the glass structure (Section 1), but in the LMG glass the low Mg introduced with the flux needs to be balanced by higher Ca in order to prevent the weathering and 'dissolution' of glass. If the sand used does not have the proper quantity of shells and/or lime is not voluntarily added, the resulting glass may be easily degraded with time. As suggested by some authors (Sayre and Smith, 1961; Reade *et al.*, 2005; Shortland *et al.*, 2006) this may be the reason for the lack in the archaeological record of a large amount of glass in the early two centuries of the first millennium BC, both in Egypt and the Near East. The spread of LMG is rapid and LMG glass is known in Europe as early as the 9th century BC (see Section 5). From the 6th–5th centuries BC natron is "the flux used west of the Euphrates in the great majority of glass" (Shortland *et al.*, 2006). In the east natron did not displace totally plant ash and during the Iron Age HMG glass are still present in Mesopotamia, Iran and Central Asia. Whether the plant ash glass had such a long life in the east due to difficulty in the supply of natron in the area or because the glassmakers preferred to comply with the old and traditional glass-making recipes is a matter of debate (Shortland *et al.*, 2006).

From the 7th–6th centuries BC to Early Roman time the variety of beads, pendants, arming, moulded vessels, core-formed vases and bottles that circulate in the Mediterranean area, Egypt, Near East and Europe is extremely wide and also the variety of colour and shapes increased significantly with respect to the Bronze Age.

Among this large variety of glass objects the rod-formed head pendants (Fig. 12) merit mention because of how widespread they are and the significant aesthetic and technological values. The head pendants have a Phoenician style but are present largely in the Mediterranean world also in non-Phoenician sites. There is no archaeological evidence of the pendants' origin and the existence of Phoenician production is not confirmed. Beside Phoenicia, Rhodes and Carthage have also been suggested as production provenance. The Phoenicians play an important role in the spreading of

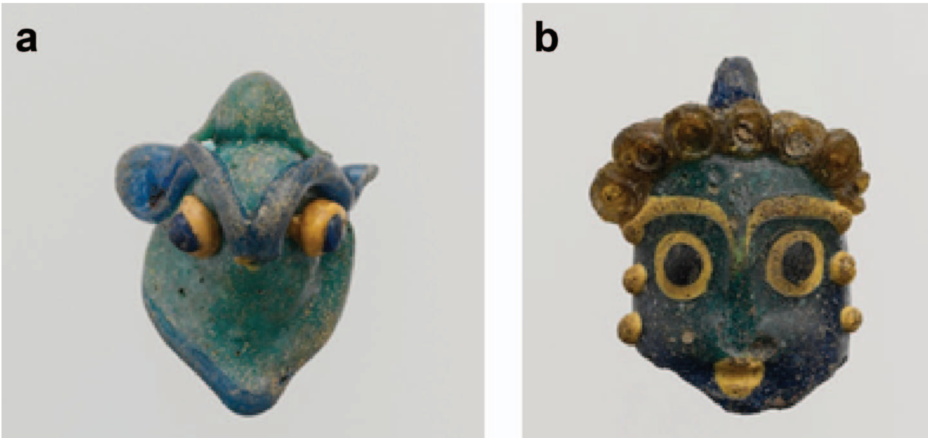


Figure 12. (a) Rod-formed glass pendant in the form of a demonic mask (type 1 in the text). Phoenician style dated to the 6th–5th century BC; (b) rod-formed glass pendant with an elaborate male face (type 4 in the text). Phoenician or Carthaginian, 5th century BC. [Images from the MET website].

glass throughout the Mediterranean (Spaer, 2001). The head pendants are known between the 7th/6th centuries BC to the 4th/3rd centuries BC but the different types have specific distribution zones and ages. The rod-formed head pendants are classified in four main group: (1) demon mask or grotesque; (2) double-faced cylindrical male heads; (3) single-faced cylindrical male heads; and (4) elaborate heads, male and female (Spaer, 2001). Only a few head pendants have been analysed to date: two are known from Mozia (Sicily) and are LMG glass with blue body coloured by traces of Co and large amounts of Fe (Arletti *et al*., 2012). The yellow decoration is composed of LMG-Pb antimonate glass. A systematic archaeometric study of these wonderful ornaments is still lacking.

The production of core-formed vases, known since the Bronze Age (Section 2) was revitalized between the 6th and the 1st century BC when small polychrome vases were one of the most widespread glass objects throughout the entire Mediterranean area. According to their shape and decorative style they are divided in three groups, labelled Mediterranean groups I, II and III. The studies of these classes of objects are numerous and according to some of the more quoted works (Barag, 1970; Harden 1981; McClelland, 1984; Grose, 1989; Stern and Schlick-Nolte, 1994; Triantafyllidis, 2003), the characteristics of the Mediterranean Groups may be summarized as follows:

(1) Group I (late 6th century–mid-4th century BC; Fig. 13a). This comprises four main types of vase: *aryballoi*, *oinochoai*, *alabastra* and *amphoriskoi*. It is the largest of the three groups and is characterized by homogeneous production. The body is generally dark blue, blue or opaque white and they are decorated by threads in yellow, turquoise, purple or white opaque glass.

(2) Group II (mid-4th–late 3rd centuries BC; Fig. 13b). The same type of vases present in Group I were also produced in Group II, with stylistic

Figure 13. (a) Core-formed vessel of the Mediterranean Group I; Greek, Eastern Mediterranean, late 6th–5th century BC. From left to right: an *aryballos*, an *alabastron*, an *amphoriskos* and one *oinochoe*. (b) Hellenistic core-formed *hydriske* belonging to the Mediterranean Group II, late 4th–3rd century BC. (c) Hellenistic core-formed *alabastron* of the Mediterranean Group III, 2nd –mid-1st century BC. [Images from the MET website].

differentiation. In Group II, new shapes were created, such as *hydriai*. These vases usually have, in general, a dark blue body with white and yellow decoration. Some authors note the existence of a chronological gap of about two generations between Group I and Group II (McClelland, 1984; Grose, 1989; Henderson, 2013b). The beginning of production of Group II is more or less coeval with the conquest of the Persian Empire by Alexander the Great.

(3) Group III (mid-2nd century BC–early 1st century AD; Fig. 13c). The types of vessel produced was reduced, *alabastra* and *amphoriskoi* being used mainly. The body is generally made with translucent blue or green glass, decorated with opaque yellow, white, blue and green threads.

Over the past ten years numerous chemical analyses of major, minor and trace elements have been done so that a good set of data is now available in the literature. The finds analysed are: Mediterranean Group I and II vases from: Italy (Arletti *et al*., 2011a, 2012; Panighello *et al*., 2012; Oikonomou *et al*., 2018); Rhodes, Greece (Triantafyllidis *et al*., 2012); mainland Greece (Blomme *et al*., 2017; Oikonomou, 2018) and Georgia (Shortland and Schroeder, 2009). The glass used for the body and decoration of the vases is always LMG glass produced using sand and natron. The range of colourants and opacifiers used is usually the same as used in the previous glass production tradition: Pb antimonate, Ca antimonate, Cu and Co minerals and Mn. Considering the results of the archaeometric studies, both major and trace elements seem to form different chemical groups that provide links between finds from different regions. The authors still debate the origin of the production, but generally it has been suggested that the Mediterranean Group I, II and III vessels may be produced in Rhodes, southern Italy and the Syro-Palestinian (or Syro-Cypriot) regions, respectively (Harden, 1981; McClelan, 1984; Grose, 1989; Oikonomou, 2018). Nevertheless, isotopic study performed on some Group I vessels from Pydna and Methoni (northwestern Greece) suggest an origin from the Syro-Palestinian coast, at least of the raw glass (Blomme *et al*., 2017). To date no confirmed evidence of primary or secondary production sites are known for these classes of objects.

Hellenistic glass production flourished between the 3rd and 1st centuries BC. The core-formed vessels of the Mediterranean Groups II and III are also considered to be Hellenistic productions. Besides the core-formed vessels, an incredible variety of moulded vessels was produced during the Hellenistic time using the slumping and casting techniques (Fig. 14). A variety of colours and decoration motifs was created, such as the mosaic vessels, gold sandwich glass, *millefiori* glass, lacework or network glass. Based on historical texts and archaeological evidence, production centres of Hellenistic vases are said to be present in Rhodes, Sidon (or generally on the Syro-Palestinian coast), Alexandria (Egypt), Tyre (Lebanon) and southern Italy (Henderson, 2013b). Once again, no confirmed archaeological data have been found to prove the origin of these Hellenistic vessels.

Chemical analyses of Hellenistic glasses prove that they are composed of natron glass with Sb used as decolourant (Henderson, 2013b, and literature quoted therein). Sb is employed to obtain colourless glass from the 7th century BC to the 1st century BC. Mn started to replace Sb as a decolourant from the 2nd century BC. A large set of Hellenistic mosaic vessel fragments from nine sites in France, Italy, Greece and from Tebtynis in Egypt have been analysed recently using LA-ICP-MS in order to investigate the composition of the glass and compare the materials from different sites. In their summary, the authors outlined some interesting preliminary results (Nenna and Gratuze, 2009). The majority of the glasses are LMG, but plant ash glasses are also present. In some cases, the composition seems to present a homogeneity within materials from the same site, such as the mosaic glass fragments from Delos. Generally, a correlation between the composition and the colour is observed: red and orange glass are mainly plant ash glass, and ~1/4 or1/3 of green and amber colour glass are also produced with plant ash. With a few exceptions, the other glasses are usually natron glass.

During the Hellenistic phase new capabilities in glass-working and colouring techniques were developed. This is evident in the production of mosaic glass and in the

Figure 14. (a) Glass-ribbed bowl cast, tooled and cut. Late Hellenistic, 1st century BC; Greek, Eastern Mediterranean; (b) glass mosaic jar cast and cut ('agate' glass). Hellenistic, 2nd–early 1st century BC; Greek, probably Eastern Mediterranean; (c) cast glass mosaic dish. Hellenistic, 2nd–mid-1st century BC; Greek, probably Eastern Mediterranean. [Images from the MET website].

creation of a large variety of inlays applied to wooden furniture and architectural elements (Fig. 15). In addition, the glass inlays are often made of mosaic glass. The glass inlays are also referred to as enamels by numerous authors. In a general sense 'enamel' is used for any type of glass applied on a body made with different materials, such as metals (as in Byzantine enamel), or wooden (as in the Egyptian furniture) or even plasters or stone. The inlay is glass, often opacified and coloured. Glass inlay appears in Egypt as early as the New Kingdom, but it is in the Ptolemaic and Early Roman time that their production is developed strongly. Secondary workshops related to the activities of temples are present along the whole Nile. In a recent study, new data from the inlay workshop of Tebtynis (Fayum, Egypt) have been obtained by a review of the literature, a study of the unpublished excavation reports and thanks to archaeometric analysis of ~130 glasses (Bettineschi, 2018; Bettineschi *et al.*, 2019a,b). In Egypt, secondary workshops are present: between the 5th and the 4th centuries BC in Ayn Manawir; in Ptolemaic and probably Early Roman time in Tebtynis, Gumaiyima, Tanis, Soknopaiou Nesos, Karnak and Dyonisias; after the 2nd century AD in Apollinopolis Magna; and in Late Antiquity (and some sites also in later time) in Alexandria, Akoris, Antinopolis and Hermothis (Bettineschi, 2018; Bettineschi *et al.*, 2019a). The site of Tebtynis is particularly interesting because during the excavation in 1931, besides the glass inlay and finished objects, raw glass, glass cans, ceramic moulds, small ceramic trays, weights, and bronze tools were also found in the workshop. Moreover, the presence of a furnace has been properly located thanks to the old excavation diary and satellite images of the sites (Bettineschi *et al.*, 2019b). Similar to what was observed by Nenna and Gratuze (2009) the glasses are both plant-ash and natron based. The red and the orange colours are mainly plant ash-lead

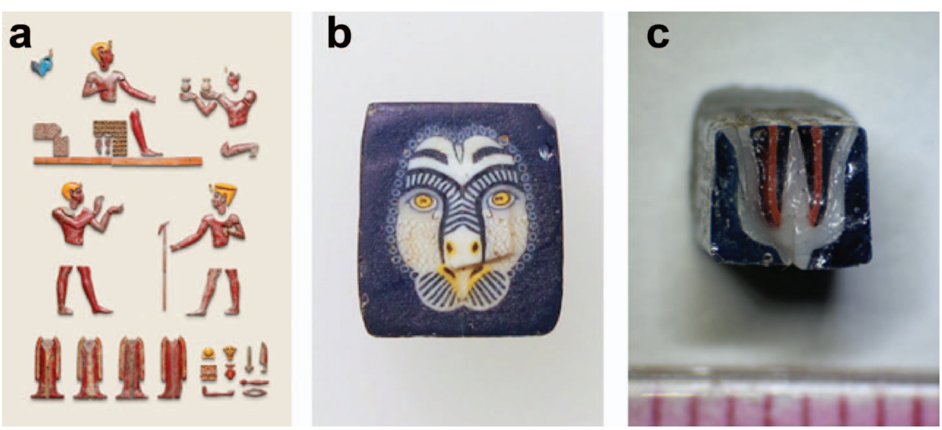


Figure 15. (a) Inlays and shrine elements from Egypt, Late Period–Ptolemaic Period, (~380–30 BC); (b) mosaic glass inlay probably Egyptian, Late Hellenistic or Early Imperial (~1st century BC–1st century AD); (c) 3D micro-photography of a small mosaic cane slice from Tebtynis with millimetric scale, Ptolemaic [(a) and (b) images from the Metropolitan Museum of Art website; (c): image courtesy of C. Bettineschi, object Museo Egizio, Torino, Tebtynis collection].

glass coloured by cuprite and/or Cu metallic segregation. HMG glasses are observed in some green glasses and in a few blue ones; however, they are generally natron glass. The colouring techniques used are a mix of the recipes related to the old glass-making traditions and the new knowledge and techniques that were to be used in Roman times. For example, yellow glasses are coloured both by the use of Pb antimonate or by the use of very small cuprite crystals (Bettineschi, 2018).

Glass production was revolutionized completely at the end of the 1st century BC when the Hellenistic phase faded and glass blowing was discovered.

2.3. Antiquity and Late Antiquity

At the end of the Iron Age, natron glass continued to prevail. As the volume of glass recovered, taken as indicative of the volume of glass produced, increased tremendously, large groups of glass with more homogeneous compositions were observed. The discovery of glass blowing in the 1st century BC is possibly linked to the rapid increase in glass production capacity (Israeli, 1991; Stern, 1999; Cummings, 2002). However, it is still possible to distinguish fairly distinct groups among the glasses named as Syro-Palestinian or Roman and a diachronic evolution of the composition is observed during Antiquity (Grose, 1979; Jackson-Tal, 2004; Henderson, 2013b).

A large number of secondary glass workshops have been unearthed in western Europe . Thanks to the excavation of different shipwrecks in the western Mediterranean Sea (Les Embiez, Cap Corse, Julia Felix; see for example: Fontaine and Foy, 2007; Silvestri *et al.*, 2008) and of several primary glass workshops in the Near East (Freestone *et al.*, 2000; Freestone, 2006; Rosenow and Rehren, 2014), the supply of these European secondary glass workshops is well documented. It has thus been shown that finished objects as well as raw glass and recycled glass wastes were exported from the Near-East towards western Europe (Baxter *et al.*, 2005; Freestone, 2015; Foy, 2018). From the Augustan Age to Late Antiquity, different groups of glass were identified and named according to the raw materials used or by the decolourizing recipes (Table 2). In addition to these well defined groups the presence of mixed glasses resulting from the recycling of the prevailing groups is also observed. The recycling and the mixing of the different glass groups are highlighted particularly by secondary glass workshop studies where analysis reveals the presence of pure glass groups but also of mixed glass (Foster and Jackson, 2009; Jackson and Paynter, 2016; Schibille *et al.*, 2017).

From a recipes point of view, starting from the Augustan period, blue-green un-decoloured glass, manganese decoloured glass and antimony decoloured glass are encountered (Foy *et al.*, 2004; Jackson, 2005; Gliozzo, 2017). In the same way, during the 4th century, antimony was replaced progressively by tin as the main opacifier for white and yellow opaque glass. Consider the raw materials used, and considering that sand is characterized mainly by the contents of alumina, lime, titanium and iron, the main recognized groups of glass are mainly: Syro-Palestinian, Levantine I and II, or Egyptian HIMT I and II (for high iron, magnesium and titanium) (Freestone *et al.*, 2000; 2005; Rosenow and Rehren, 2014). According to recent isotopic studies all these glass objects were produced in the Near East, from the Syrian coast to the Egyptian coast (Degryse and Shortland, 2009; Brems and Degryse, 2014). For that period other specific geographic groups of natron glass of less importance have also been recognized such as Egypt I and II, as well as the continuous presence of plant-ash glass in some Roman glass production. Analytical work carried out on Sasanian glass attests to the continuous production of plant-ash glass to the east of the Euphrates during that period (Mirti *et al.*, 2008; Rehren and Freestone, 2015).

At the end of Late Antiquity, an intensification of recycling is observed, resulting in increasing concentrations of copper, lead, tin and antimony in the glass composition. Some new groups of glass such as the high-boron high-alumina glass identified in Turkey at Pergamon also appear (Schibille, 2011; Swan *et al.*, 2018).

2.4. Early Middle Ages and later

Depending on the different regions, the production of natron glass in the Near East and its importation into Europe seems to break off progressively from the 9^{th} to the 11^{th} or 13^{th} centuries AD. In the Near East, glasses produced from soda coastal plant ash replace natron glass (Phelps *et al.*, 2016). In western Europe, the end of the first millennium was also a period of transition resulting in the emergence of a new glass production period: Near Eastern imported glass is partially replaced by new locally produced glass types, containing potash, lime or lead. Thus, in the Mediterranean world during the 9^{th} century a radical change is observed in glass production recipes resulting in the systematic use of plant ash instead of natron (Gratuze and Barrandon, 1990).

In the course of the 9^{th} century, in the eastern Mediterranean and Mesopotamia, soda lime glass, produced from the ashes of halophytic plants, became the prevailing type of glass. This recipe was adopted all around the Mediterranean and became predominant before the end of the 12^{th} century (Henderson, 2013b).

At the same period in western continental Europe, the development of the production of potash-lime glass using forest plant ashes was observed (Hartmann, 1994; Hartmann and Grünewald, 2010). The main fluxing agent is no longer soda but a mixture in variable proportions of potash, lime containing large amounts of magnesia, phosphorus and also manganese (Jackson and Smedley, 2004, 2008). However, although these types of glass became the prevailing types in continental Europe in the 10^{th} century, the supply to some glass workshops of natron glass seems to have persisted until the end of the 12^{th} century as is highlighted by some typical glass productions (Pactat *et al.*, 2017), *e.g.* cobalt blue stained glass or cobalt blue glass vessels such as the bowl of Saint-Savin (Simon-Hiernard and Gratuze, 2011).

The existence of another type of glass in which the calc-alkaline flux is partly or totally replaced by lead oxide must also be pointed out (Table 2). These types of glass start to develop from the 7^{th} century AD, in the eastern part of Europe (Wedepohl *et al.*, 1995), and form two main families:

(1) The lead glasses, strictly speaking, made only from lead and sand, characterized by a lead oxide content generally $\geqslant$60%, and the absence of alkaline elements.

(2) The lead-alkali glasses, made from a ternary mixture of lead oxide, sand and ash. Among them can be distinguished lead-sodium glass, lead-potassium glass and glass mixed lead-soda-potash.

Until the 12th century, lead glass seems to have been distributed mainly in eastern Europe (Poland, Russia) and in the Caucasus region. Within Fatimid glass, around the late 10th and early 11th centuries, an emerald green glass category is also made up of >60% lead (Henderson *et al.*, 2004; Henderson, 2013b). But it is not known whether there are links between the productions of the Christian and Muslim worlds.

2.5. Modern period

Between the 12th and 15th centuries, plant ash soda glass characterizes the Mediterranean coastal regions while forest plant ash glass is produced in continental Europe. Since the beginning of the Modern period, sodium plant ash glass, which characterizes the Venetian productions (*e.g.* Common Glass, Vitrum Blanchum and Cristallo) were then adopted gradually throughout Europe. Its use is well illustrated by the production and spread of façon-de-Venise glass vessels (Šmit *et al.*, 2004). However, several other different glass types were still in use or under development in Europe during the same period. If, until the Modern period, glass compositions were linked mostly to the geographical location of the glass workshops rather than to the types of production, a progressive specialization of glass compositions according to their uses is observed. Typical glass types of the period are the HLLA glass (for High Lime Low Alkali) used mainly for window panes (Schalm *et al.*, 2007; Dungworth, 2012; Kunicki-Goldfinger *et al.*, 2014); a high-alumina HLLA glass was used for bottle production from the 17th century (Dungworth, 2003; Dungworth *et al.*, 2006).

From the end of the 16th century many innovations were developed in the glass industry. The main ones were probably related to the development of lead glass known as crystal or flint glass and to the progressive use of coal fuel. But a lot of less well known innovations were developed such as the use of kelp ash or of basalt as ingredients in glass manufacturing and at the end of the eighteenth century the synthesis of artificial soda which replaced plant ashes.

2.6. Notes on Indian and Chinese glasses

This section provides a rapid overview of Indian Ocean glass compositions compared to those circulating in the Mediterranean world. Note that in contrast with the variety of glass finds recovered from Mediterranean archaeological sites, glass material recovered from early South Asian archaeological sites consist mainly of beads, bangles and other ornaments. Glass vessels are rare and often identified as imported. Based on pioneering work by Dussubieux (2001) and others, Lankton and Dussubieux (2006) proposed a basic scheme for the compositions, based on major and minor elements, of early glasses found in the maritime trade from India to southern China. Although high-alumina soda glasses seemed to be characteristic of Indian productions, many other different glass types were identified in south Asia and southeast Asia. More recent data can be found in Lankton and Dussubieux (2013) and Dussubieux and Gratuze (2013). Fuxi *et al.* (2009, 2016) provide novel data on Chinese materials. Among the most famous and peculiar are the typical lead-barium Chinese glasses (Table 2). Potash glasses are also found commonly at early southeastern Asian sites and it is possible to suggest that at least three types of potash glass, based on levels of lime and alumina were produced. Different types of mixed alkali glass have also been identified. More recently, the availability of high-quality trace element analyses using LA-ICPMS has led to the identification of at least five groups of Asian alumina soda glasses based on levels of uranium and cesium (Dussubieux *et al.*, 2010; Dussubieux and Gratuze, 2013). Using these trace elements, it is possible to distinguish between north Indian production (high uranium, high cesium) and south Indian production (moderate uranium, low cesium). For potash glass, the situation is less clear, although the ratio of rubidium to strontium does appear to help separate groups in the low-lime range. From a chronological point of view, a diachronic evolution model of the composition, beginning with potash glass and ending with alumina soda glass can be sketched. The recent discovery of glass ingots in the Godavaya shipwreck, dated between the 1st century BC and the 1st century AD, has provided physical evidence for the early exchange of raw glass in south Asia (Muthucumarana *et al.*, 2014). The analytical results show that the glass in the ingots belongs to the m-Na-Al1 type defined by Dussubieux (2001). Its trace element contents appear to share many chemical features with glasses found or produced on the Tamil coast of south India. These samples help open new doors to the study of glass exchange and production in these regions.

3. Glass-making transition at the beginning of the 1st millenium BC

The revolution in the glass-making recipes occurred at the beginning of the Iron Age: the introduction of natron as flux, as described previously. This change started in the 10th century BC and involved the whole Egyptian, European, Aegean, Levantine and Near Eastern world. The questions of how and when the introduction of natron occurred, and what type of glass compositions were present at the same time vary region by region, especially in the early Iron Age. General trends may be established, as discussed above (Section 2.2), but in some geographical areas the chemical composition and the shape typologies of the glass are so variable that many questions about the origins and the production of some glass recipes are still far from being understood. Europe is one area where variations in the glass composition in the early Iron Age are particularly complex. During the Final Bronze Age up to its end (beginning at or near the end of the 9th century BC depending on the zone) the glass had essentially LMHK composition. In Italy, the mixed alkali glasses disappear in the early Iron Age: only a few beads are known from the north (Golasecca Culture, Angelini *et al.*, 2011; and Villanovan Culture, Arletti *et al.*, 2011b) and only one in the south (Conte *et al.*, 2019). In Poland, LMHK glass are present from HaA2 to HaB2 (about end of the 12th–middle of the 9th century BC), but only a few are known from the HaB3 and none is dated to the HaC, so from the 8th century BC they ceased to exist (Purowski *et al.*, 2018). The early Iron Age LMHK beads are few in number and spread over a large geographical area, therefore they are more likely to be related to reuse of older materials than to local production. The only exception seems to be the 9th−7th centuries BC LMHK glass from Rathgall (Ireland) where a significant number of beads is present (Henderson, 1988).

In early Iron Age Europe, LMG is not the only class of glass that appeared with respect to the Final Bronze Age production; HMG glass also began to be present. Plant-ash glasses re-appear, because they are typical in Europe during the 14th−13th centuries BC (Section 2.1), but with a slightly different chemistry. In Poland HMG are present in the early and full Iron Age, in the HaC–beginning HaD (~8th–end of the 6th century BC), and the authors do not report significant differences from the oldest materials (Purowski *et al.*, 2014, 2018). The oldest HMG in Poland have been interpreted mainly as having a Mesopotamian origin and a few with an Egyptian origin. The few differences in the chemistry between the Polish HMG glass and the Egyptian and Mesopotamian ones are interpreted as variations introduced during the recycling or working process (Purowski *et al.*, 2018). On the contrary, the HMG from Germany dated to 800−750 BC show a composition different from the oldest German HMG, in particular the trace elements pattern suggests a different origin and also the possibility of local production (Mildner *et al.*, 2014). In Italy, HMG glasses were present throughout the 9th to 7th centuries BC in northern (Villanovian Culture, Polla *et al.*, 2011; Arletti *et al.*, 2011b) and in southern Italy (in the Campania and Calabria regions, Conte *et al.*, 2018, 2019). Some of these HMG glass are characterized by a lower K content with respect to the classical Near Eastern or Egyptian glass, so that a different production is possible.

Natron glass dated as early as the 9th−7th centuries BC is known from France (Gratuze, 2009) and Italy, both in the north and in the south of the peninsula (Polla *et al.*, 2011; Arletti *et al.*, 2011b; Conte *et al.*, 2018, 2019). During the early Iron Age in France and Italy, glasses with particular compositions are also present: (1) natron glass with Co, high Al and Mg; (2) natron black glass with very high Fe contents (FeO > 7 wt.%, generally around 10%) (Gratuze, 2009; Conte *et al.*, 2018, 2019). For the natron glass from Italy differences in the trace elements suggest the existence of diverse production centres, but there are no confirmed indications of the origin. Isotopic analysis of some natron black beads from Bologna (northern Italy) are compared by the authors with sand and sandstone from Egypt and a possible Egyptian origin of the beads is suggested (Conte *et al.*, 2018).

Other peculiar vitreous materials are known from northern Italy and central Europe. For example there are beads dated to the 7th−6th centuries BC and made in glassy faience rich in Pb present in the Golasecca Culture in northen Italy (Angelini *et al.*, 2011) and in Poland (Purowski *et al.*, 2014). These beads have a black or dark blue body and are decorated with circles of yellow glass, coloured with Pb antimonate. This bead typology is widespread in central Europe, northern Italy and the Balkans, so the production had to be located somewhere in this area (Angelini *et al.*, 2011; Purowski *et al.*, 2014).

During HaC and HaD (about the 8th century to the middle of the 5th century BC) in Poland natron glass, natron glass with Pb and glass with low Mg and K (named LMMK, Purowski *et al.*, 2012, 2014) were also present. The LMMK glassy faience shows a small Ca content and the type of flux used is unknown, possibly plant ash. Its unique composition is not reported from Egypt or the Near East so that a local production is probable (Purowski *et al.*, 2012, 2014).

From the 6th century BC up to early Roman time in the whole of Europe mainly natron glass is found, even if the composition may vary slightly depending on the region and age. 'Classical' natron glass is typical *e.g.* of second Iron Age Italy (Olmeda *et al.*, 2015; Arletti *et al.*, 2010), France (see a summary in Gratuze, 2009), and in northern and central Europe during the La Tène Culture. The Celtic glass production of beads and bangles is all natron-based and presents a high variety of colour and shape.

Considering the previous discussion it is clear that the study of the glass composition in Europe during the early part of the 1st millennium BC is an extremely complex topic. The open questions are still many and varied and the dataset available is limited, often restricted to some geographical areas, and needs to be improved.

4. Glass-making transition at the end of the 1st millenium AD

As discussed above, important changes were observed in western Europe concerning glass manufacture during the Carolingian period. While an increase in soda glass recycling was observed throughout the Merovingian period, a slow but constant increase of the potash content in the glass was observed from the end of the 8th century in continental Europe. Within the same period of time, a shift from natron glass towards soda plant-ash glass is also observed in Mediterranean Europe, while the sporadic presence of lead glass is encountered according to the different European and Near Eastern regions. In recent years, the increasing number of analyses carried out on glass materials dated to this transition period has highlighted the presence of a great variety of different compositions. This important variability seems to reflect the use by glassmakers of local raw materials which enabled them to face the decreasing availability of natron glass (both raw and recycled).

Three main examples will illustrate the different solutions developed by European glassmakers to face the lack of natron glass at the end of the 8th century in western Europe.

The first two originate from the studies carried out on two glass workshops, dated from the 9th–10th centuries and located in the northeast and in the west of France. The third one shows how glassmakers have recycled metallurgical glassy slag to make glass objects.

In 2008, an archaeological evaluation conducted in the municipality of Meru (Oise, between Paris and Beauvais) revealed the presence of a mediaeval site of ~3000 m^2 in area characterized by a glass workshop, which was probably abandoned after a fire and was not subsequently reoccupied. Despite the relative isolation of that site, far from large towns or important religious sites, it is located along a major thoroughfare and has all the necessary resources (wood, clay and water). Although the site has not been fully excavated, the evaluation enabled recovery of different elements which prove undoubtedly the presence of a glass workshop: vitreous slag and vitrified furnace walls, crucibles (with three complete ones), several glass production wastes and glass objects. According to the ceramics and to the glass vessels, the site can be reliably dated to the 9th century. The presence among the finds of a lead glass smoother (see below, the production of glass around Melle) corroborates this dating (Pactat *et al.*, 2015).

In order to understand which types of glass were worked and produced at Meru, 58 samples were analysed using LA-ICP-MS. They represent the whole variability of the finds associated with glass working (raw glass, cullet, glass working waste, glass drops, crucibles, glass vessels and glass panels). The presence on the site of Roman tesserae, glass beads, Roman and Merovingian glass vessels (such as bottles and mosaic glass bowl), indicates recycling activities. Only few tiny raw glass fragments have been unearthed on the site, therefore, the main raw material might have been glass cullet.

The analysis reveals the presence of two main glass compositional groups which correspond to two different glass recipes. They are mainly distinguished by their contents of soda (Na_2O), potash (K_2O), lime (CaO) and phosphorus oxide (P_2O_5). The first recipe is in continuity with Antique glassmaking traditions and is based on reused natron glass. It is, however, probable that during the 9th century, this way of working was not able to meet the demand for glass, therefore glass-workers had to adapt by developing new recipes using local raw materials to increase their production. The second recipe, which corresponds to a potash-lime glass containing fairly large amounts of soda, is based partly on the reuse of natron glass, but the glass has increasing contents of potash, magnesia and phosphorus. This particular feature could be interpreted either by the mixing of two different type of glass (natron and potash-lime), or by the addition of increasing amount of forest plant ash into the reused natron glass cullet. The ratio between silica and the fusing elements (Na+Mg+K+Ca+P+Cl) tends to decrease with the potash content for the potash-lime-soda glass (2.7 to 1.6, while the average value is 2.7 for natron glass). This second compositional group can be further divided into two sub-groups. In the first there is an inverse relationship between soda on the one hand and, potash magnesia and phophorus on the other: soda decreases from 14% to 5.5% while potash increases from 1.7% to 9%. This glass corresponds to a gradual transition between natron glass and forest plant-ash glass. The second sub-group has more stable contents of soda and potash (Na_2O 4.1% and K_2O 10.5%) and seems to characterize the forest plant-ash glass produced and worked in Meru. While all the raw glass and the glass cullet belong to the natron group, the other categories of objects (crucible, glass wastes and glass vessels) are represented in the two main groups and sub-groups.

Among the different glass vessels unearthed at Meru, one, a funnel beaker made with three different glasses (colourless, cobalt-blue and light-blue), is particularly interesting. The analyses reveal that the different parts of the beaker have different soda, potash, lime and magnesia contents (Fig. 16). The presence of that particular object and the repartition of the different types of objects (crucible, glass wastes and glass vessels) among the different compositional groups of glass show undoubtedly that the transition in glass making (from natron glass towards forest plant-ash glass) occurred at Meru. The important recycling of natron glass is shown by the presence of glass cullet and a block of raw glass with that composition. The discovery of a blown sleeve glass window shows that the production of stained glass was probably also one of the vocations of that workshop.

The archaeological site of Bois Beslan at La Milesse (Sarthe, 10 km northwest of Le Mans) was discovered and excavated by the National Institute for Preventive Archaeology in 2012–2013. It consists mainly of an iron metallurgical site (extraction and production) dated from Late Iron Age to Antiquity (Raux *et al*., 2015). A glass workshop implemented in the northeast part of the site, in the dumps of abandoned mining, has also been identified. In one of the pits excavated in that part of the site, archaeologists have recovered abundant elements characteristics of glass-working activity such as glass fragments of crucibles and processed glass waste. Seven crucibles, with the presence of glass or vitrified matter on their internal or external walls have been identified, and >20 kg of glass waste has been recovered. Half of the weight consists of waste originating from glass crafts (wires and rods of drawn glass, with round or flat sections, glass drops, small raw glass fragments and shapeless drips of various sizes), the other half being composed of scoriaceous glassy material.

According to radiocarbon analyses and to the typologies of the glassware and ceramic containers originating from the pit, the workshop can be dated from the 10th century AD. The most documented forms are goblets, with straight or returning edge, concave base and ovoid body. They are decorated with horizontal or spiral, threaded inserts. They are similar to several exemplaries dated from the 9th–10th centuries. All the glass samples have a deep green colour.

Fourteen samples, representative of the variability of the finds (crucibles, raw glass, glass waste and vessels) were analysed using LA-ICP-MS. The various samples form a homogeneous chemical group, characteristic of lime-potash glass, obtained from forest plant-ash glass. Compared with coeval lime-potash glass objects, the glass objects originating from La Milesse are characterized by larger amounts of alumina, iron, titanium and zirconium and smaller sodium concentrations. The chemical homogeneity

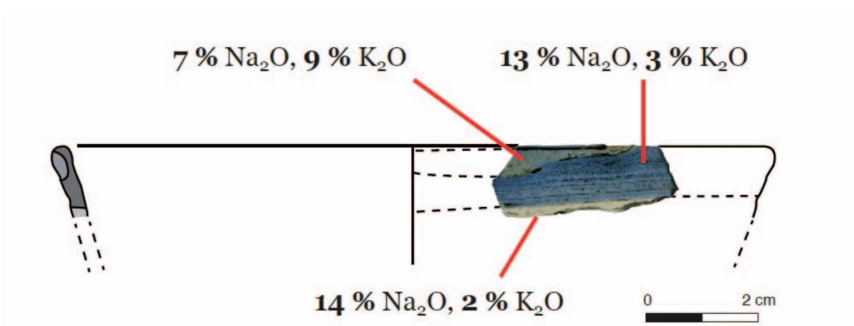


Figure 16. Soda/potash ratios measured in one funnel beaker edge from Meru. © MSHE, I. Pactat.

of this group of objects favours the presence of primary glass production on the site. The large iron content of these glasses shows that the glass-workers used the ferrous sand present at the site. From the small soda content of La Milesse's glass (0.54±0.10%), it can be concluded that the recycling of natron glass was not carried out by La Milesse's glass-workers, due either to the total lack of this sort of glass in that area or to its later production period than Meru's glass workshop.

In 1992, Julia Scapova published an uncommon composition for a 10th century linen glass smoother discovered in Novgorod (Russia) (Scapova, 1992). This object was made from a silica-lime-alumina-lead glass characterized by the presence of large amounts of iron, barium and antimony. Over the following decades, several linen glass smoothers of similar composition were described from Germany, France, England, Ireland and Norway and more recently Denmark and Belgium. All these objects, which are distributed along Viking trade routes, share the same type of composition and are dated between the end of the 8th century and the end of the 10th century. Until 2013, this composition seemed to be specific to the smoothers as no other analysed lead-glass objects of this period were found with a similar composition. At the end of the 1990s, based on chemical and lead isotope analyses, a study carried out on the Carolingian lead-silver mines of Melle (Deux-Sevres, west of France, 30 km south of Niort and 50 km southwest of Poitiers) allowed us to establish a relationship between the glassy slag produced on that mining site and the silica-lime-alumina-lead of all the linen glass smoothers originating from Europe. From 2012, thanks to the systematic analysis of the glass objects originating from different Carolingian archaeological sites located to the north and west of Melle (Bressuires, Fayes-sur-Ardin, Pussigny, Poitiers) it became possible to identify several glass vessels sharing this particular composition. Most of these objects are beakers made of strongly coloured green glass with an externally thickened rim and decorated by several rows of opaque white glass on the neck. The site of Faye-sur-Ardin also yielded many different glass fragments, with that composition. However, it was not possible to relate them to well established typologies (Gratuze *et al.*, 2014).

The analyses carried out on these different objects show that all of them were made by recycling the glassy slag produced during the metallurgical process leading to the production of silver from galena. The comparison between the composition of the glassy slag and the glass of the beakers and the linen smoothers reveals the following features: (1) soda glass cullet was added systematically to the melting batch; (2) soda glass cullet was added in a lesser extent for the production of linen smoothers (Na_2O 1.3±0.3%) and to a greater extent for the production of glass vessels (2.4±1.3%); and (3) the white glass was produced by adding tin oxide to the same base glass used to make the beaker, therefore the tin white opacified glass was produced directly in the glass workshop.

This workshop, which has not yet been discovered, is up to now known only by its products (glass smoothers and vessels), but we can hypothesize that it was located around the mining site of Melle.

This direct use of lead slag in glass production remains to this day without equivalent for that period. The valorization of metallurgical byproducts presents two main advantages for Melle's glass-workers. On one side, it allowed them to obtain a cheap raw material for dealing with the natron glass shortage encountered at that time in the whole of western Europe. Secondly, it allowed them to make a significant saving of combustible material. Glass making requires a significant amount of energy. The manufacture of potash glass, developed at that time in western Europe, needed a large amount of wood or other plants. These are necessary on the one hand as a raw material for the preparation of ash used as fusing agent, and secondly as a fuel to melt the mixture of sand and ash. The valorization of the slag significantly reduced the wood needs of the glass-workers, which are then limited to the re-melting of the slag and the natron glass cullet. The use of slag could thus be considered as the response of Melle's glass-workers to the two main challenges they faced: the lack of natron glass at the European scale and the fierce local competition for the exploitation of combustible materials due to mining and metallurgical activities on the site. These activities are also major consumers of wood (mining using fire-setting, roasting and reduction of ore; coin minting).

Thanks to the discovery at Meru of a glass linen smoother produced by the Melle glass-workshop, it can be hypothesized that these two glass workshops are coeval.

The adaptability of glass workers and their search for new recipes in order to continue to produce glass is also highlighted by the studies carried out on several typical Carolingian productions (bowls, beakers and vessels decorated with reticulated glass, and/or rows of opaque glass; Pactat *et al.*, 2017) and by the composition of two coeval glass objects, unearthed at Vernou-sur-Brenne (Indre-et-Loir, 15 km east of Tours, France), and dated from the 9th–10th centuries. These two pieces which were produced by an unknown glass workshop might, as in the case of Meru, represent a transition between natron soda lime glass and forest plant-ash glass. While the first is a soda lime glass containing a small amount of plant ash (3% K_2O and 1.4% MgO), the second is a lime potash glass containing a large amount of soda (5%). Based on the analytical data from Meru and other consumption sites, it seems there was a two-step process: at first, an increase in potash concentration, up to 3–4%, a change that is not correlated with an increase in magnesia, phosphorus and lime, which may be the consequence of pollution by wood's fly ash, and, secondly, a correlated increase in potash, magnesia, phosphorus and lime, which really indicates the introduction of forest plant ash.

This transition period seems to end between the end of the 12th century and the beginning of the 13th century. From that period, several glass production areas, characterized by well defined chemical compositions, can be identified in western Europe: plant-ash soda-lime glass on the Mediterranean coastal areas, potash-lime glass in northwestern Europe and high-lime glass in continental Europe.

The variations in chemical composition of glass through time are summarized in Fig. 17.

5. Techniques for the investigation of glass

Several analytical methods are used commonly for chemical analysis of ancient glass. A rapid survey of recent publications dealing with this subject (*e.g.* Barca *et al.*, 2009; Giussani *et al.*, 2009; van der Werf *et al.*, 2009; Walton *et al.*, 2009; Carmona *et al.*,

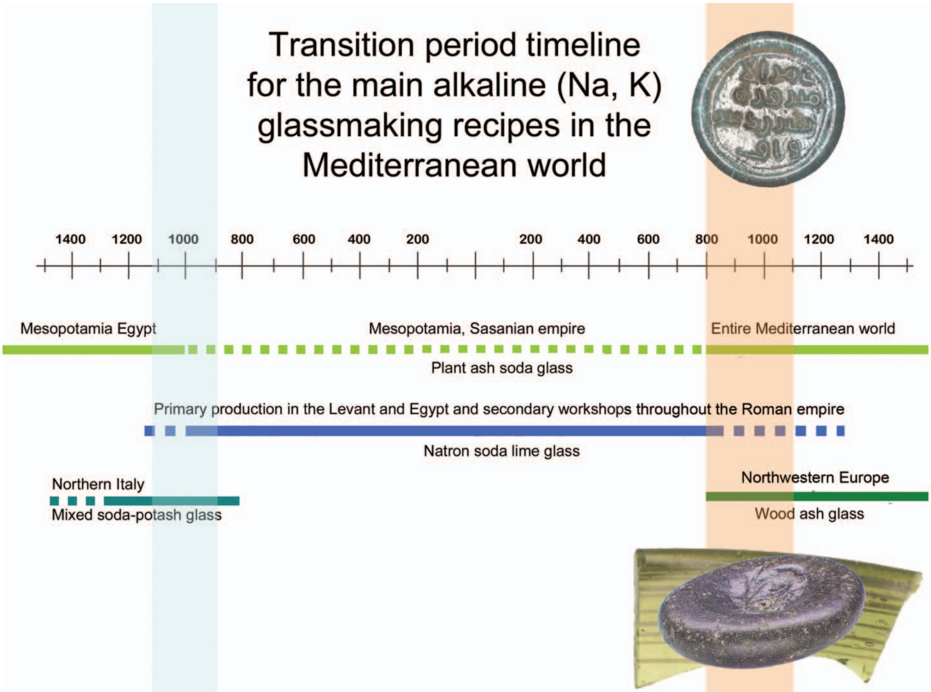


Figure 17. Timeline of the main glass-making recipes based on alkaline fluxes used in the Mediterranean and European world between the second half of the 2nd millennium BC and the first half of the 2nd millennium AD. Adapted from Wedepohl (1997). The recipes based on lead oxide fluxes are not illustrated.

2010a; Wedepohl *et al.*, 2011a,b) shows that the most common analytical methods are electron probe micro-analysis (EPMA) and scanning electron microscopy with energy or wavelength dispersive X-ray Spectroscopy (SEM-EDX or WDX). Then there are all the other methods, X-ray fluorescence spectroscopy (XRF), particle-induced X-ray emission (PIXE) which is often associated with particle-induced γ-ray emission (PIGE), ICP-MS (either in its liquid mode or in its laser mode, LA-ICP-MS) and to a lesser extent instrumental thermal neutron activation analysis (INAA) and laser induced breakdown spectroscopy (LIBS). Of course isotopic characterization towards glass provenancing, diffusion, and interpretation of glass technology needs measurements performed by mass spectrometry (Degryse *et al.*, 2009). Spectroscopic characterization of structural or chromophore elements in glass is performed commonly by X-ray absorption spectroscopy (XAS), either in extended fine-structure mode (EXAFS) or in near-edge mode (XANES) (see *e.g.* Quartieri *et al.*, 2002; Veiga and Figueiredo, 2008; Quartieri and Arletti, 2013). Such investigations are fundamental to understanding the colouring/decolouring mechanisms of the chromophore ions and the structural role (*i.e.* network forming or network modifier) of the chemical species in the glass.

The investigation of glass materials typically poses peculiar problems, related to the facility of weathering, and to the substantial heterogeneity of the glassy materials, which often contain crystalline components of various natures (Artioli *et al.*, 2008), as discussed above (Table 1). Figure 18 shows a representative example of the micro-structural complexity of ancient glass materials.

Mineralogical, crystallographic and textural analyses are therefore important to observe and decode the single crystalline components, and thus obtain information on production processes, recycling, phase transitions, physicochemical properties, and degradation. Bulk X-ray diffraction (XRD) or neutron diffraction (ND) allow detection and quantification of the crystalline components, though spatial information is lost, unless measurements are carried out with microbeams to map the distribution of the crystal phases, *e.g.* with synchrotron micro- or nano-X-ray beams or with electron diffraction (ED). XRD is of course mandatory when investigating *in situ* the mechanisms of crystallization of opacifiers in the glass matrix, simulating ancient production techniques (Lahlil *et al.*, 2008, 2010). Characterization performed by Raman microbeams, including point analyses or maps (Figs 19 and 20) may also be very important for identifying the nature of the crystalline phases present in the glass matrix and to extract mineralogical, chemical and crystallographic information such as crystal

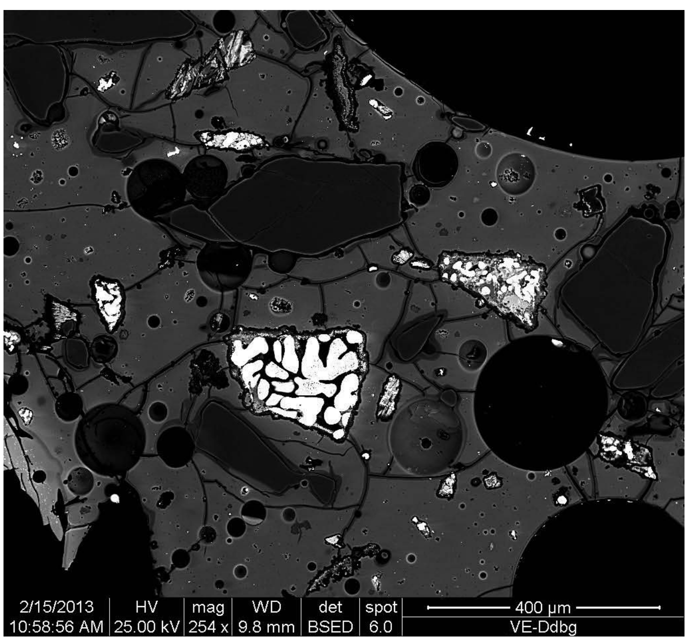


Figure 18. SEM backscattered electron image of a fragment of an Etruscan blue-green glass bead from Verucchio, Italy (Phase V, 7th century BC). The image clearly shows the complex micro-structure composed of small fragments of wüstite-rich slags from iron metallurgy (white), quartz fragments (dark grey) and gas bubbles embedded in the glass matrix. (Image I. Angelini).

morphology, chemical zoning, phase transformations, *etc*. (see *e.g.* Colomban, 2003; Ricciardi *et al.*, 2009). Of course multi-analytical characterization yields complementary information and therefore a more complete interpretation of complex materials (see *e.g*. Welter *et al.*, 2007).

Whenever complex multiphasic and heterogeneous materials are to be investigated, imaging techniques are mandatory to retrieve spatially resolved information. Optical microscopy (OM) operated in transmitted light, reflected light, or confocal modes is of course a primary tool for the visualization of the micro-structure (Fig. 21), though SEM imaging is also a very versatile and widespread tool (Fig. 18). Optical coherence tomography (OCT) has been used to analyse the interaction layer in faience materials (Kunicki-Goldfinger *et al.*, 2009; Liang *et al.* 2012), though the silica grains, the voids, and the permeation of the glass matrix in the interstices of the faience can be visualized efficiently by high-resolution computed X-ray tomography (CT) (Fig. 22).

Imaging methods reaching atomic or molecular resolution, such as high-resolution transmission electron microscopy (HRTEM) or atomic force microscopy (AFM) are seldom applied, though they may be important for decoding the fine features of the glassmaking processes. TEM techniques have been applied to investigate lustre, glazes and glass coloured by nanoparticles (Angelini *et al.*, 2004; Darque-Ceretti *et al.*, 2005;

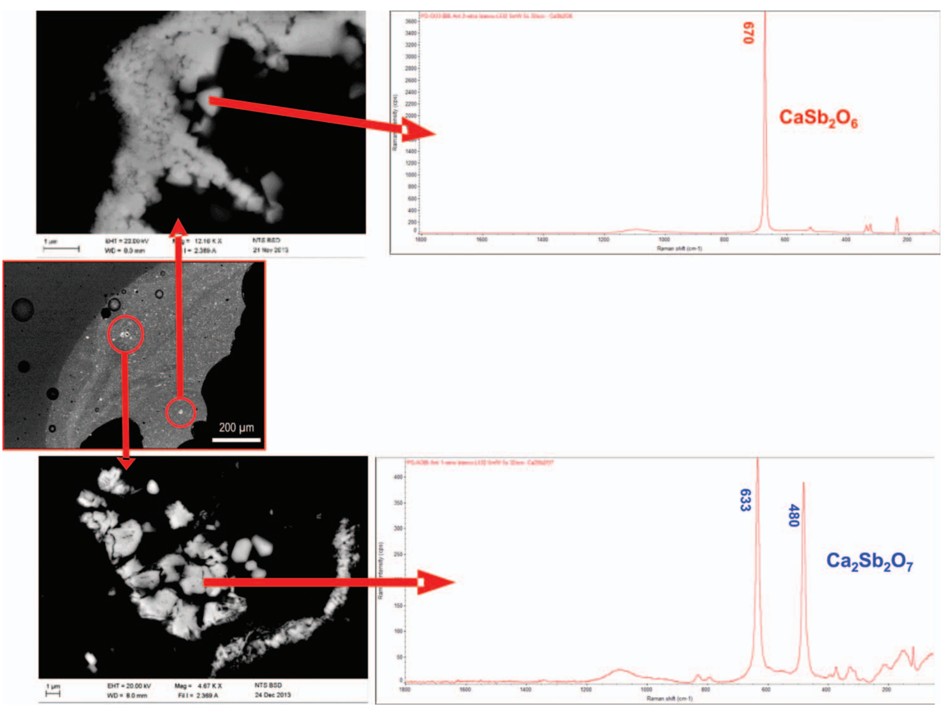


Figure 19. SEM backscattered electron images and Raman characterization of the Ca antimonate crystals present in the matrix of a white glass bead from Villa di Villa, Treviso, Italy (Iron Age). (Image and data: I. Angelini and G. Olmeda).

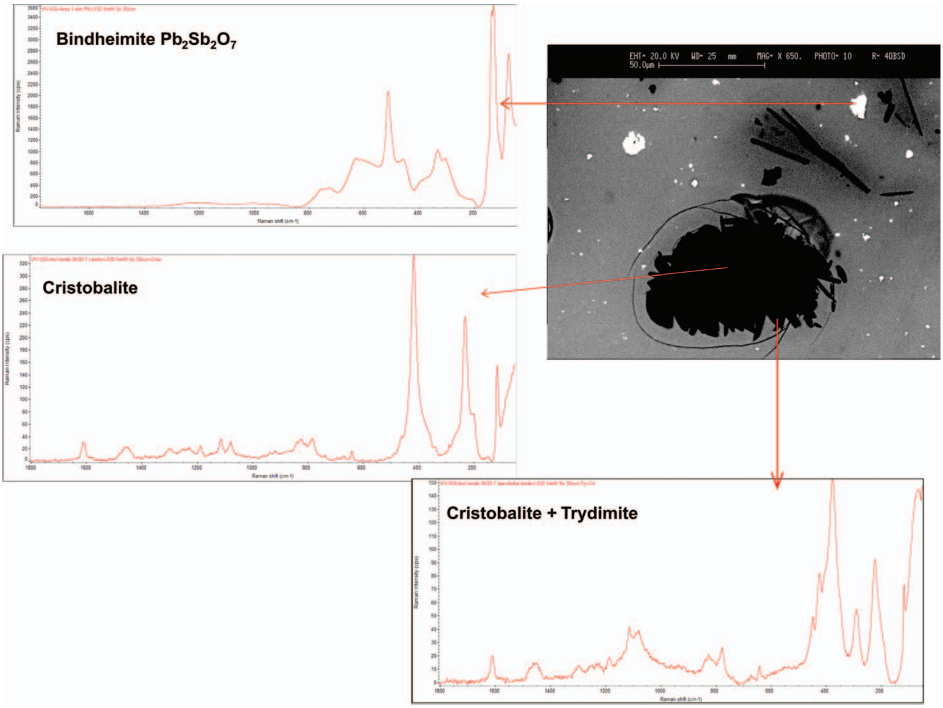


Figure 20. SEM backscattered electron image and Raman characterization of the crystals present in the matrix of a yellow glass eye-bead from Villa di Villa, Treviso, Italy (Iron Age). The white inclusions are Pb antimonate crystals accounting for the yellow colour of the bead, whereas the dark crystal clusters are composed of cristobalite and trydimite. The volume reduction during the phase transition in the silica cluster causes the circular fracture in the glass matrix. (Image and data: I. Angelini and G. Olmeda).

Roqué *et al.* 2006; Colomban, 2009). Recent developments of advanced crystallographic TEM analysis (by 3D electron diffraction tomography) open the possibility of identifying, characterizing, and even determining the crystal structure of nm-sized particles in the glass (Zacharias *et al.*, 2018). AFM microscopy has been used to understand surface alteration processes at the molecular level (Carmona *et al.*, 2010b).

5.1. Surface vs. bulk chemical analysis

Ancient glass artefacts are often weathered, thus the corroded surface of these objects has a different composition from the intact glass underneath. Depending on the type of glass and on the intensity of the weathering, this perturbed layer may be several hundreds of μm thick. Most X-ray methods only measure material to a depth of a few microns, and thus typically do not reach intact glass. Moreover, these methods are highly sensitive to surface effects and need to be applied on very flat surfaces. Embedding glass samples in resin and polishing is often necessary, which can be considered as destructive, time consuming and expensive. It should also be noted that

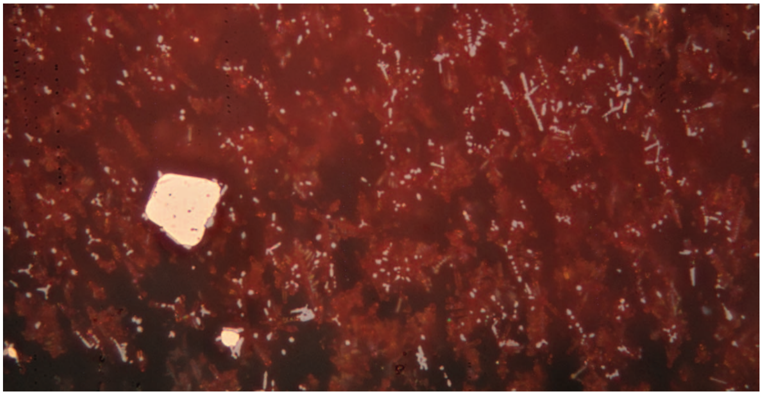


Figure 21. Deep-focused image of a red Pb glass from Tebtunis, Fayum, Egypt (Hellenistic Age). The combination of stacked OM images focused at different depths allows the perception of the cuprite dendrites embedded in the transparent glass matrix. A couple of copper metal droplets are surfacing. (Image courtesy of C. Bettineschi, UNIPD).

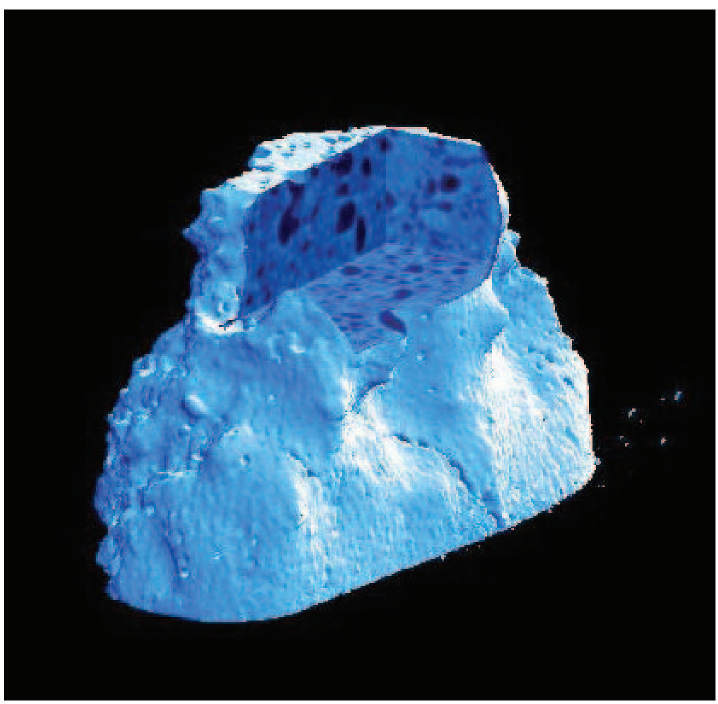


Figure 22. Computed X-ray micro-tomographic image of a faience bead from Lavagnone, Brescia, Italy (Early Bronze Age) (Angelini *et al.* 2006). The virtual sectioning of the reconstructed 3D image allows visualization and quantification of the voids, the quartz grains, and the glass interaction layer. (Image: G. Artioli).

energy-dispersive X-ray methods suffer matrix effects and interferences. For example, detection limits of bismuth or gold in glass are affected when lead is also present in high concentrations. Compared to X-ray methods, LA-ICP-MS analysis can be done on unprepared objects and allows the measurement of a large number of chemical elements (present either as major, minor or trace components) with only a few chemical or spectrometric interferences (Gratuze, 2016). LA-ICP-MS also offers lower detection limits than any energy- or wavelength-dispersive X-ray method. However, the spatial resolution of LA-ICP-MS analysis is not as good as that of EPMA, and LA-ICP-MS is also less relevant and selective for characterizing mineral inclusions.

As mentioned above, glass is a complex material made by mixing at least two main compounds: sand or crushed quartz pebbles (for silica) and plant ashes, mineral deposit or other oxides (for the fluxing agent: soda, potash or lead) to which different materials can also be added in order to modify its physical properties (colourants and opacifiers such as metallic oxides).

Until the 19^{th} to 20^{th} centuries, all these components had frequently relatively high levels of impurities, which reflected their origin or their manufacturing processes. The major elements typically characterize the recipes followed by the glass workers, and the minor- and trace-element associations reflect the origin of the materials used, thus representing the chemical fingerprints of the glass.

Chemical analysis of ancient glass items should, therefore, on the one hand, allow identification of the different recipes used for their production (soda, potash, lime, lead or other type of glass) and, if possible, the nature and origin of the raw materials (sand, quartz pebbles, fluxing agent from mineral deposits or from plant ash, colouring and opacifing agents), and on the other, allow us to follow the objects from the workshop to the consummation site. However glass objects, like metals, can be recycled and mixed easily, which makes interpretation of the analytical data more delicate, and often limits the conclusions of glass provenance studies.

More recently, the geochemical signature (isotopic composition) of some glass components (such as lead, strontium, neodymium, boron, oxygen) has been used to identify the origin of the raw materials (Degryse *et al.*, 2009). Isotopic analysis can also help to follow the diffusion of the manufactured objects or to locate geographically the primary glass workshops.

According to the analytical methods used, some or all of the different types of information are accessible. Using scanning electron spectroscopy coupled with X-ray energy-dispersive analysis (SEM-EDX), only major elements are determined, therefore this method allows only classification of the main glass type according to the fluxing agents used. However, due to the different imaging techniques (backscattered electron, secondary electron and X-ray mapping) it provides good identification of all the different mineralogical phases present in the glass (glass, devitrification structures, crystals, bubbles ...), giving the possibility to distinguish between unmelted relict phases (quartz, zircon, feldspars, metallic particles, opacifier ...) and *in situ* newly formed crystals (opacifier, wollastonite, metallic crystals ...). All this information provides a valuable tool to understand glass-making processes and opacifying recipes (*in situ* crystallization, addition of previously formed crystals, or mixing of clear and opaque glass). Compared to SEM-EDX, electron probe micro analysis offers the same imaging facilities with better detection limits (WDS improves detection limits by an order of magnitude or so, *vs*. EDS), giving access to the main minor elements (*i.e*. colouring element such as Co, and minor compound such as Ti, Sr, Ba ...). One of the main interests of SEM-EDX and EPMA is the option to carry out both bulk and point analyses.

Other X-ray and associated γ-ray methods (XRF, PIXE, PIGE) often offer better detection limits (ppm level instead of hundreds of ppm), but they are not associated with imaging facilities. These methods are particularly relevant for provenance study based on trace-element bulk analysis, but suffer the needs of expensive and complex analytical facilities such as Van de Graaff accelerators or Synchrotron lines. For similar reasons, access to facilities and cost, instrumental neutron activation analysis (INAA), which has been largely used to determine rare-earth elements and other trace elements for glass provenance studies, is used less nowadays.

More recently developed, inductively coupled plasma mass spectrometry techniques (either in liquid mode or laser ablation mode) offer a good compromise for trace-element analyses. Different options are offered according to the type of mass analyser (quadrupole, magnetic sector or time of flight) and the introduction mode (liquid, laser wavelength: Nd-YAG or Excimer laser). If ICP-MS in liquid mode offers only the possibility of bulk analysis on dissolved glass samplings, LA-ICP-MS offers more possibilities. Compared to EPMA or SEM-EDX analysis, analysis can be done directly on the sample without any preparation. Removal of the corrosion layer is easily carried out with a pre-ablation of the area to be analysed, regardless of the thickness of the corrosion layer. It is possible to obtain reliable results down to 1 mm below the surface. As the laser sampling is invisible to the naked eye, it is thus possible to analyse a greater number of objects and to get a better representation of compositional variation within a population of such glass objects. But laser ablation techniques can be applied with a great flexibility on a large range of sample types, it is hence also possible to analyse objects or sections of samples embedded in resin previously characterized by SEM-EDX or EPMA and to carry out either point analysis of inclusions or bulk analysis of the whole glass. It is thus possible to characterize fully (for major, minor and trace elements) the glass but also the different large inclusions present inside its structure. To characterize inclusions with great selectivity and good sensitivity, their size should not be $<40-50$ μm. Characterization of smaller inclusions (down to 10 μm) is possible, but it is done to the detriment of detection limits and selectivity.

EPMA and LA-ICP-MS appear then as perfect complementary techniques. The first allows us to carry out a full analysis of the different phases present in the glass (morphologies and compositions) as well as to determine the bulk composition of the major and main minor elements of the glass, while the second offers the options of achieving trace-elements analysis of the various structures encountered for trade and provenance studies.

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