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ISOTOPES ON THE BEACH, PART 2: NEODYMIUM ISOTOPIC ANALYSIS FOR THE PROVENANCING OF ROMAN GLASS-MAKING*

D. BREMS,[1]† M. GANIO,[1] K. LATRUWE,[2] L. BALCAEN,[2] M. CARREMANS,[1] D. GIMENO,[3] A. SILVESTRI,[4] F. VANHAECKE,[2] P. MUCHEZ[1] and P. DEGRYSE[1]

[1]*Division of Geology, Department of Earth and Environmental Sciences, K.U. Leuven, Celestijnenlaan 200E, B-3001 Leuven, Belgium*

[2]*Department of Analytical Chemistry, Ghent University, Krijgslaan 281—S12, B-9000 Ghent, Belgium*

[3]*Departament de Geoquímica, Petrología i Prospecció Geològica, Facultat de Geologia, Universitat de Barcelona, 08028 Barcelona, Spain*

[4]*Dipartimento di Geoscienze, Università di Padova, Via Gradenigo 6, 35131 Padova, Italy*

In this study, we have evaluated the applicability of Nd isotopic analysis for the provenancing of Roman glass and we present a database of Nd isotopic compositions of possible sand raw materials from the western Mediterranean, as a means of comparison for the growing number of isotopic studies on ancient glass. The $^{143}Nd/^{144}Nd$ *isotope ratio of sands is a good indicator for their geological (and sometimes geographical) provenance. The use of the isotopic signature of Nd as a proxy for the source of silica in glass is, however, not always straightforward because of the possible overlap of signatures from different suppliers.*

KEYWORDS: NEODYMIUM, ISOTOPES, PROVENANCE STUDIES, ROMAN, NATRON GLASS, RAW MATERIALS, BEACH SAND, WESTERN MEDITERRANEAN

INTRODUCTION

The provenance determination of ancient natron glass is one of the most challenging problems in the field of archaeometry. A good understanding of the production processes and the sources of the raw materials used to produce them can provide very important insights into the organization of ancient economies and the distribution of trading routes. However, whereas the physicochemical analysis of other commodities such as ceramics and marble is well advanced, this is not the case for glass (Wilson and Pollard 2001). The main reason for this is the complex nature of glass itself and the non-straightforward relationship between glass and the raw materials from which it is made. Natron glass is essentially a mixture of three components: quartz-rich sand, an evaporitic mineral flux rich in soda and a source of lime, either shell or limestone. During glass melting many characteristics of the raw materials—such as mineralogy, grain size and shape—are lost, so that only bulk chemical data can be used. Unfortunately, the major elemental composition of ancient natron glass was found to be relatively uniform and specific objects could hardly ever be uniquely assigned to their origin (Sayre and Smith 1961; Freestone 2006; Wedepohl *et al*. 2011a). In the past decade, several attempts have been made to determine the provenance of ancient glass on the basis of trace elements, rare earth element patterns and isotopic signatures of O, Pb, Sr and Nd (e.g., Wedepohl and Baumann 2000; Freestone *et al*. 2003; Henderson *et al*. 2005; Shortland *et al*. 2007; Degryse and

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†Corresponding author: email dieter.brems@ees.kuleuven.be

Schneider 2008; Degryse and Shortland 2009; Degryse *et al*. 2009a). In particular, trace elements and Sr–Nd isotopic signatures appear to be promising tracers for raw materials in glass production, since they may show systematic variations around the Mediterranean Sea as a consequence of the differing geological environment. The use of Sr isotope ratios as a provenance indicator for the lime source used in Roman glass-making is discussed elsewhere (Brems *et al*. 2012a).

Nd isotope ratios are a powerful tracer for detritus in sedimentary basins (e.g., Banner 2004). Sand being the major component of Roman natron glass, Nd isotope ratios can be useful to determine its provenance. Over recent years, an increasing amount of Nd isotope ratio data of ancient glasses has become available (Degryse and Schneider 2008; Degryse *et al*. 2009b, 2010; Henderson *et al*. 2009, 2010; Ganio *et al*. in press a,b). However, until now there has been no database of Nd isotopic signatures of possible sand raw materials available for comparison. In this paper, we present such a database for beach sand deposits from the western part of the Mediterranean area.

THE Sm–Nd ISOTOPIC SYSTEM

Samarium and neodymium are both light rare earth elements (LREE) belonging to the lanthanide series. Both Sm and Nd have seven naturally occurring isotopes. The applicability of the Sm–Nd isotopic system to geochemical studies is the result of the radioactivity of ^{147}Sm, which decays through the emission of an alpha particle to ^{143}Nd.

Variations in the isotopic composition of Nd result from the radiogenic growth of ^{143}Nd in reservoirs with varying Sm/Nd ratios (DePaolo and Wasserburg 1976). These variations in Nd isotopic composition are traditionally expressed relative to the stable, non-radiogenic isotope ^{144}Nd (the ^{143}Nd/^{144}Nd ratio). However, Nd and Sm are only fractionated from one another to a very small extent during partial melting and crystallization, because of their very similar ionic radii and, consequently, similar geochemical properties. This results in a very small range of different ^{143}Nd/^{144}Nd ratios (0.510–0.514; Best 2003). To make these small differences more apparent, the isotopic composition of a system is frequently shown normalized to the chondritic meteorite standard in the form of $\varepsilon_{\mathrm{Nd}}$ values:

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

where CHUR stands for Chondritic Uniform Reservoir, which represents the bulk earth Nd isotopic composition deduced from measurements in chondrites (DePaolo and Wasserburg 1976; Jacobsen and Wasserburg 1980). The present-day chondritic value of ^{143}Nd/^{144}Nd is 0.512638.

Neodymium is a little bit less compatible than samarium. Therefore, Sm is preferentially incorporated into the mantle. Nd will be more enriched in a partial melt and, as a result, Nd will be relatively concentrated in the earth's crust (Wedepohl 1995). The mantle is marked by higher Sm/Nd ratios and, hence, the ^{143}Nd/^{144}Nd ratio (and the $\varepsilon_{\mathrm{Nd}}$ value) is higher in the mantle than in the crust. Mid-ocean ridge basalts tend to have the highest $\varepsilon_{\mathrm{Nd}}$ values, of up to 12 (Goldstein and Hemming 2003). Young volcanic arcs show $\varepsilon_{\mathrm{Nd}}$ values of 0–7 (Grousset *et al*. 1988, 1998). Typical continental crust has $\varepsilon_{\mathrm{Nd}}$ values lower than the bulk earth (that is, between about –20 and –5) depending on the age of the rocks (Goldstein *et al*. 1984). The oldest parts of the continental crust, such as the Precambrian craton of Greenland and Mauritania, can have $\varepsilon_{\mathrm{Nd}}$ values as low as –54 (Grousset *et al*. 1998; Banner 2004).

The application of variations in the isotopic composition of Nd to sediments is based on the fact that accumulated clastic sediments are basically just the mechanical disintegration products of igneous, metamorphic and older sedimentary rocks exposed in the source areas (Goldstein *et al*. 1984; DePaolo 1988; Grousset *et al*. 1988; Jeandel *et al*. 2007, and references therein). The Nd isotopic signature of the source terrains is generally preserved in the resulting sediments. Consequently, variations in the isotopic composition of Nd are very useful as tracer in sediment provenance studies (Linn and DePaolo 1993; Banner 2004; Grousset and Biscaye 2005).

THE Nd ISOTOPIC COMPOSITION OF ANCIENT GLASS

Together with the other light rare earth elements, Sm and Nd are enriched in accessory minerals, such as apatite, titanite, allanite, perovskite, xenotime and monazite (Wedepohl 1978; Foster and Vance 2006; McFarlane and McCulloch 2007). They also occur in trace concentrations in many rock-forming minerals, such as feldspar, biotite, amphibole and clinopyroxene, in which they replace major ions (Best 2003; Faure and Mensing 2005). Because of the large difference between the ionic radii of Sm^{3+} (0.104 nm) and Nd^{3+} (0.108 nm) and that of Si^{4+} (0.026 nm) (Shannon 1976), quartz contains virtually no Sm or Nd. The concentration of Nd in siliciclastic sediments and sedimentary rocks is usually in the order of 5–50 ppm (Faure and Mensing 2005). In limestone and shell, the absolute Nd content is even lower (between 0.5 and 10 ppm: Wedepohl 1978; Faure and Mensing 2005; Wedepohl *et al*. 2011b). Natron appears to contain hardly any Nd—that is, of the order of 20–40 ppb Nd (Wedepohl *et al*. 2011b; Shortland *et al*. unpublished data)—and consequently has no influence on the Nd budget and the Nd isotopic signature of the glass. The Nd in Hellenistic, Roman and Early Byzantine period glass (i.e., natron-based glass) thus originates from the heavy or non-quartz mineral fraction of the silica raw material (Degryse and Schneider 2008).

Due to the varying sediment influx from the Nile (fluvial), the Sahara (aeolian) and the European continent (fluvial), the Nd isotopic composition of deep-sea sediments in the eastern Mediterranean Sea varies significantly. The River Nile has an exceptionally high ε_{Nd} value in its sediment load, of around −1 (Weldeab *et al*. 2002; Scrivner *et al*. 2004), as it is dominated by young volcanic rocks from the Ethiopian Plateau. Sediments dominated by input from wind-blown Saharan dusts, on the other hand, show typically low (old) ε_{Nd} values of around −13 (Grousset *et al*. 1988, 1998; Henry *et al*. 1994). Sediments entering the Ionian Sea from the Calabrian Arc and the Adriatic Sea are characterized by low ε_{Nd} values of around −11.06 (Weldeab *et al*. 2002). Aegean Sea sediments show average ε_{Nd} values of around −7.89 (Weldeab *et al*. 2002). When these sediments enter the Mediterranean Sea, they are redistributed by the dominant sea currents (Pinardi and Masetti 2000; Weldeab *et al*. 2002; Hamad *et al*. 2006). For example, the Nile sediments are transported eastwards along the Egyptian and Israeli coasts, possibly up to Turkey. Because of the combination of all these different sources and currents, the isotopic pattern of the eastern Mediterranean surface sediments shows a pronounced east–west gradient, from as high as $\varepsilon_{Nd} = -1$ at the mouth of the River Nile and the coasts of Egypt and Israel to $\varepsilon_{Nd} = -12$ south of Sicily (Goldstein *et al*. 1984; Frost *et al*. 1986; Weldeab *et al*. 2002). Sediment samples from Alexandria (Egypt) show ε_{Nd} values between −8 and −6 (Freydier *et al*. 2001; Tachikawa *et al*. 2004). These values are significantly lower than the pure Nile end-member, and suggest mixing between Nile particles and sediment with a Sahara origin coming from the west with the dominant sea currents. Raw natron glass from the known primary production centres in Egypt and Syro-Palestine has a relatively small variation in ε_{Nd}, with values between −6.0 and −5.1 (Degryse and Schneider 2008; Freestone *et al*. unpublished data).

In the western Mediterranean, the distribution of the Nd isotopic signatures is less well known. Only a few results for particulates from the Rhône and the Po Rivers and deep-sea sediments near Gibraltar and the southern French coasts are published, and they all show rather low signatures, with ε_{Nd} between –10.8 and –9.7 (Frost *et al*. 1986; Grousset *et al*. 1988; Henry *et al*. 1994). One result from the Tyrrhenian Sea shows an ε_{Nd} value of –7.6 (Frost *et al*. 1986). Although the number of analyses is small, there seems to be a significant difference in Nd isotopic signatures between the easternmost part of the Mediterranean Sea and the rest of the basin. If the same regional variations in Nd isotopic signatures occur in sand deposits across the Mediterranean, this can be used to trace ancient glass artefacts to their primary origin.

OBJECTIVES

Nd in ancient glass is incorporated with the source of silica. The variation in Nd isotopic signature observed in deep-sea sediments across the Mediterranean Sea offers great potential to distinguish possible sand raw materials and primary glass from the eastern and western part of the basin. However, it is of course not possible to directly compare the Nd isotopic signature of glass to that of seafloor sediments. Sand deposits are often much more locally derived and it is not certain that these beach sands show the same regional variation in Nd isotopic composition.

In this study, we have therefore investigated whether variations in Nd isotopic signatures can distinguish sand deposits around the Mediterranean. Seventy-six beach sand samples from Spain, France and Italy (Fig. 1) were analysed for their Nd isotopic composition and we have assessed whether the regional pattern in Nd isotopic signatures of deep-sea sediments can be recognized in these beach sands. Some of these sands have been previously identified as suitable raw materials for Roman natron glass production (Brems *et al*. 2012b, in press a).

METHODS

Backshore sediment samples were collected from 76 sandy beaches along the coasts of Spain, France and Italy. The sample locations are shown in Figure 1, and their geographical coordinates are given in Table 1. About 2 kg of sediment sample was collected from the upper 10 cm of sand, representing the contemporaneous sedimentation layer.

For separation of Nd from the sample solutions, the sequential extraction procedures developed by Pin *et al*. (1994), Pin and Zalduegui (1997) and Míková and Denková (2007) were combined and slightly modified. An extensive evaluation of the isolation protocol used is given by Ganio *et al*. (in press c). Nd isotope ratios were determined using a Thermo Scientific Neptune multi-collector ICP–MS instrument, equipped with a micro-flow PFA-50 Teflon nebulizer coupled on to a spray chamber consisting of a combination of a cyclonic and a Scott-type spray chamber. The measurements were carried out in static multi-collection mode. The JNdi-1 standard was used to correct for instrumental mass discrimination during the measurements of ^{143}Nd/^{144}Nd. The Nd concentration of all samples and the standard were matched to 300 μg l^{-1} Nd. The intensity for $^{147}Sm^{+}$ was measured to correct for potentially remaining isobaric interferences from $^{144}Sm^{+}$ on the corresponding Nd nuclide. The ^{143}Nd/^{144}Nd isotope ratios were measured with an average internal precision (2σ) of 0.0000219.

The determination of the Nd concentration in the samples was carried out using a Thermo-Scientific Element XR sector field ICP–MS instrument, in its standard configuration. In order to maintain maximum sensitivity, the instrument was operated in low-resolution mode. The Nd concentration was determined by measuring the intensity of ^{143}Nd, as both isobaric overlap and

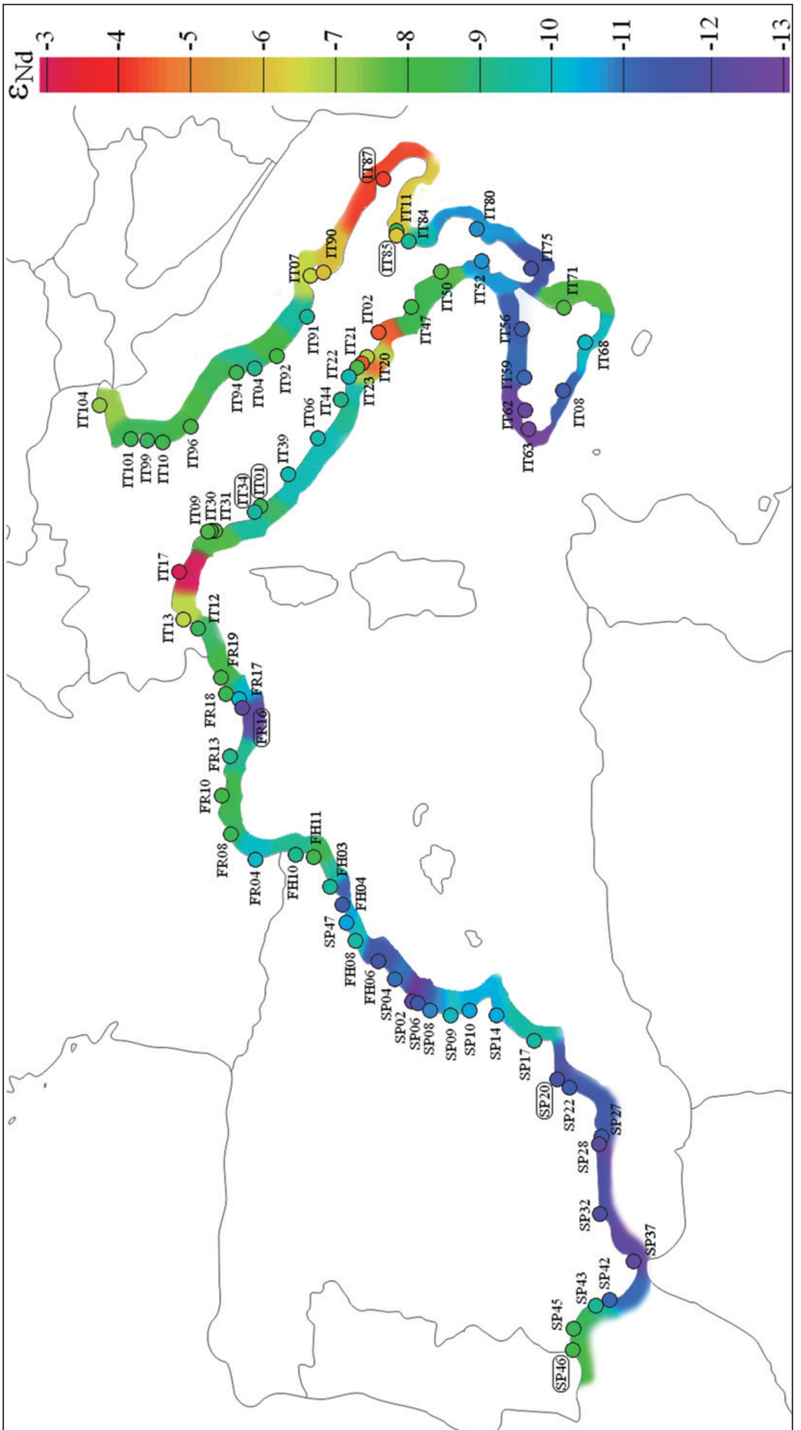

Figure 1 *A map of the western Mediterranean, showing the sample locations and the* ε_{Nd} *values of the beach sands analysed. Sand samples IT34, IT85 and IT87 have previously been identified as good glass-making sands (Brems* et al. *2012b). Sands SP46, SP20, FR16 and IT01 can be used to make Roman natron glass after the addition of extra lime to the glass batch.*

Table 1 *The sampling locations and results of the Nd isotopic analysis of beach sands from Spain, France and Italy*

Sample	*Location*	*Latitude (°N)*	*Longitude (°E)*	$^{143}Nd/^{144}Nd$	2σ	ε_{Nd}	*Nd (ppm)*
Spain							
SP46	Isla Canela	N37°10′34.08″	W007°21′15.58″	0.512229	0.000070	–7.99	9.2
SP45	Mazagón	N37°07′44.86″	W006°49′29.42″	0.512193	0.000042	–8.68	5.6
SP43	Sanlúcar de Barrameda	N36°46′48.43″	W006°21′59.54″	0.512167	0.000037	–9.20	5.6
SP42	El Puerto de Santa Maria	N36°34′40.86″	W006°13′38.77″	0.512076	0.000051	–10.96	7.3
SP37	Carteya-Guadarranque (San Roque)	N36°10′51.65″	W005°24′45.42″	0.512007	0.000073	–12.30	5.8
SP32	Málaga	N36°43′11.69″	W004°24′14.53″	0.512026	0.000032	–11.93	14.6
SP28	Adra	N36°44′38.17″	W003°00′45.75″	0.512012	0.000050	–12.22	n.d.
SP27	Almerimar	N36°42′07.46″	W002°48′03.33″	0.512049	0.000090	–11.50	9.4
SP22	Las Marinas de Vera (Garrucha)	N37°11′50.56″	W001°48′44.82″	0.512057	0.000037	–11.33	9.1
SP20	El Rubial	N37°24′02.10″	W001°35′33.26″	0.512035	0.000050	–11.76	7.0
SP17	Mil Palmeras	N37°52′54.13″	W000°45′13.59″	0.512141	0.000053	–9.69	5.4
SP14	Villajoyosa	N38°30′23.71″	W000°13′38.11″	0.512109	0.000055	–10.32	n.d.
SP10	Cullera	N39°09′23.94″	W000°14′24.51″	0.512100	0.000047	–10.50	6.9
SP09	Valencia	N39°24′27.55″	W000°19′54.16″	0.512126	0.000059	–9.99	5.5
SP08	Sagunto	N39°39′36.15″	W000°12′34.58″	0.512090	0.000047	–10.70	n.d.
SP06	Castellón de la Plana	N39°59′44.86″	E000°01′43.78″	0.512044	0.000036	–11.58	12.6
SP02	Benicassim (Castellon)	N40°02′45″	E000°03′56″	0.512018	0.000101	–12.10	n.d.
SP04	Benicarló	N40°25′09.84″	E000°26′13.06″	0.512075	0.000035	–10.98	n.d.
FH06	Riumar	N40°43′49″	E000°50′30″	0.512049		–11.49	9.2
FH08	Cambrils	N41°03′57.6″	E001°04′06.3″	0.512133	0.000082	–9.84	16.3
SP47	Coma-Ruga	N41°11′00.68″	E001°32′46.71″	0.512104	0.000058	–10.42	8.1
FH04	Castelldefels	N41°15′51.7″	E001°57′02.0″	0.512065	0.000091	–11.18	12.2
FH03	Vilassar de Mar	N41°30′46.6″	E002°24′46.3″	0.512161		–9.30	10.9
FH11	Platja d’Aro	N41°49′02.08″	E003°04′11.10″	0.512193		–8.68	3.6
FH10	Sant Pere Pescador	N42°11′21.43″	E003°06′38.18″	0.512166	0.000088	–9.20	6.6

France							
FR04	Le Barcarès	N42°46′57.21″	E003°02′20.30″	0.512124	0.000063	−10.03	14.5
FR08	Le Grau-d'Agde	N43°16′57.91″	E003°26′59.95″	0.512190	0.000058	−8.74	17.0
FR10	Saintes-Maries-de-la-Mer	N43°26′57.43″	E004°24′57.79″	0.512212	0.000065	−8.31	16.2
FR13	L'Estaque, Plage des Corbières	N43°21′27.36″	E005°17′26.53″	0.512170	0.000121	−9.14	n.d.
FR16	Les Bormettes, La Londe-les-Maures	N43°07′16.69″	E006°15′38.86″	0.512002	0.000043	−12.40	9.1
FR17	Cavalaire-sur-Mer	N43°10′57.28″	E006°32′28.29″	0.512118	0.000087	−10.14	11.7
FR18	Saint-Aygulf	N43°24′31.78″	E006°44′06.80″	0.512203	0.000058	−8.48	n.d.
FR19	Cannes	N43°32′55.72″	E007°00′13.63″	0.512227	0.000113	−8.03	8.0
Italy							
IT12	Pigna, Andora SV	N43°56′49.79″	E008°08′27.84″	0.512185	0.000090	−8.83	7.7
IT13	Finale Pia, Finale Ligure	N44°10′18.48″	E008°21′30.08″	0.512292	0.000070	−6.75	10.2
IT17	Sestri Levante	N44°16′21.51″	E009°23′35.56″	0.512482	0.000049	−3.05	n.d.
IT09	Torre del Lago Puccini, Viareggio	N43°49′28.23″	E010°15′15.36″	0.512236	0.000070	−7.84	n.d.
IT30	Migliarino, Vecchiano	N43°47′33.04″	E010°15′55.95″	0.512207	0.000073	−8.41	12.1
IT31	Marina di Pisa	N43°40′00.06″	E010°16′30.89″	0.512234	0.000086	−7.87	15.0
IT34	Torre del Sale, Piombino	N42°57′14.50″	E010°36′00.71″	0.512156	0.000028	−9.40	7.0
IT01	Cala Violina	N42°50′19.53″	E010°46′29.46″	0.512184	0.000009	−8.86	6.6
IT39	Montalto Marina	N42°19′41.71″	E011°34′29.44″	0.512133	0.000088	−9.85	n.d.
IT06	Ostia	N41°43′41.45″	E012°16′40.78″	0.512138	0.000037	−9.76	n.d.
IT44	Terracina	N41°16′50.95″	E013°11′47.24″	0.512168	0.000106	−9.16	11.1
IT22	Gaeta (BRILL 4556; Degryse and Schneider 2008)	N41°12′47″	E013°32′33″	0.512133	0.000010	−9.90	25.2
IT23	Volturno, coastal strip of Mondragone (MN1; Silvestri *et al*. 2006)	N41°07′32.85″	E013°51′55.31″	0.512233	0.000054	−7.90	39.1
IT21	Castel Volturno, mouth of Volturno River (BRILL 4554; Degryse and Schneider 2008)	N41°01′15″	E013°55′50″	0.512411	0.000006	−4.40	296.3
IT20	Licola Mare (BRILL 4553; Degryse and Schneider 2008)	N40°52′5″	E014°02′37″	0.512284	0.000009	−6.90	59.5
IT02	Amalfi	N40°37′07.16″	E014°34′38.54″	0.512415	0.000008	−4.35	n.d.
IT47	Foce, Marina di Casal Velino	N40°09′41.95″	E015°08′41.66″	0.512203	0.000070	−8.48	n.d.

Table 1 (Continued)

Sample	Location	Latitude (°N)	Longitude (°E)	$^{143}Nd/^{144}Nd$	2σ	ε_{Nd}	Nd (ppm)
IT50	Paola	N39°22′00.36″	E016°01′38.86″	0.512243	0.000146	−7.71	n.d.
IT52	Pizzo	N38°46′20.22″	E016°11′50.19″	0.512086	0.000051	−10.77	n.d.
IT56	Scafa, Brolo	N38°09′19.65″	E014°47′57.53″	0.512062	0.000035	−11.23	n.d.
IT59	San Nicola l'Arena	N38°00′35.31″	E013°37′26.32″	0.512072	0.000110	−11.04	7.3
IT62	Castellammare del Golfo	N38°01′28.21″	E012°54′20.29″	0.511999	0.000102	−12.47	n.d.
IT63	Marausa, Trapani	N37°56′05.62″	E012°28′53.98″	0.511979	0.000114	−12.85	6.7
IT08	Torre Salsa	N37°22′12.78″	E013°19′01.45″	0.512067	0.000116	−11.14	n.d.
IT68	Marina di'Acate	N36°58′58.28″	E014°21′31.86″	0.512122	0.000051	−10.07	n.d.
IT71	Catania	N37°27′08.69″	E015°05′11.40″	0.512235	0.000092	−7.86	13.4
IT75	Bova Marina	N37°55′37.60″	E015°53′24.66″	0.512042	0.000057	−11.63	n.d.
IT80	Steccato	N38°55′58.25″	E016°55′12.79″	0.512087	0.000045	−10.75	38.7
IT84	Lido di Policoro	N40°11′53.62″	E016°43′37.65″	0.512164	0.000116	−9.24	7.7
IT85	Metaponto Lido	N40°20′34.11″	E016°49′23.68″	0.512325	0.000078	−6.11	10.5
IT11	Castellaneta Marina	N40°27′45.63″	E016°56′18.41″	0.512194	0.000011	−8.66	n.d.
IT87	Masseria Maime	N40°33′27.00″	E018°02′36.73″	0.512424	0.000076	−4.17	10.7
IT90	Siponto, Manfredonia	N41°35′32.58″	E015°53′41.45″	0.512329	0.000089	−6.03	n.d.
IT07	Gargano	N41°56′11.64″	E015°56′50.84″	0.512245	0.000036	−7.67	n.d.
IT91	Campomarino	N41°58′39.04″	E015°01′52.56″	0.512160	0.000033	−9.32	7.2
IT92	Pescara	N42°28′28.71″	E014°12′40.47″	0.512222	0.000071	−8.12	n.d.
IT04	San Benedetto del Tronto	N42°57′57.45″	E013°52′48.24″	0.512173	0.000011	−9.07	n.d.
IT94	Civitanova Marche	N43°17′44.25″	E013°44′30.80″	0.512199	0.000066	−8.57	8.5
IT96	Gabicce Mare	N43°58′03.83″	E012°44′25.39″	0.512230	0.000092	−7.95	n.d.
IT10	Casalborsetti	N44°33′17.84″	E012°17′00.57″	0.512211	0.000059	−8.34	n.d.
IT99	Lido delle Nazioni	N44°43′54.17″	E012°14′31.82″	0.512187	0.000083	−8.79	n.d.
IT101	Boccasette	N45°01′37.79″	E012°25′25.92″	0.512209	0.000063	−8.37	n.d.
IT104	Bibione, Lignano Sabbiadoro	N45°37′53.58″	E013°03′23.80″	0.512274	0.001189	−7.10	n.d.
Shell	Mixture of shell fragments from southern France and north-west Italy			0.512297	0.001068	−6.66	1.0

interference by oxide or hydroxide ions of other elements present in the sample are negligible for this nuclide. External calibration (based on four standards, with concentrations ranging between 0.5 and 10 μg l^{-1} Nd) was used for quantification, and the use of Ru as internal standard allowed us to correct for potential matrix effects, signal drift and instrument instability. All standard solutions were prepared by diluting 1 g l^{-1} single-element standards with 0.3 M sub-boiled HNO_3. The sample solutions obtained after digestion were appropriately diluted prior to ICP–MS analysis, resulting in samples with a final acid concentration of 0.3 M HNO_3, a dilution factor of 250 and an internal standard (Ru) concentration of 3 μg l^{-1}. Procedure blanks were used for blank correction.

RESULTS AND DISCUSSION

The results are shown in Table 1 and Figure 1. The ε_{Nd} values of the beach sands analysed are broadly related to the large geological regions and vary relatively gradually along the coastlines (Fig. 1). The Spanish and French sands all show relatively low ε_{Nd} values, from –12.40 to –7.99, in close agreement with the data from the deep-sea sediments. The Italian sands, however, show a wide range of ε_{Nd} values, between –12.85 and –3.05. The Nd concentration of most sands lies between 3 and 60 ppm Nd. One sample (IT21), however, contains 296 ppm Nd. In this section, we will discuss the isotope ratio results in relation to the composition of the beach sands and their broader geological setting. A more extensive description of the composition of the beach sands analysed and the local geology is published elsewhere (Brems *et al*. 2012b).

The Iberian Massif and the Betic Cordillera

In southwestern Spain, the beach sands (SP46, SP45 and SP43) are mostly derived from the crystalline basement rocks of the Iberian Massif and are characterized by ε_{Nd} values between –9.20 and –7.99. In the Bay of Cádiz (SP42), detritus from Triassic–Neogene sedimentary rocks of the western Subbetic Zone make up the local beach sands. Here, the ε_{Nd} value has fallen to –10.96. This lower Nd isotopic signature can be attributed to the starting influence of the Internal Zones of the Betic Cordillera. This part of the Betic mountain range stretches along the southern coast of Spain from the Gibraltar Promontory to Cartagena. It is mostly composed of Palaeozoic metasedimentary successions of the Malaguide, the Alpujárride and the Nevado–Filábride Complexes. All of the beach sands analysed along this coast (SP37, SP32, SP28, SP27, SP22 and SP20) have rather low ε_{Nd} values, between –12.30 and –11.33.

In the southern Gulf of Alicante, sandy sediments (SP17) are derived from the recycling of Miocene to Quaternary post-orogenic siliciclastic and carbonaceous sedimentary rocks. The ε_{Nd} value of the sands in this area is –9.69. In the northern part of the Gulf of Alicante, the beach sands are the erosion products of Jurassic to Miocene limestones and sandstones of the Prebetic External Zone of the Betic Cordillera. The ε_{Nd} value remains relatively low, at –10.32.

The Iberian System, the Catalonian Coastal Ranges and the Pyrenees

In the eastern part of the Iberian Peninsula, the Hercynian rocks of the Iberian Massif are covered by Mesozoic and Tertiary siliciclastic, carbonate and evaporitic sedimentary rocks of the Iberian System, which were deformed during the Alpine orogeny. Between Cullera and the Ebro Delta, most sediments derived from these rocks (SP10, SP09, SP08 and SP04) have ε_{Nd} values between

−10.98 and −9.99. Locally, near Castellon de la Plana (SP06 and SP02), however, recycling of Carboniferous greywackes lowers the ε_{Nd} values to −12.10 to −11.58.

The drainage basin of the Ebro River lies between the northern side of the Iberian Ranges and the southern flanks of the Pyrenees. Within the drainage basin, abundant Tertiary sedimentary successions crop out. The ε_{Nd} value of sediments delivered to the Ebro Delta (FH06) is relatively low, at −11.49. Along the coast between the Ebro Delta and Barcelona, the sandy sediments are derived from Cenozoic and minor Mesozoic sedimentary rocks. The ε_{Nd} values along this small stretch of coast (FH08, SP47 and FH04) vary quite a lot, lying between −11.18 and −9.84. Magmatic rocks of the Catalonian Coastal Ranges crop out north-east of Barcelona. In the eastern Pyrenees, similar plutonic rocks occur, together with Palaeozoic metamorphic rocks. These rocks produce beach sands with ε_{Nd} values between −10.03 and −8.68 along the Catalonian Coastal Ranges (FH03 and FH11) and at the eastern side of the Pyrenees in northern Spain and southern France (FH10 and FR04).

The Massif Central, the Rhône Basin and the Western Alps

The southern part of the Massif Central is partly covered by Jurassic and Cretaceous limestones and Cenozoic siliciclastic sedimentary rocks. Erosion products of these rocks are deposited in the central part of the Gulf of Lion. These beach sands (FR08) are characterized by an ε_{Nd} value of −8.74. The Rhône River drains an extensive area, spreading from the Massif Central over the Vosges and the Jura to the Western and Northern Alps. The ε_{Nd} value of −8.31 for sand from the Rhône Delta (FR10) can be seen as an average value of the exposed rocks in the river's drainage basin. The Bay of Marseilles is dominated by Cretaceous and Jurassic limestone cliffs. Locally, however, recycling of Oligocene sedimentary rocks produces very mature quartz-rich beach sand (FR13), with an ε_{Nd} value similar to those of beach sands more to the west, at −9.14.

Near the city of Hyères (FR16), along the metamorphic Maures–Tanneron Massif in south-east France, the beach sands have a very low ε_{Nd} value of −12.40. These sands are derived from the Precambrian metagranites of Bornes, Cambrian quartzites and gneiss, and Ordovician–Silurian schists. Further east along the Maures Massif (FR17), the ε_{Nd} value of the beach sands increases again, to −10.14. On the beaches in the Gulf of Fréjus and the Gulf of Napoule, sediments from Cambrian–Ordovician quartzites, schists and granites, and Permian sedimentary and volcaniclastic rocks, are mixed with detritus from Triassic to Cretaceous limestones. These sediments (FR18 and FR19) have ε_{Nd} values between −8.48 and −8.03.

Sand from a beach near Imperia (IT12) has an ε_{Nd} value of −8.83. These sediments are composed of calcareous and siliciclastic grains derived from Cretaceous–Paleogene turbidites. In the Gulf of Genoa, similar turbidites alternate with extensive outcrops of Jurassic metaophiolites. These ultramafic rocks, with their very high ε_{Nd} values of up to 10 (Rampone *et al*. 1998), have a strong influence on the bulk Nd isotopic signature of the beach sands in this area. This is already conspicuous near Finale (IT13), with an ε_{Nd} value of −6.75, but even more so in sands further to the eastern part of the gulf (IT17), where the ε_{Nd} values are as high as −3.05. The ultramafic source of sands in this area results in very high Fe_2O_3, MgO and Al_2O_3 concentrations (Brems *et al*. 2012b). As a consequence, these sands cannot have been used to produce Roman natron glass.

The Tuscan and Roman Magmatic Province

The beach sands between Viareggio and Livorno (IT09, IT30 and IT31) are brought to the coast by the Arno River. This river drains an area covered with Cretaceous to Pleistocene sedimentary rocks. The ε_{Nd} values of these beach sands show a small range from −8.41 to −7.84. In the Gulf of Follonica (IT34 and IT01), relatively mature sands derived from turbidite sequences and coastal-plain sediments have ε_{Nd} values varying between −9.40 and −8.86.

Along the Tyrrhenian Sea margin of the Lazio region, the Northern District of the Roman Magmatic Province is found (Avanzinelli *et al.* 2008). The Pliocene to Holocene potassic volcanic rocks of the Vulsini, Vico, Cimini, Sabatini and Alban Hill volcanoes have rather low ε_{Nd} values of around −11 to −8 (Di Battistini *et al.* 2001; Conticelli *et al.* 2002; Peccerillo *et al.* 2010). Since detritus from these volcanic sources contributes to the local beach sands, the sands found between Monte Argentario and Sperlonga (IT39, IT06 and IT44) all have similar ε_{Nd} values, between −9.85 and −9.16. Further south, Pleistocene–Holocene rhyolitic volcanic rocks belonging to the Neapolitan District of the Roman Magmatic Province (Avanzinelli *et al.* 2008) have much more variable ε_{Nd} values (Conticelli *et al.* 2002, and references therein). In particular, the Roccamonfina volcanic rocks have a wide range of possible ε_{Nd} values, between −11 and −3. The ε_{Nd} values of the Somma-Vesuvius suite are generally higher; that is, between −5 and 0. Sediments brought to the Campanian beaches by the Garigliano and Volturno Rivers can therefore have a wide range of Nd isotopic signatures. The four samples analysed in this study (IT20, IT21, IT22 and IT23) vary between −9.90 and −4.40 ε_{Nd}. These sands contain high percentages of heavy minerals, resulting in high Fe_2O_3 and Al_2O_3 levels, making them unsuitable as raw materials for glass production (Brems *et al.* 2012b, in press b). Also, the Nd concentrations of these sands are rather peculiar. Whereas most sands analysed in this study have Nd contents below about 25 ppm, sands from this area all contain more Nd. One of the samples (IT21) even has a concentration of 296 ppm. South of Mount Vesuvius, near Amalfi, small pocket beaches alternate with high calcareous cliffs. Sand from one of these beaches (IT02) is composed of 60% calcareous fragments from the Mesozoic carbonates and abundant volcanic detritus. The ε_{Nd} value of the sand (−4.35) is in agreement with the relatively high values reported for Vesuvius. Further south, along the Cilento promontory, quartz-rich beach sand (IT47) derived from Jurassic to Oligocene quartzo-feldspathic turbidites has an ε_{Nd} value of −8.48.

Calabria and Sicily

The coastlines of Calabria and the northeastern tip of Sicily (IT50, IT52, IT56, IT75 and IT80) are dominated by sands derived from Hercynian low- to high-grade metamorphic and plutonic rocks, and the overlying sedimentary cover. These sands generally have ε_{Nd} values between −11.63 and −10.75. Along part of the western coast of Calabria, near Cosenza (IT50), however, small amounts of detritus from local ophiolitic sequences result in a higher ε_{Nd} value of −7.71. At the centre of the northern coast of Sicily, in the Termini Imerese Gulf (IT59), quartz-rich beach sands have an ε_{Nd} value of −11.04.

The most negative ε_{Nd} values encountered in this study were found in the northwesternmost part of Sicily. Sediments from the Gulf of Castellammare (IT62) and south of Trapani (IT63) are mainly derived from Miocene sedimentary rocks and have ε_{Nd} values between −12.85 and −12.47. The sediments deposited in this area during the Miocene were probably derived from old (Palaeozoic or even Precambrian) rocks with a crustal affinity. The southwestern part of Sicily (IT08 and IT68) is characterized by ε_{Nd} values between −11.14 and −10.07. Although the beach sands from the Gulf of Catania, on the east coast of Sicily (IT71), are mainly derived from Oligocene–Pleistocene sedimentary rocks, small contributions from volcanic rock fragments from Mount Etna result in a slightly elevated ε_{Nd} value, at −7.86 (Conticelli *et al.* 2002, and references therein). Sandy sediments closer to the Etna volcano will most probably show higher ε_{Nd} values.

Adria

The eastern part of the Italian peninsula, which approximately coincides with the Apulia region, is geologically distinct from the rest of Italy. This area forms part of the so-called Adria microplate, which acted as the Adriatic and African foreland during the peri-Adriatic orogeny (Bosellini 2004, and references therein). Geologically, it has more affinity with the African Plate than with Europe. The area is mostly composed of Jurassic to Miocene platform carbonates, overlain by a thin layer of Neogene and Quaternary sedimenticlastic deposits. The results of the Nd isotopic analysis of beach sands along the coast of this part of Italy are rather peculiar. In the Gulf of Taranto, north-east of the Cape of Spulico, detritus is still mostly derived from the sedimentary successions exposed in the Southern Apennines. These sediments (IT84) are delivered to the coast by the Sinni and Agri Rivers and have an ε_{Nd} value of –9.24. Further to the north of the Gulf of Taranto, between the mouths of the Basento and the Bradano Rivers (IT85), the ε_{Nd} value of the beach sand increases to –6.11. The only clear potential source for this relatively high Nd value are the Mount Vulture volcanic rocks, which have ε_{Nd} values between 1 and 3 (Conticelli *et al*. 2002, and references therein). Although these volcanic rocks are exposed about 10 km outside the Bradano River drainage basin, volcaniclastic material rich in mafic minerals (mostly pyroxenes) derived from Mount Vulture is also reported to be present in the Middle Pleistocene sediments covering the platform carbonates of the Adria microplate (Acquafredda *et al*. 1997; Mastronuzzi and Sansò 2002). Recycling of these sedimentary sequences also delivers unradiogenic Nd to the beaches in the area. Closer to the city of Taranto (IT11), the ε_{Nd} value of the beach sand decreases again, to –8.66. South-east of Brindisi, on the northeastern side of the Salentina peninsula (IT87), the ε_{Nd} value of the beach sand is –4.17. This sand is derived from the Pliocene–Pleistocene siliciclastic sedimentary rocks overlying the limestones of the Apulia platform. The presence of layers rich in pyroxene and garnet coming from the Mount Vulture volcano in the Pleistocene successions in the area (Mastronuzzi and Sansò 2002) can explain this high Nd isotopic value. Another possibility is that mafic minerals from Mount Vulture get transported from the mouth of the Ofante River to the south, along the Adriatic coast of Apulia, and incorporated into the local beach sands (Caldara *et al*. 1998; Mastronuzzi *et al*. 2007). A relatively high ε_{Nd} value of –6.03 is also encountered in the Gulf of Manfredonia (IT90). However, this value can also be attributed to detritus from Mount Vulture, brought to the gulf by the Ofante River and then transported to the north in a clockwise motion along the coast (Fabricius and Schmidt-Thomé 1972). Carbonate-rich sand from the Gargano promontory (IT07) shows a lower ε_{Nd} value of –7.67.

The Central Apennines, the Po Basin and the Southern Alps

North of the Gargano promontory and up to Pesaro (IT91, IT92, IT04 and IT94), the beach sands are derived from the eastern flanks of the Central Apennines. The ε_{Nd} values for these sands range from –9.32 to –8.12. Between Pesaro and Rimini (IT96), a beach sand with abundant calcareous fragments has an ε_{Nd} value of –7.95. Sedimentary material derived from the eastern side of the Northern Apennines is deposited along the beaches near Ravenna (IT10). The ε_{Nd} value of these sands is very similar to those of the beach sands along the Central Apennines; that is, –8.34.

The Po River derives its sediment load from the Western, Central and Southern Alps and the northwestern side of the Northern Apennines. Mixing of detritus from diverse source rocks exposed in this large drainage basin results in ε_{Nd} values between –8.79 and –8.37 for the beach sands along the Po Delta (IT99 and IT101). Erosion of the extensive carbonate rocks exposed in the eastern Dolomites results in highly calcareous beach sands along the coast of north-east Italy (IT104). These sediments have an ε_{Nd} value of –7.10.

THE ε_{ND} VALUE AS A PROVENANCE INDICATOR FOR THE SILICA SOURCE?

The sands under investigation were previously evaluated for their suitability for Roman natron glass production by comparing their major and minor elemental compositions to the compositional ranges of Roman imperial natron glass (Brems *et al*. 2012b). Seven sand raw materials from six limited areas were found to be suitable for the production of natron glass, either with or without the need for an extra source of lime (Fig. 1). When we focus on these sands, we can evaluate the Nd isotopic signature as a provenance indicator for sand raw materials and raw natron glass. The four sand raw materials that can be used to produce Roman natron glass after the addition of extra lime all have relatively low ε_{Nd} values, typical for the western Mediterranean. Sand SP46, from southwestern Spain, has an ε_{Nd} value of –7.99. Suitable sand from near El Rubial in southeastern Spain (SP20) has an ε_{Nd} value of –11.76. Sand raw materials from Les Bormettes in the Provence (FR16) have an even lower ε_{Nd} value of –12.40. Finally, the sands from Calla Violina in Tuscany (IT01), which would make good natron glass after the addition of lime, have an ε_{Nd} value of –8.86. A mixture of shell fragments, collected along several beaches in southern France and north-west Italy, has a Nd concentration of 1.0 ppm and an ε_{Nd} value of –6.6. Since this Nd concentration is 5–20 times smaller than the concentration in most sands and the additional lime only makes up ~10% of the total glass batch, the additional source of lime only has a very small influence on the final Nd budget of a glass. Glass produced with either of these sand sources would thus be readily distinguishable from glass from the eastern Mediterranean, since raw glass from Egypt and Syro-Palestine has relatively low variation in ε_{Nd}, with values between –6.0 and –5.1 (Degryse and Schneider 2008; Freestone *et al.* unpublished data).

Three sands from Italy were identified as being suitable for Roman glass production in their present form (Brems *et al*. 2012b). Sand IT34 from Tuscany also has a rather low ε_{Nd} value, of –9.42. The two other suitable glass-making sands found in the Basilicata (IT85) and Apulia regions (IT87) in south-east Italy, however, have relatively high ε_{Nd} values of –6.1 and –4.2, respectively. These values coincide with the range of Nd isotopic signatures previously thought to be characteristic for an eastern Mediterranean origin (Degryse and Schneider 2008; Freestone *et al.* unpublished data). This shows that the use of Nd isotopic signatures as a provenance indicator for Roman glass is not as straightforward as previously thought. Nd isotopic analysis is not the miracle cure for the provenancing of Roman natron glass, but it has certainly proven its value. On the basis of the Nd isotopic signature of glass artefacts, certain possible areas of production can be suggested or excluded. For further differentiation, other techniques will have to be applied. A pilot study is currently being performed to see whether trace element geochemistry can be used to distinguish between suitable sand raw materials from Italy and Syro-Palestine, which happen to have similar Nd isotopic signatures.

CONCLUSIONS

The aim of this study was to evaluate the use of Nd isotopic signatures for the provenance determination of Roman natron glass. To do this, 76 beach sands from the coasts of Spain, France and Italy were analysed for their Nd isotopic composition. Nd in Roman natron glass originates from the heavy mineral fraction of the sand raw material, and its isotopic composition is an indication for the source of the silica. Suitable glass-making sands from Spain, France and the western part of Italy all have relatively low ε_{Nd} values and glass that would be produced from them could be readily distinguished from glass from the known primary production sites in Egypt and Syro-Palestine. Two good sand sources in the Basilicata and Apulia regions (south-east Italy), however, have ε_{Nd} values that coincide with those of glass with an eastern Mediterranean origin. Further research is required to determine whether these possible sources of glass can be distinguished from each other by relying on trace element patterns.

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