Pliny the Elder and Sr−Nd isotopes: tracing the provenance of raw materials for Roman glass production

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Abstract

In Roman and Byzantine times, natron glass was traded throughout the known world in the form of chunks. Production centers of such raw glass, active from the 4th to 8th century AD, were identified in Egypt and Syro-Palestine. However, early Roman primary glass units remain unknown from excavation or scientific analysis. The ancient author Pliny described in 70 AD that besides Egyptian and Levantine resources, also raw materials from Italy and the Gallic and Spanish provinces were used in glass making. In this study, the primary provenance of 1st−3rd century AD natron vessel glass is investigated. The use of combined Sr and Nd isotopic analysis allows the distinguishing and characterizing of different sand raw materials used for primary glass production. The isotope data obtained from the glass samples are compared to the signatures of primary glass from known production centers in the eastern Mediterranean and a number of sand samples from the regions described by Pliny the Elder as possible sources of primary glass. Eastern Mediterranean primary glass has a Nile dominated Mediterranean Nd signature (higher than −6.0 ε Nd), while glass with a primary production location in the western Mediterranean or north-western Europe should have a different Nd signature (lower than −7.0 ε Nd). Most Roman glass has a homogeneous $^{87}Sr/^{86}Sr$ signature close to the modern sea water composition, likely caused by the (intentional) use of shell as glass raw material. In this way, strontium and neodymium isotopes now prove that Pliny's writings were correct: primary glass production was not exclusive to the Levant or Egypt in early Roman days, and factories of raw glass in the Western Roman Empire will have been at play.
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1. Introduction

For all archaeological artefactual evidence, the study of the provenance and trade of raw materials must be based on archaeometry, the application of mineralogical and geochemical techniques to archaeological problems. Whereas the study of the provenance and trade of stone and ceramics is already well advanced, this is not the case for ancient glass. The nature of the mineral raw materials used and the geographical location of their transformation into finished artifacts largely remain unclear.

The great majority of ancient glass was based upon silica, fluxed with either soda or potash. Chemically, soda-based glass (soda-silica-lime glass) falls into two categories (Sayre and Smith, 1961): (1) plant ash glass, combining a plant ash with quartz pebbles; and (2) natron glass, combining soda-rich mineral matter with quartz sand. Before the middle of the first millennium BC, plant ash glass was produced from its raw materials in Egypt and Mesopotamia. Thereafter, natron glass became the predominant type of ancient glass in the whole Mediterranean area and in Europe, this until the ninth century AD (Freestone et al., 2002a; Shortland, 2004). Using plant ashes as a flux again became the dominant practice from the ninth century AD onwards (Freestone, 2006).

It is generally accepted that raw glass was already traded as 'ingots' or chunks from late Bronze age to early Medieval times (Foy et al., 2000; Nicholson et al., 1997; Rehren and

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Pusch, 1997). 'Primary' workshops produced raw glass and were distinct from 'secondary' workshops that shaped glass into specific objects. A single primary workshop could then supply many secondary workshops over a large geographical area (Nenna et al., 1997). Archaeological excavations revealed that large quantities of 4th–8th century AD natron glass were made in a limited number of 'primary' glass production centers mainly in Egypt and the Levant (Brill, 1988, 1999; Freestone et al., 2000, 2002a; Picon and Vichy, 2003). It has been argued that the similarities between Roman blue–green glass and later glass produced in the Levant are sufficiently similar that Roman glass is likely to have been made there, although the archaeological evidence is difficult to interpret (Nenna et al., 1997; Picon and Vichy, 2003; Foy et al., 2003). Some authors have suggested that early Roman primary production may have taken place elsewhere in the Hellenistic and early Roman world (Leslie et al., 2006), as small-scale glassmaking has been reported from Roman York (Jackson et al., 2003) and fourth century AD Hambach, Germany (Wedepohl et al., 2003). The ancient author Pliny the Elder writes in his Natural History (Hist. Nat XXXVI, 194), that also sands from the coast of Italy and Gaul and Spain were used. This, however, was never confirmed by excavations or through scientific analysis, although the suitability of some of the sands explicitly described by Pliny has been proven (Silvestri et al., 2006).

The concept of this *division of production* leads to a specific interpretation of analytical data, as glass compositions reflect the origins of the raw materials of the 'primary' sources, rather than the 'secondary' workshops (for example Nenna et al., 1997; Foy et al., 2000; Freestone et al., 2000, 2002b). Natron glass hence provides an excellent case for the importance of a production model in the interpretation of archaeometrical data and vice versa, and archaeologically for studying organized trade in raw materials. 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 rarely been possible. For example, all Roman glass was found to be relatively homogeneous natron glass with little variation in major element composition (Freestone, 2006). However, elements like lime, iron, magnesium and alumina are useful, as they can be related to the concentrations of specific minerals (for example, feldspars, clays) in the glassmaking sand. Also, trace elements in glass can help to separate compositional groups and assign individual objects to them (Freestone, 2006). However, the presence of elevated transition metals indicates that scrap glass, including small quantities of intentionally colored glass, was incorporated in the glass batch, pointing to 'recycled' material, which complicates the picture. Studies by Freestone et al. (2000, 2002b) and Aerts et al. (2003), however, have investigated trace elements as more specific indicators of origin of glass raw materials. Especially Rare Earth Element (REE) patterns have proved promising to distinguishing between sand raw materials (Freestone et al., 2002b) as these may be typical for the geological environment of the sand, but these characterizations remain mostly unexplored. Conversely, recent advances (Wedepohl and Baumann, 2000; Freestone et al., 2003; Degryse

et al., 2005, 2006a,b) have shown that the use of radiogenic isotopes, specifically those of strontium and neodymium, allows developing new approaches for provenance determination of primary glass, even after its transformation or recycling in secondary workshops.

2. Aims

In this study, the primary provenance of 1st–3rd century AD natron vessel glass is investigated. The use of combined Sr and Nd isotopic analysis of vessel glass allows distinguishing and characterizing different sand raw materials used for primary glass production. The isotope data obtained from the glass samples are compared to the signatures of primary glass from known production centers in the eastern Mediterranean and a number of sand samples from the regions described by Pliny the Elder as possible sources of primary glass. In this way, the occurrence of factories of raw glass outside the Levant and Egypt, for example in Italy and the Gallic provinces, is investigated.

3. Methodology

3.1. Glass and Sr–Nd isotopes

Radiogenic isotope systems are often used for dating the time of formation of minerals or rocks, but are also very useful in tracing the sources of for example detrital matter in sedimentary and biogeochemical cycles (Banner, 2004). They may hence be used in tracing raw materials in craft production. The isotopic composition of a raw material is dependent on its geological age and origin. Due to their relatively high masses at low internal mass differences, Sr and Nd isotopes are not fractionated by the temperatures involved in ancient technical processes such as glass melting (Faure, 1986, 2001). The isotopic composition of the artifact will hence be identical, within analytical errors, to the raw material from which it was derived, while the signature of different raw materials used, and hence the resulting artifacts, may differ (Brill and Wampler, 1965; Gale and Stos-Gale, 1982).

Sr in ancient glass is mainly incorporated with the lime-bearing material, such as shell, limestone or plant ash (Wedepohl and Baumann, 2000). It has been demonstrated that natron has no significant influence on the Sr budget in glass (Freestone et al., 2003). However, minor influences may be attributed to feldspar or heavy minerals in the sand (Degryse et al., 2006a). Where the lime in glass was derived from Holocene sea shell, the Sr isotopic composition of the glass reflects that of modern sea water (Wedepohl and Baumann, 2000). Where the lime was derived from 'geologically aged' limestone, the signature of the glass reflects that of the limestone, possibly modified by diagenesis (Freestone et al., 2003). Also the Sr content is a useful indicator. Shell may contain a few thousand ppm Sr (for example Brill, 1999), while, because of diagenesis, limestone will incorporate only a few hundred ppm of Sr (Freestone et al., 2003). In effect, 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 according to their origin (Brill, 2006).

Nd isotopes have been 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 from the heavy mineral content of the silica raw material (Degryse et al., 2006b). Raw natron glass from late Roman to early Byzantine primary production sites in Egypt and the Levant has already been successfully analyzed for its Sr and Nd isotopic composition (Degryse et al., 2006a,b; Freestone et al., submitted for publication). The consistency of the Nd isotope composition of this glass with Nile dominated sediments (Weldeab et al., 2002; Stanley et al., 2003) concurred with its origin in between the Nile delta and the southern Levant.

3.2. Samples and archaeological context

Samples of twenty-seven vessel individuals from several locations in the Roman Empire (Fig. 1) were selected for Sr and Nd isotopic analysis. All samples represent free-blown vessel glass and their chronology was determined by stratigraphical association. The glass from Sagalassos (SW Turkey) originates from Roman excavation contexts dated from the first half of the first century AD to the third century AD (layers 3–11 of site L; Poblome, 1999). The glass from Maastricht (Netherlands) was found during excavations in a cellar. A first sample was found in a peat layer where finds of the Flavian period were discovered (Hulst and Dijkman, 1999). A second sample originated from a rubble layer under the floor of the cellar and could be assigned to the second quarter of the second century AD. The finds from Kelemantia originate from the Roman

Fig. 1. Map of the sampling localities of glass (stars) and sand (diamonds) – 1: Bocholtz, 2: Maastricht, 3: Tienen (glass was also sampled here), 4: Kelemantia, 5: Sagalassos, 6: Antwerp, 7: river Belus, 8: Wadi-el-Natrun, 9: river Volturno.

auxiliary fort of Iža in Slovakia, situated about 4 km east of the confluence of the river Waag and the Danube. The finds all belong to one single construction phase dating between 175 and 179 A.D. The glass from Bocholtz (the Netherlands) originates from an underground burial chamber in a known Roman graveyard (de Groot, 2006). The chamber was dated to the last quarter of the second to the first quarter of the third century AD. The glass from Tienen (Belgium) was found in the context of a, excavated glass furnace dated to the second century AD (Cosyns and Martens, 2002–2003).

In addition to the glass, (possible) silica raw materials for primary glass production were mineralogically characterized and analyzed for their Sr–Nd isotopic signature (Fig. 1). Quartz sands from the mouth of the river Belus, the present day river Na'aman south of the city of Akko on the coast of Israel (near the primary glass factories of the Levant) were sampled by R.H. Brill in the sixties (Brill, 1999). Samples BRILL 674 and BRILL 679 are fine sands from the beach at the mouth of the river and sample BRILL 681 is a mixture of samples taken 400 m south of the former beach. Quartz sands from the river Volturno between Castel Volturno and Cumae, near the coast of Naples in Italy, were sampled by R.H. Brill in the early eighties (Brill, 1999). Samples BRILL 4553 and BRILL 4556 are fine, light colored to yellowish beach sands while sample BRILL 4554 is coarse black sand found in pockets. From Tertiary (Eocene) sand dunes near lake Fazda in Egypt (next to the glass factory of Wadi-el-Natrun), two samples were taken, one next to the glass factory and one north of the lake. All three sampling locations described above are mentioned in Pliny the Elder's Natural History (Hist. Nat XXXVI, 194) as locations for primary glass production using the local mineral raw materials. Also, two Tertiary deposits in Belgium were mineralogically and geochemically characterized. Sample TIE2-A-2 was taken from Oligocene sands near the glass furnace excavated at Tienen, Belgium while sample ANT-M12 is a Miocene sand from Antwerp (Laga et al., 2001). These locations are sampled for regional comparison of Sr–Nd isotopic signatures and as possible sand sources in the Gallic provinces as described by Pliny.

3.3. Analytical techniques

For isotope analysis, samples were weighed into Teflon screw-top beakers and dissolved in a 3:1 mixture of 22 M HF and 14 M HNO_3 on a hot plate. Solutions were dried and dissolved in aqua regia. Aliquots of these solutions were spiked with a highly enriched ^{84}Sr and ^{150}Nd tracer for separate concentration analyses by isotope dilution, whereas unspiked aliquots were used for determination of isotope ratios. For separation of Sr and Nd from the same sample solutions, sequential extraction methods developed by Pin et al. (1994) were utilized and slightly modified. Sr and REE were separated using 2 M HNO_3 on coupled miniaturized Teflon columns containing 50 μl of EICHROM Sr and TRU resin, respectively, and eluted with deionized H_2O. For separation of Nd, the REE cut was further passed trough a column containing 2 ml EICHROM Ln resin. For this, the column was

washed with 5.5 ml 0.25 M HCl after adding the sample. Nd was then stripped off using 4 ml 0.25 M HCl.

All measurements were performed on a six-collector FINNIGAN MAT 262 thermal ionization mass spectrometer (TIMS) running in static multicollection mode. Sr isotopic ratios were normalized to $^{86}Sr/^{88}Sr = 0.1194$, Nd isotopic ratios were normalized to $^{146}Nd/^{144}Nd = 0.7219$. Repeated static measurements of the NBS 987 standard over the duration of the study yielded an average $^{87}Sr/^{86}Sr$ ratio of 0.71025 ± 2 (2σ, $n = 22$). Repeated measurements of the La Jolla Nd standard yielded $^{143}Nd/^{144}Nd = 0.511848 \pm 0.000009$ (2σ, $n = 8$). Total procedural blanks ($n = 6$) did not exceed 30 pg Sr and 50 pg Nd and were found to be negligible.

4. Results

Sr and Nd isotopic compositions and elemental concentrations of the glass and sand samples are given in Tables 1 and 2. $^{143}Nd/^{144}Nd$ ratios are also represented in parts per 10^4 deviation from the present-day value of a model evolution of Nd isotopes in a chondritic Earth (Chondritic Uniform Reservoir, CHUR) according to DePaolo and Wasserburg (1976)

$$\varepsilon Nd = \left(\frac{(^{143}Nd/^{144}Nd)_{sample}}{(^{143}Nd/^{144}Nd)_{CHUR}} - 1 \right) \times 10^4$$

with $^{143}Nd/^{144}Nd_{CHUR} = 0.512638$.

The $^{87}Sr/^{86}Sr$ ratios of most glass samples ($^{87}Sr/^{86}Sr$ 0.70865–0.70910) correspond to the present-day seawater composition. However, three samples show clearly distinct Sr isotopic compositions, with $^{87}Sr/^{86}Sr = 0.70759$ for sample TIE 49, $^{87}Sr/^{86}Sr = 0.70958$ for sample BO 119, and $^{87}Sr/^{86}Sr = 0.70966$ for sample KEL 234/88. The Sr contents of the glasses vary widely between 55 and 363 ppm. Likewise, the Nd isotopic data show a wide range in isotopic composition and Nd content, with $^{143}Nd/^{144}Nd = 0.512083–0.512511$ (ε Nd = − 10.8 and −2.5) and Nd = 3.2−28.9 ppm.

The Sr isotopic composition of the sand samples (Table 2) varies between $^{87}Sr/^{86}Sr = 0.70796$ and 0.71923. The sands have low Sr contents between 0.005 and 0.04% SrO (Brill, 1999). Nd isotope ratios for the sands again vary greatly

Table 1
Sr–Nd isotopic data of the 1st–3rd century AD glass analyzed

Sample	$^{143}Nd/^{144}Nd$	2 σ	Nd (ppm)	ε Nd	$^{87}Sr/^{86}Sr$	2 σ	Sr (ppm)
Maastricht							
Ma 1 c	0.512214	0.000007	nd	−8.3	0.70875	0.00003	nd
Ma 2 b	0.512205	0.000010	nd	−8.4	0.70898	0.00002	nd
Tienen							
Tie 11	0.512511	0.000009	15.4	−2.5	0.70893	0.00001	55
Tie 12	0.512267	0.000009	13.9	−7.2	0.70899	0.00002	131
Tie 17	0.512378	0.000010	18.7	−5.1	0.70902	0.00001	363
Tie 24	0.512376	0.000013	18.7	−5.1	0.70902	0.00002	266
Tie 35	0.512219	0.000009	nd	−8.2	0.70886	0.00001	186
Tie 37	0.512083	0.000006	nd	−10.8	0.70891	0.00002	241
Tie 41	0.512337	0.000009	28.9	−5.9	0.70901	0.00001	363
Tie 45	0.512174	0.000008	nd	−9.1	0.70904	0.00001	304
Tie 48	0.512262	0.000005	nd	−7.3	0.70896	0.00001	355
Tie 49	0.512249	0.000010	nd	−7.6	0.70759	0.00001	241
Tie 50	0.512362	0.000008	18.2	−5.4	0.70898	0.00001	241
Bocholtz							
Bo 106	0.512296	0.000008	4.1	−6.7	0.70905	0.00001	283
Bo 109	0.512298	0.000008	3.2	−6.6	0.70903	0.00002	229
Bo 119	0.512223	0.000006	5.9	−8.1	0.70958	0.00002	279
Bo 123	0.512291	0.000009	4.4	−6.8	0.70906	0.00002	340
Kelemantia							
Kel 82/91	0.512325	0.000010	14.4	−6.1	0.70904	0.00001	nd
Kel 229/06	0.512266	0.000012	13.1	−7.3	0.70901	0.00002	nd
Kel 229/88	0.512325	0.000009	22.6	−6.1	0.70877	0.00002	nd
Kel 234/88	0.512177	0.000011	11.8	−9.0	0.70966	0.00002	nd
Sagalassos							
Sag 573	0.512294	0.000005	nd	−6.7	0.70865	0.00003	nd
Sag 574	0.512464	0.000002	nd	−3.4	0.70905	0.00001	330
Sag 709	0.512308	0.000006	nd	−6.4	0.70910	0.00002	nd
Sag 575	0.512434	0.000002	nd	−4.0	0.70894	0.00001	nd
Sag 717	0.512410	0.000002	nd	−4.4	0.70879	0.00001	nd
Sag 718	0.512291	0.000005	nd	−6.8	0.70882	0.00002	nd

nd: not determined.

Table 2
Sr−Nd isotopic data of the sand analyzed

Sample	Location	$^{143}Nd/^{144}Nd$	2 σ	Nd (ppm)	ε Nd	$^{87}Sr/^{86}Sr$	2 σ	SrO (%)
TIE2-A-7	Tienen, Belgium	0.512052	0.000011	11.0	−11.4	0.71923	0.00001	nd
ANT-M12	Antwerp, Belgium	0.511986	0.000007	47.7	−12.7	0.71487	0.00002	nd
FAZDA 1	Wadi-el-Natrun, Egypt	0.512289	0.000008	14.7	−6.8	0.71046	0.00001	nd
FAZDA 2	Wadi-el-Natrun, Egypt	0.512199	0.000007	13.1	−8.6	0.70951	0.00001	nd
BRILL 674	River Belus, Levant	0.512393	0.000010	19.7	−4.8	0.71159	0.00001	0.01
BRILL 679	River Belus, Levant	0.512392	0.000009	25.9	−4.8	0.70920	0.00002	0.005
BRILL 681	River Belus, Levant	0.512588	0.000010	23.7	−1.0	0.70925	0.00003	0.04
BRILL 4553	River Volturno, Italy	0.512284	0.000009	59.5	−6.9	0.70969	0.00001	nd
BRILL 4556	River Volturno, Italy	0.512133	0.000010	25.2	−9.9	0.70922	0.00001	0.02
BRILL 4554	River Volturno, Italy	0.512411	0.000006	296.3	−4.4	0.70796	0.00002	0.05

nd: not determined, data on SrO contents after Brill (1999).

between $^{143}Nd/^{144}Nd = 0.511986−0.512588$ (ε Nd = −12.7 and −1.0). The Nd contents of the sands range between 11 and 296 ppm.

5. Discussion

Raw glass from late Roman to early Byzantine primary production sites in Egypt and the Levant has already been analyzed for its Sr and Nd isotopic composition (Degryse et al., 2006a,b; Freestone et al., submitted for publication). Strontium is considered a proxy for the lime-rich component(s) in the glass raw materials (Freestone et al., 2003). In Levantine samples, $^{87}Sr/^{86}Sr$ signatures close to the present-day marine signature of 0.7092 indicated the use of shell as a lime source in the glass (Wedepohl and Baumann, 2000; Freestone et al., 2003). This shell was naturally included in the beach sand of the Levantine coast, which was used to manufacture the glasses (Brill, 1988). The lower $^{87}Sr/^{86}Sr$ signature of the Egyptian samples pointed to the use of either limestone (Freestone et al., 2003) or the influence of other minerals in the sand (Degryse et al., 2005; Freestone et al., 2005) that are characterized by less radiogenic strontium. The low variation in $^{143}Nd/^{144}Nd$ for Levantine and HIMT (Egyptian) primary glass, with ε Nd values between −6.0 and −5.1, was consistent with the values given for Nile dominated sediments in the Eastern Mediterranean (Weldeab et al., 2002; Stanley et al., 2003). It is well established that the heavy minerals in eastern Mediterranean coastal sands South of Akko are very homogeneous and dominated by amphibole and pyroxene derived from the Nile (Emery and Neev, 1960). Though it is not possible to directly compare the ε Nd of the glasses exactly with sea-floor sediment, the correspondence for the Levantine and Egyptian glasses is remarkable. These analyses hence provide a regional signature for the Nd isotopic composition of eastern Mediterranean glass, from the Nile delta up north to the Levant.

Moreover, it is clear from the study of for example Goldstein et al. (1984), Grousset et al. (1988) and Weldeab et al. (2002) that the Sr and Nd ratios of sediments in the Mediterranean vary significantly, offering a great potential to distinguish primary glass from Egypt and the Levant from other primary glass producers. If production units situated in the western Mediterranean or north-western Europe use a local sand raw material, the glass will reflect a local Sr−Nd geochemical signature. The Nd isotopic composition of particulates from major river systems and atmospheric dusts was studied by Goldstein et al. (1984). River water and wind are the primary media by which surface material is eroded, mixed and transported. It was shown there that the Nd isotopic composition of the sediment input of most river systems into the oceans is fairly homogenous, where the material flux from the continents has an average ε Nd of −11.4. For instance, the sediment load of the river Cam (UK) discharging into the North Sea has ε Nd = − 10.9. This homogeneity is explained by either thorough mixing of isotopically heterogeneous material by erosion processes on a short time scale or overall sampling of crustal segments with similar compositions (Goldstein et al., 1984). Conversely, the sediment load of the Nile has an exceptional Nd isotopic composition, dominated by East African volcanic rocks from the Ethiopian Plateau. This leads to an average ε Nd of −3.3 for eastern Mediterranean sediments. Sediments dominated by input from wind-blown Saharan dusts, on the other hand, show a typical isotopic composition with ε Nd = − 12 to −13.5. Moreover, detrital deep-sea surface sediments in the North Atlantic and the Mediterranean were measured by Frost et al. (1986) and Grousset et al. (1988). This study showed that the sediments in the east-west axis of the Mediterranean ranged from −10.1 at Gibraltar to −3.3 at the mouth of the river Nile, with a maximum of +4.6 of the Greek−Turkish coast. Western Mediterranean sediments around the Spanish and southern French coasts have a homogeneous composition between −9.7 and −10.1. Sediments around the Italian coasts, show a range in between ε Nd = − 12.4 and −7.6 in the Tyrrhenian Sea, and an ε Nd value of −10.8 in the Adriatic Sea. Sediments of the coast of Sicily range between −5.0 and −6.8. The varying values around the Italian peninsula are explained by the influence of African aerosols and Saharan dust (Grousset et al., 1988).

The data obtained in earlier studies correspond well to the results for the sand samples in this study (Fig. 2). Sands BRILL 674, BRILL 679 and BRILL 681 from the Levant
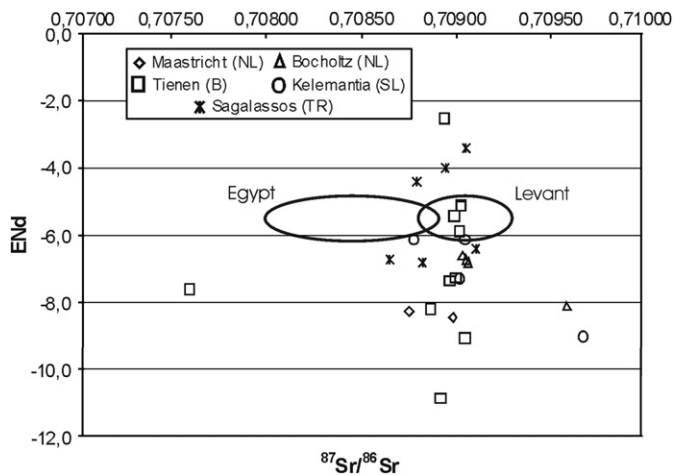
Fig. 2. $^{87}Sr/^{86}Sr$ versus ε Nd biplot of the analytical data for glass obtained in this study. The typical composition of primary glass from the Levant and Egypt is indicated (Freestone et al., submitted for publication; Degryse et al., 2006a,b).

show a composition of ε Nd = − 4.8 to −1.0, consistent with the literature (Goldstein et al., 1984; Frost et al., 1986; Grousset et al., 1988). In addition, the former two sands have ε Nd values (both −4.8) consistent with earlier analyses of primary glass from the Levant (Degryse et al., 2006a,b) and were considered silica raw materials for glass production (Brill, 1988). The latter sample has a higher ε Nd (−1.0) than archaeological glass analyzed in previous studies, but also shows a higher feldspar content (Brill, 1999). The $^{87}Sr/^{86}Sr$ ratios of the Levantine sands vary between 0.70920 and 0.71159. These results are consistent with analyses by Brill and Fullagar (Brill, 2006). Samples with a higher CaO content and with lime present in the form of sea shell, have a $^{87}Sr/^{86}Sr$ close to modern sea water, while the sample with the lowest CaO and hence shell content, has the highest $^{87}Sr/^{86}Sr$ value, reflecting the influence of other minerals with higher radiogenic Sr isotope signatures.

Sand samples BRILL 4553, BRILL 4556 and BRILL 4554 from the beach near the river Volturno show ε Nd = − 4.4 to −9.9, values consistent with the literature (Goldstein et al., 1984; Frost et al., 1986; Grousset et al., 1988). The former two samples are sands chemically suitable for glass production (Brill, 1999) and have the lower ε Nd values (−6.9 and −9.9). The latter sand sample is coarse black sand, with a very high content in heavy minerals (diopside, augite, hydrogrossular) and is not suitable as a glass raw material (Brill, 1999). It has the highest ε Nd value of −4.4. The Sr isotopic signature of the Volturno sands varies between 0.70796 and 0.70969. These results are consistent with analyses by Brill and Fullagar (Brill, 2006). The coarse black sand BRILL 4554 has the lowest $^{87}Sr/^{86}Sr$ signature, reflecting the influence of the heavy minerals with less radiogenic strontium than the other samples. Sand samples BRILL 4556 and BRILL 4553 contain some shell and have signatures close to modern sea water, but the latter sample shows some influence of other minerals (likely feldspars) with a higher radiogenic Sr isotope signature.

Sand samples FAZDA 1 and FAZDA 2 from Wadi-el-Natrun in Egypt and TIE2-A-7 and ANT-M12 from Belgium have $^{87}Sr/^{86}Sr$ = 0.70951, 0.71046, 0.71487, and 0.71923, respectively. These $^{87}Sr/^{86}Sr$ values reflect the presence of minerals with higher radiogenic strontium than modern sea water. Therefore, they are clearly not influenced by shell material, which is absent in sand. Moreover, the CaO contents of these sands are less than 1%. ε Nd of the Belgian samples (ε Nd = − 11.4 and −12.7) is consistent with values from the literature for north-western Europe and the North Sea (Goldstein et al., 1984). No reference values are available for the region of Wadi-el-Natrun (ε Nd = − 6.8 and −8.6, Table 2).

The glass analyzed has not been deliberately colored or opacified, avoiding contamination of the primary raw materials of the base glasses by materials from other sources. Roman glass from Sagalassos, Tienen, Bocholtz and Kelemantia (samples TIE11, TIE17, TIE24, TIE41, TIE50, SAG574, SAG575, SAG717, KEL229/88, KEL82/91) has a Sr−Nd isotope signature identical or very similar to the composition of the known 4th−8th century AD primary production locations in the Levant and Egypt (ε Nd = − 5.0 to −6.0, Fig. 2). These values may also be compared to ε Nd signatures of the Levantine sands in this study and of the eastern Mediterranean sands in Goldstein et al. (1984), Frost et al. (1986) and Grousset et al. (1988). It is therefore likely that primary production was taking place in the eastern Mediterranean also in the 1st−3rd century AD, although not necessarily in the same geographical area as the aforementioned primary glass units. Especially samples TIE11, SAG574, SAG575 and SAG717, with ε Nd between −4.4 and −2.5, may have their origin in the eastern Mediterranean, but their silica raw materials would not originate from exactly the same locations as the primary glass factories studied by Degryse et al. (2006a,b) and Freestone et al. (submitted for publication). The $^{87}Sr/^{86}Sr$ ratios of these glass types are very homogeneous, between 0.70877 and 0.70905. This is nearly identical to the Sr signature of the sands and points to shell as a lime source of the glass.

Conversely, glass from Maastricht, Tienen, Bocholtz and Kelemantia clearly has an exotic Sr−Nd isotopic composition, not corresponding to sediment signatures from the eastern Mediterranean basin (Fig. 2). Samples TIE12, TIE35, TIE37, TIE45, TIE48, BO106, BO109, BO123, KEL229/06, SAG573, SAG709, SAG718, MA1C and MA1B have ε Nd −6.4 and −10.8 and $^{87}Sr/^{86}Sr$ ratios between 0.70865 and 0.70910. This Nd isotopic composition is inconsistent with any sediment in the eastern Mediterranean but for the lower ε Nd values 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. However, for the intermediate ε Nd values of some of this glass (ε Nd between −6.4 and −6.8), it cannot be discarded that recycling of glass or mixing of primary sources from the eastern and western Mediterranean area has given the material its isotopic composition. Moreover, on the basis of the limited amount of sand samples analyzed in this study, it

may prove difficult to source glass of this intermediate isotopic composition, as it may correspond to several sand signatures. The Sr isotope signature of this glass is very homogeneous, but not always identical to that of the sands analyzed. Moreover, the CaO of the sands is often too low for glass production (for example Brill, 1999). This may be an indication of the intentional addition of shell as a lime source for the glass as suggested by Wedepohl and Baumann (2000) and in particular for sand from the river Volturno by Silvestri et al. (2006).

Some glass samples show exotic Sr−Nd isotopic signatures. For instance, sample TIE 49 has ε Nd = − 7.6 and $^{87}Sr/^{86}Sr = 0.70759$. This is consistent with the Nd isotopic composition of Egyptian sands and that of previously analyzed early-Byzantine/Islamic Egyptian glass (Freestone et al., submitted for publication; Degryse et al., 2006a). This may be a suggestion towards the primary origin of this sample. Sample BO 119 has ε Nd = − 8.1 and $^{87}Sr/^{86}Sr = 0.70958$. Sample KEL 234/88 has a signature of ε Nd = − 9.0 and $^{87}Sr/^{86}Sr = 0.70966$. The Nd signature of these glass samples suggests an origin in the Western Roman Empire. The Sr signature points to the influence of a Sr source different from shell or limestone, characterized by a higher radiogenic Sr isotopic composition than modern seawater.

6. Conclusion

It has been demonstrated that the combined use of Sr and Nd isotopes allows the origin of primary glass to be traced. Nd is characteristic of the mineral fraction other than quartz in the silica raw material used for the glass, while Sr is in most cases characteristic of the lime component, either attributed to the sand raw material or as a separate constituent in the form of shell. Eastern Mediterranean primary glass has a Nile-dominated Mediterranean Nd isotopic composition (ε Nd higher than −6.0), while glass with a primary production location in the western Mediterranean or north-western Europe should have a different Nd isotope signature (ε Nd lower than −7.0). Most Roman glass has a homogeneous $^{87}Sr/^{86}Sr$ signature close to the modern sea water composition, likely caused by the (intentional) use of shell as glass raw material. It can hence be proven what Pliny the Elder suggested in his Natural History: primary glass was also manufactured outside the Levant and Egypt in the 1st−3rd century AD.

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