AN INAUGURAL LECTURE TO THE SOCIETY

TRACE ELEMENTS IN PROVENANCING RAW MATERIALS FOR ROMAN GLASS PRODUCTION

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(3 figures and 1 table)

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ABSTRACT. It has been shown before that the combined use of Sr and Nd isotopes allows the geographical origin of Roman primary glass production to be traced. Nd isotopes are characteristic of the mineral fraction other than quartz in the silica sand used for the glass, while Sr isotopes are in most cases characteristic of the lime component, either attributed to the sand or as a separate constituent in the form of shell. In this study, the relationship between a sand raw material and the resulting ancient glass in terms of their trace element and Sr-Nd isotopic compositions is investigated. Especially the relevance of REE versus the use of isotopic techniques in the provenance determination of glass production is evaluated. The REE content of Roman glass is shown to be dependent on the clay fraction of the sand, and is identical for most possible provenance areas in the Mediterranean. Conversely, elements such as Zr, Hf, Ti, Sn are controlled by heavy mineral concentrations in sand and offer great potential as indicators of glass provenance.

KEYWORDS: Archaeometry, LA-ICP-MS, mineral resources, Nd isotopes, Sr isotopes

1. Introduction

Research of archaeological artefacts is aimed at reconstructing how daily life was organised in the past. The better we understand the context in which people used and produced artefacts, the more likely we are to understand the agency of underlying practices in a society. Artefacts are then not simply raw material for classification by archaeologists or evidence of production, but they can reveal how trade relations or productions evolved (Gosden, 1994). The scientific examination of archaeological and historic artefacts has many possible aims, but one which has long excited archaeological scientists is their provenance determination. Such a study thus not only answers questions on mining and quarrying, arts and crafts or trade, but also documents social stratigraphy (e.g. presence of exotic goods), subsistence strategies (e.g. provenance of food based on the provenance of their containers) and chronological changes in the standard of living (e.g. changing proportions of import versus local production) (Degryse, in press). All these topics are extremely important to the evaluation of the ancient socio-economy of a site or region. Provenancing relies on the assumption that there is a scientifically measurable property that will link an artefact to a particular source or production site. Elemental chemical composition has been used to try and identify where artefacts were produced; it has been suggested that artefacts might have a compositional ‘fingerprint’ (Henderson, 1989). However, the use of major elemental analysis data for provenance studies has recently been subjected to close scrutiny, especially for materials such as glass and metals, where the direct relationship between mineral raw material and artefact has been obscured. Archaeological scientists have become increasingly aware that smelting or melting may have dramatic effects on the concentrations of many minor and trace elements (Wilson & Pollard, 2001). Recently, new approaches are developed for provenance studies on such materials, including the use of trace elements (e.g. Shortland et al., 2007) and radiogenic isotopes (e.g. Degryse et al., 2007; Degryse & Schneider, 2008).

Chemically, the great majority of ancient glass was made up of silica, fluxed with soda and stabilized with lime. This soda-lime-silica glass was the first type produced in the late Bronze Age of Mesopotamia and Egypt and continued as the dominant compositional type across Western Asia and the Mediterranean through to the modern period (Freestone, 2006). From the point of view of raw materials, this glass type falls into two broad categories (Sayre & Smith, 1961): (1) plant ash glass, combining a soda-based flux rich in lime produced from plant ashes with quartz pebbles as a silica source and (2) natron glass, combining a soda-based flux of mineral matter (mostly natron Na₂CO₃·10 H₂O and trona...
Na₃H(CO₃)₂·2H₂O; Shortland, 2004) with quartz sand. Natron glass is the predominant type of ancient glass in the Mediterranean and Europe from the middle of the first millennium BC through to the ninth century AD (Freestone et al., 2002a). Plant ash glass is mainly produced before that time in Egypt and Mesopotamia and from the ninth century onwards throughout the Mediterranean and Europe (Freestone, 2006). It has been shown from shipwrecks such as Ulu Burun that raw glass was already traded as ingots in the Late Bronze Age (Nicholson et al., 1997; Rehren & Pusch, 1997) and as lumps of glass in the Roman and early medieval periods (Foy et al., 2000).

‘Primary’ workshops made raw glass from its raw materials and appear to have been distinct from ‘secondary’ workshops that shaped glass into specific objects in most of the early periods. To complicate matters, the chemical composition of glass reflects its primary origin rather than the location where it was shaped or formed, but also the fact that glass may have been recycled many times. Its chemical composition may hence be influenced by mixing of several primary sources or by the addition in the recycling process of strong coloured or decoloured glasses with high trace element contents, e.g. lead, cobalt or antimony.

Excavations made it clear that large quantities of 4th to 8th century AD natron glass were made in a limited number of ‘primary’ glass production centres, mainly in Egypt and Syro-Palestine (Brill, 1988, 1999; Freestone et al., 2000, 2002a; Picon & Vichy, 2003). Earlier, in the Roman period, suggestions towards the existence of similar units in Egypt (Nenna, 2003) and Syro-Palestine have been made (Nenna et al., 1997; Foy et al., 2003) although some authors have indicated that primary production also took place elsewhere in Hellenistic and early Roman times (Wedepohl et al., 2003; Jackson et al., 2003; Leslie et al., 2006). Moreover, the ancient author Pliny the Elder writes in his Natural History (Hist. Nat XXXVI, 194) that also sands from the coast of Italy, Gaul and Spain were used. This, however, was never confirmed up to now by excavations. Recently, however, the existence of primary glass producing units in the western Mediterranean was proven through scientific analysis (Degryse & Schneider, 2008). In this paper, the use of combined trace element and Sr and Nd isotopic analysis for the primary provenance determination of archaeological natron glass is evaluated. The relationship between the sand raw material and the trace element and isotopic composition of an ancient glass is investigated and, more importantly, the relevance of trace element analysis (REE and other elements) versus the use of isotopic techniques in the primary provenance determination of glass production is evaluated.

2. State-of-the-art

2.1. Glass and elemental analysis

Substantial databases of major element analyses of glass exist (Brill, 1999), but meaningful groupings with respect to the geographical origin of the mineral resources have seldom been possible. For example, all Roman glass was found to be relatively homogeneous natron glass with little variation in major element composition (Freestone, 2006). Hence, though significant advances have been made, for many, if not most, ancient periods an understanding of the exploitation of raw materials, technology and trade through major and trace element analysis still remains limited (Freestone, 2006). Major elements like calcium, iron, magnesium and aluminium can be of limited use, as they can be related to the concentrations of specific minerals (feldspars, clays…) in the glassmaking sand. Trace elements in glass can help to separate compositional groups and assign individual objects to them (Freestone, 2006). For example, the presence of elevated transition metals (Zn, Cu…) or Pb contents indicates that scrap glass, including small quantities of coloured glass, was incorporated in the batch, pointing to ‘recycled’ material. Recent studies have investigated some trace elements as more specific indicators of origin of glass raw materials. Rare Earth Element (REE) patterns (Freestone et al., 2002b), Zr-Ti (Aerts et al., 2003), Zr-Ti-Cr-La (Shortland et al., 2007) and Zr-Ba (Silvestri et al., 2008) have proved promising in distinguishing between various sand (silica) raw materials, as these elements may be typical for a geological environment.

2.2. Glass and isotope analysis

Radiogenic isotopes are often used for dating the time of formation of minerals or rocks, but are also very useful in tracing the sources of detrital matter (Banner, 2004). They can hence be used in tracing raw materials in craft production. The isotopic composition of a raw material is dependant on the geological age and origin of that material. The heavy isotopes of e.g. lead, strontium and neodymium, due to their relatively small mass differences (Faure, 1986, 2001), are not fractionated during technical processing. The isotopic composition of the artefact will hence be identical, within analytical errors, to the raw material from which it was derived, while the signature of different raw materials used may differ (Brill & Wampler, 1965).

Recent advances (Wedepohl & Baumann, 2000; Freestone et al., 2003, in press; Degryse & Schneider, 2008; Degryse et al., 2005, 2006a, 2006b) have shown that the use of Sr-Nd radiogenic isotopes allows provenancing of primary glass, even after its transformation or recycling in secondary workshops. Sr in ancient glass is mainly incorporated with the lime bearing material, being shell, limestone or plant ash (Wedepohl & Baumann, 2000). It is assumed that natron has no influence on the Sr isotopic ratio of glass (Freestone et al., 2003). However, minor influences may be attributed to feldspar or heavy minerals present in a sand (Degryse et al., 2006a). Where the lime in glass has been derived from Holocene sea shell, the Sr isotopic composition of the glass reflects that of modern sea water (Wedepohl & Baumann, 2000). Where the lime has been derived from ‘geologically aged’ limestone, the isotopic signature of the glass reflects that
of the limestone, possibly modified by diagenesis (Freestone et al., 2003). Also the bulk Sr content may be a useful indicator. Shell may contain a few thousand ppm Sr (e.g. Brill, 1999). Because of diagenesis, limestone will incorporate not more than a few hundred ppm of Sr, however, without substantially modifying the Sr isotopic composition (Freestone et al., 2003). A first survey of the Sr isotopic composition of glass throughout the ancient world has indicated the promising nature of the technique in classifying glasses essentially according to the origin of the lime material (Brill, 2006).

Nd isotopes are used as an indicator of the provenance of detrital sediments in a range of sedimentary basin types (Banner, 2004). Nd in glass is likely to have originated partly from the clay mineral content and partly, but principally, from the heavy mineral content of the silica raw material (Degryse et al., 2006b; Degryse & Schneider, 2008). This offers great potential in tracing the origins of primary glass production in ancient times. Moreover, the effect of recycling on the Nd isotopic composition of a glass batch is not significant, and neither is the effect of colorants (Freestone et al., 2005). The first example of this approach was shown in the provenance determination of early Byzantine 4th to 8th century glass from Syro-Palestine and Egypt (Degryse et al., 2006b; Freestone et al., in press). The consistency of the Nd isotope composition of the glass with Nile dominated sediments (Weldeab et al., 2002; Stanley et al., 2003) suggested an origin of these glass types situated in between the Nile delta and what is now Lebanon-Israel. In a second study (Degryse & Schneider, 2008), a Roman 1st to 3rd century glass showed exotic Sr-Nd isotopic compositions, which does not correspond to the signatures from the known production centres in Egypt and Syro-Palestine. These signatures were moreover not consistent with any possible glass raw material in the eastern Mediterranean, but do correspond well to sediments from the western Mediterranean, from the Italian peninsula to the French and Spanish coasts. Therefore the primary production location of this glass most likely lies in the western Roman Empire.

3. Methodology

All samples represent free-blown Roman (1st to 3rd century AD) vessel glass. The chronology of the glass was determined by stratigraphical association. The main element chemistry of the samples is described in Degryse et al. (in press). All glasses can be characterised as low-magnesia, soda-lime-silica glasses (Henderson, 1985), where most is natron glass. However, sample KEL2 has elevated MgO, K₂O and P₂O₅ contents. This leads to presume that this glass is not a pure natron based glass, but that plant ashes were (partly) used as a flux. The high Al₂O₃ and Na₂O contents of this sample are an indication of its mixed origin. The blue and green glasses in this study are naturally coloured by the presence of Fe₂O₃, the nature of colourless glass can be attributed to decolouration of the material with Sb and Mn (e.g. Degryse et al., 2005).

The isotopic data used here were obtained from Degryse & Schneider (2008).

For this study, samples were chemically characterised through comprehensive elemental analyses by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Trace element analyses were carried out using a New Wave UV-213 laser ablation system in conjunction with an Agilent 7500a ICP-MS instrument. Samples were mounted in standard electron microprobe resin blocks and ablated under an atmosphere of argon. Ablation conditions were: 80 µm laser spot diameter operated at 10 Hz and a laser power of ~7 J/cm², each sample was analysed in spot mode. Ablated material was transported to the plasma source using a gas flow control system at a flow rate of approximately 1.2 l min⁻¹, and the plasma was operated at a power of 1400 W. These conditions produce a beam with an intensity of 10³ cps/ppm with a Th⁴⁺/ThO⁺ ratio of >0.5%. Signals from the ablated sample were recorded in time-resolved mode over a period of 240 s, during the first 120 s of which the laser shutter remained closed to allow the measurement of the 'gas blank'. The complete signal was subsequently interpreted using the ‘GLITTER’ software package with Ca as the internal standard element. Analyses were calibrated against NIST SRM 610, a glass reference material doped with a nominal concentration of 500 ppm for most trace elements (Pearce et al., 1997). Replicate analyses indicated that individual analyses of most elements are subject to analytical uncertainties of <10% precision and accuracy, and detection limits for most elements are in the sub-ppm range.

4. Results

Analytical results for trace elements and isotopes are given in Table 1. The Sr isotopic composition of the ancient glass for most samples lies very near to the modern-day sea water composition (⁸⁷Sr/⁸⁶Sr 0.7092; Fig. 1). Some samples show a clearly differing Sr isotopic

![Figure 1. ⁸⁷Sr/⁸⁶Sr vs. εNd biplot of the glasses analysed. A wide spread in Nd isotopic composition can be observed.](image-url)
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composition ($^{87}\text{Sr}/^{86}\text{Sr}$ range between 0.70759 and 0.72548). Sr contents of the glasses very between 133 and 554 ppm. The Nd isotopic data show a wide range in composition, varying between -13 and -3.8 for $\varepsilon_{\text{Nd}}$ (Fig. 1), concentrations varying between 3.15 and 8.40 ppm.

The glasses in the sample clearly have elevated transition metal contents due to the decolouring agents, as elevated contents (over 1000 ppm) in Sb and/or Mn can be observed. Moreover, much of the glass analysed has elevated contents, over hundreds of ppm, in Mn, Pb, Cr, Ni and sometimes Cu and Zn, typically pointing to the recycled nature of the materials. Remarkable in the analyses is the homogenous REE content (Fig. 2). Most glasses have an identical chondrite normalized REE pattern, showing LREE enrichment, flat HREE distributions and a significant negative Eu anomaly. Variations only seem to exist in the absolute abundance of the REE as a group in the glass, and some variation in the Eu anomalies in the chondrite-normalized data can be seen.

![Figure 2. Chondrite-normalized REE pattern of the glasses analysed.](image)

5. Discussion

It is clear from the study of e.g. Goldstein et al. (1984), Grousset et al. (1988) and Weldeab et al. (2002) that the Sr and Nd ratios of sediments in the Mediterranean do vary significantly, offering a great potential to distinguish primary glass from Egypt and Syro-Palestine from other primary glass producers. The Nd isotopic composition of the sediment input of river systems into the oceans is fairly homogeneous with an average composition of -11.4 $\varepsilon_{\text{Nd}}$ (Goldstein et al., 1984). This homogeneity is explained by thorough mixing of heterogeneous material by erosion processes and/or overall sampling of the crust with similar composition. The isotopic composition can hence be interpreted as an estimate for the average age of the mantle origin of the various provenance components of that deposit, thus constraining a provenance area (McLennan, 1989). However, in the eastern Mediterranean, the river Nile has a very exceptional Nd composition of its sediment load, as it is dominated by East African volcanic rocks from the Ethiopian Plateau. This leads to an average composition of eastern Mediterranean sediments of -3.3 $\varepsilon_{\text{Nd}}$ (Goldstein et al., 1984). Moreover, sediments dominated by input of wind-blown Saharan dust, show a typical isotopic composition of -12 to -13.5 $\varepsilon_{\text{Nd}}$. As a consequence, the composition of detrital deep-sea surface sediments in the east-west axis of the Mediterranean ranges from -10.1 $\varepsilon_{\text{Nd}}$ at Gibraltar to -3.3 $\varepsilon_{\text{Nd}}$ at the mouth of the river Nile, with a maximum of +4.6 $\varepsilon_{\text{Nd}}$ off the Greek-Turkish coast (Grousset et al., 1988; Frost et al., 1986).

Some of the 1st-3rd century AD glasses used in this study have a Sr-Nd isotopic composition identical or very similar to the signature of the known 4th-8th century AD primary production locations in the Levant and Egypt (Degryse & Schneider, 2008). In Levantine samples, the $^{87}\text{Sr}/^{86}\text{Sr}$ signature is close to the modern day marine signature of 0.7092, thus indicating the use of shell as a lime source in the glass (Wedepohl & Baumann, 2000; Freestone et al., 2003), while in Egyptian samples the lower $^{87}\text{Sr}/^{86}\text{Sr}$ signature points either to the use of limestone as a stabiliser (Freestone et al., 2003) or to the influence of other minerals relatively low in radiogenic strontium in the sand raw material (Degryse et al., 2005; Freestone et al., 2005). The isotopic signature between -5.0 and -6.0 for $\varepsilon_{\text{Nd}}$ (Freestone et al., in press) points to an eastern Mediterranean origin. It is therefore likely that primary production was taking place in the eastern Mediterranean also in early Roman days, although not necessarily in the same geographical location as the aforementioned primary glass units.

Conversely, some glass clearly has an exotic Sr-Nd isotopic composition, not corresponding to sediment signatures from the eastern Mediterranean basin. These signatures (between -6.0 and -13 $\varepsilon_{\text{Nd}}$ and between 0.70759 and 0.72548 $^{87}\text{Sr}/^{86}\text{Sr}$) are not consistent with any sediment in the eastern Mediterranean but corresponds well to the range in isotopic values of beach and deep-sea sediments from the western Mediterranean, from the Italian peninsula to the French and Spanish coast, and from north-western Europe. The primary production location of this glass therefore most likely lies in the western Roman Empire (Degryse & Schneider, 2008). In addition, the large spread in the isotopic composition of the Hellenistic-Roman glass analysed here, besides proving a primary origin of the glass all over the Mediterranean basin, is also likely to reflect thorough mixing (and possibly recycling) of the glass and its resources over time. This concurs well with the information obtained from the trace element data of the glass, indicating thorough recycling of the glass, as can be seen from the elevated transition metal contents.

In addition, sediments preserve a record of their provenance within their trace element composition (McLennan, 1989). Over the past decades, there have been several reviews that discuss the use of REE geochemistry in the study of crustal evolution, and of relationships between plate tectonics, sedimentation and sedimentary processes such as diagenesis and weathering (Elderfield, 1988; Taylor & McLennan, 1985, 1988;
McLennan, 1989). Regarding the REE, some inconsistency has arisen in geochemical literature. In most geochemical discussions, the REE include lanthanide elements La-Lu as well as Y. In terms of geochemical behaviour, Y mirrors the heavy lanthanides Dy-Ho, and typically is included with them for discussion (McLennan, 1989). Sc is a smaller cation with a geochemical behaviour different from the lanthanides (but similar to elements such as Cr, Ni, V, Co), but it is sometimes included with the REE (e.g. Puddephatt, 1972) as it is of interest for sedimentary provenance studies because of the low concentrations, similar to the REE, in low temperature aqueous fluids (see below; McLennan, 1989). In this study, Sc was not included with the REE.

The variations in the physico-chemical properties of the REE make them sensitive to mineral/melt equilibria, leading to their special utility in geochemical studies of igneous systems (McLennan, 1989). For sedimentary rocks, these characteristics are equally important, but in a less direct manner. The REE contents are usually normalized to average chondritic meteorites, likely parallel to the primordial abundances in the solar nebula and parallel to bulk earth abundances (e.g. Taylor & McLennan, 1988). Sedimentary REE patterns show remarkable uniformity with light rare earth element (LREE) enrichment, flat heavy rare earth elements (HREE) distributions and a significant negative Eu anomaly in chondrite normalized diagrams, quite in contrast to the considerable diversity shown in igneous rocks. It has been suggested that the process of erosion leads to an efficient sampling of the REE in the exposed upper continental crust. In common weathering conditions, REE are transported from the weathering profile by mechanical processes (Nesbitt, 1979). The major assumption behind equating the REE patterns of sedimentary materials to the average REE patterns of the source rocks is that the REE are quantitatively transferred in the terrigenous component during erosion and sedimentation without fractionation during sedimentation (McLennan, 1989). Elements such as Zr, Hf, Ti, Cr, Ni and Sn, tend to be closely associated with heavy minerals and their distribution may be dominantly controlled by heavy mineral concentration processes, which is not so for the REE (see below). In every case, the dependence of the contents in Zr, Hf, Ti and Sn in a sand on the mineralogy of the sand offers great potential for using these elements as indicators of glass provenance.

As described by McLennan (1989), three major factors of sedimentary sorting may affect REE patterns in sedimentary processes: grain size contrasts, general mineralogy and heavy mineral fractionation. The bulk of the REE resides in the silt and clay fraction of the sediment (Cullers et al., 1979) though there is no correlation with the clay mineralogy, suggesting that the trivalent REE are readily accommodated in all clay minerals (McLennan, 1989). Silt fractions have lower absolute REE abundances than clays, although the shape of their REE pattern is identical, suggesting that quartz, with a very low REE abundance, only has a dilution effect. Calcite and dolomite, also low in REEs, have a similar effect, reducing REE abundances, but not changing the REE pattern (Taylor & McLennan, 1985).

In principle, non-heavy mineral concentrations may also affect REE patterns. An example of this is plagioclase enrichment in sedimentary sorting, which may influence Eu-anomalies in REE patterns. REE mostly exist in a trivalent state, but under reducing conditions, Eu may exist in a divalent state, and be enriched as for Sr in feldspar, especially plagioclase, leading to a distinct behaviour of Eu compared to other REE. In this way, REE patterns may be modified when plagioclases are concentrated or enriched in sedimentary sorting (e.g. Nance & Taylor, 1977). In sediments that are more mature, with little plagioclase, such enrichments have not been documented. In addition, the presence and magnitude of Eu-anomalies is similar for all grain sizes of sediment (McLennan, 1989). Heavy minerals may also be concentrated during sedimentary sorting due to their high density and resistance to weathering. Such minerals may contain significant abundances of REE (e.g. monazite and zircon) and when their patterns differ significantly from the average source rock composition, an effect on sedimentary REE patterns may occur (McLennan, 1989). However, the importance of these minerals in sedimentary REE patterns can be judged through the concentrations of elements other than the REE that are found in trace levels in most sedimentary rocks, like Zr and Hf for the mineral zircon and Th for the mineral monazite (Taylor & McLennan, 1985). For example, the average Zr content of the exposed upper continental crust is between 160 and 237 ppm (Rudnick & Gao, 2003), while typically shales have about 200±100 ppm Zr (Taylor & McLennan, 1985) and thus show no substantial enrichment or depletion in zircon (McLennan, 1989). Also, concentrations of e.g. zircon and monazite result in Gd/Yb anomalies in sedimentary REE patterns (for further information, see McLennan, 1989). In effect, the dominating influence of heavy minerals on the REE distribution in most sedimentary rocks can be excluded by examining the sedimentary REE patterns themselves. Indeed, it has been shown by McLennan (1989) that, though sands may be prone to effects of heavy minerals, substantial enrichments in these minerals do not result in significant changes in the sedimentary REE patterns of silt, clay or shales.

The homogeneity in REE abundances and patterns of the glass analysed here can be explained in this respect. Some variations in the Eu anomalies can be seen in the REE patterns, which may be explained by different plagioclase contents in the sand raw material, but, overall, the REE abundances and patterns do not seem to be correlated with the provenance, and thus be of little use. The only sample showing a somewhat different REE pattern is KEL2, but this sample if clearly of a different nature, as it consists of a (mixed natron-) plant ash glass, made up of a fundamentally different raw material mixture. Also, in the present data set, no anomalous values due to heavy mineralogy influencing the REE patterns are discernable. The REE patterns likely reflect the pattern of...
the clay fraction of the sand raw materials and, in the case of the glasses analysed here, this is not surprising as only fundamental changes in upper crustal composition would be translated into a discernable change in sedimentary compositions (Veizer & Jansen, 1979; McLennan, 1988).

As for other trace elements, as mentioned before, the transition metal contents in a glass are sensitive to recycling of that glass. In this study, it was noted that elevated Cu, Mn, Mo, Ni, Sb, Pb and Zn contents may point to recycling, while elevated Mn, Sb contents may be related to colouring and decolouring of the glass. However, the trace elements depending on the heavy mineralogy of the sand raw material (such as Zr and Ti) do show a similar picture to that of the isotope analysis. The bi-plot of Zr vs. Ti (Fig. 3) shows mixing lines for some samples, which would point to thorough recycling of several sources, at the same time proving that several distinct sources would be involved in the primary production of these glasses. This concurs with the evidence obtained from radiogenic isotopes.

![Figure 3. Zr-Ti biplot for the glasses analysed, showing not a single mixing or recycling trend but indicating the signatures of several sand raw materials.](image)

6. Conclusion

A fundamental conclusion that may be drawn from the preceding discussion is that the REE pattern of a Roman glass is dependent on the clay fraction of the sand raw materials used in its production, with minor influences of plagioclase enrichments and a possible influence from heavy mineral concentrations. As the REE composition of such clay fractions is strongly buffered by intense recycling and mixing of upper crustal material, only fundamental changes in regional geology would be translated into a discernable REE composition. This is not to be expected for most possible provenance areas of glass in the Mediterranean.

Conversely, elements such as Zr, Hf, Ti, Sn... tend to be closely associated with heavy minerals and the distribution of these elements may be dominantly controlled by heavy mineral concentrations, which is not the case for the REE. This relation between sand mineralogy and content in these elements offers great potential for using these latter elements as indicators of glass provenance. Also, the application of radiogenic isotopes involving the REE, like the Sm-Nd and Lu-Hf systems, to solve problems of archaeological provenance, is extremely useful. Since the REE are considered immobile, the age and type of the terrigenous sedimentary deposit used for glass production will determine its isotopic composition. In contrast to the REE abundances, this will vary between source areas.

The use of combined isotopic and trace element techniques in archaeology to provenance raw materials of glass is extremely important. With such specific information, archaeologists can begin to understand ancient economies, reconstruct trade relations and unravel the organization of ancient industries, not only based on typo-morphological features as is usually done, but based on exact scientific methods.

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