An original experimental approach to study the alteration and/or contamination of archaeological ceramics originated by seawater burial

Giuseppe Montana[1,*], Luciana Randazzo[1], Cristina Maria Belfiore[2], Mauro Francesco La Russa[3], Silvestro Antonio Ruffolo[3], Anna Maria De Francesco[3], Antonino Pezzino[2], Rosalda Punturo[2], and Vincenzo Di Stefano[4]

[1] Dipartimento di Scienze della Terra e del Mare (DiSTeM), Università di Palermo, Via Archirafi 36, 90123 Palermo, Italy
[2] Dipartimento di Scienze Biologiche, Geologiche e Ambientali-Sezione di Scienze della Terra, Università di Catania, Corso Italia 57, 95129 Catania, Italy
[3] Dipartimento di Biologia, Ecologia e Scienze della Terra (DiBEST), Università della Calabria, Via Pietro Bucci, 87036 Arcavacata di Rende, CS, Italy
[4] Consiglio Nazionale delle Ricerche, Istituto per l'Ambiente Marino Costiero U.O. Capo Granitola, Via del Mare 3, 91021 Torretta Granitola, Campobello di Mazara, Trapani, Italy
*Corresponding author: giuseppe.montana@unipa.it

Abstract

This paper deals with the proposal of an original experimental methodological approach specifically designed for appraising any compositional alteration and/or contamination of archaeological ceramics after the protracted contact with seawater. A series of ceramic test-pieces (briquettes and cylinders) were purposely manufactured by mixing selected calcareous or non-calcareous clays with different varieties of sieved sand temper. The aim was to reasonably simulate the ceramic pastes most frequently found in the shipwrecks recovered in the coastal areas of western Mediterranean. The used raw materials were previously characterized in terms of mineralogical and chemical composition (XRPD, XRF). The obtained test-pieces were fired under oxidizing conditions at predetermined temperatures (800 and 950 °C) in a traditional ceramic kiln and their chemical composition was analyzed by XRF spectrometry. Briquettes were firstly fixed into customized Ertacetal® holders and then placed in open sea-bed environment under monitored oxidizing or reducing conditions by the Italian CNR-IAMC dockside at Granitola, north-western Sicily. At the same time, two customized glass containers for working in a confined system under continuous seawater flow

were designed and realized. They were filled with bottom sediments rather different in size in order to produce either reducing or oxidizing microenvironments below the water-sediment interface. Cylinder shaped test-pieces were placed in the sediment of both the glass containers. Weekly monitoring of temperature, salinity, conductivity, pH, Eh, dissolved oxygen was carried out in both the above-described experimental settings. Comparative (before/after) XRF analyses, after 3 months of exposure to seawater, were performed on the experimental ceramic briquettes and cylinders. The obtained results provided preliminary evidences that the proposed experimental strategy is efficiently working and a number of not negligible changes concerning major and trace elements were pointed out just after such a restricted time of exposure to seawater.

Introduction

The discovery of ancient artefacts used in everyday life laid under the sea in sunken wrecks exercises a particular suggestion in the collective imagination. The mysterious and dramatic context of recovery adds often a special charm to these testimonies of the past. As well acknowledged, the majority of the archaeological findings coming from shipwrecks consist of pottery and, by and large, of transport amphorae. In fact, since early antiquity, the human need to transport goods through sea crossing obliged the man to consider a container that could be easily handheld being suitable for short and long distance transport as well. Ceramic, due to the fact that is made by a mixture of raw clay and subordinate quantities of sand temper, normally fired at temperature even higher than 800 °C, is accepted as a relatively long-lasting handmade material. Nevertheless, it is important to keep in mind that, to some extent, it may also suffer alteration and/or contamination during use, manipulation and burial. The post-depositional modification in terms of composition of ancient pottery was subject of several archaeometric studies since the end of the 60's and throughout the 70's (Freeth, 1967; Millet, 1967; Matson, 1971; Duma, 1972; Coutroís, 1973; Picon, 1976; Schneider, 1978; Olin et al., 1978). From the 80's up until today the alteration and/or contamination processes involving archaeological ceramic artefacts have been studied with increasing detail mainly focusing on the specific consequences regarding the determination of "provenance" (Lemoine et al., 1981; Maggetti, 1981; Heimann and Maggetti, 1981; Lemoine and Picon, 1982; Maggetti et al., 1984; Picon, 1985a, 1985b; Pearson 1987; Picon, 1991; Buxeda, 1994, 1999; Buxeda and Cau, 1995, 1997; Buxeda and Gurt, 1995; Bearat et al., 1992; Pradell et al., 1996; Amadori et al., 2001, 2002; Buxeda et al., 2001,

2002, 2004, 2005; Cau et al., 2002; Schwedt et al., 2004; Maritan and Mazzoli, 2004) or thermoluminescence dating (Zacharias et al., 2005). However, it is important to underline that during the last 20 years, only Maurice Picon (1986) suggested to adopt a sort of mathematical correction of the concentration of the chemical elements supposed to have been contaminated during the burial period. Moreover, until today, few papers concern the alteration and contamination of archaeological ceramic after seawater burial (Amadori et al., 2002; Buxeda et al., 2005a; Maritan et al., 2009; Secco et al., 2011; Lopez-Arce et al., 2013; Martinez Ferrera et al., 2013) and a single experimental work on the same subject was published (Bearat et al., 1992). This infrequency of scientific contribution on this specific topic could be likely interpreted as due to the tangible complicatedness in simulating the processes leading to the compositional and/or physical modifications of ceramic artefacts during their marine burial. Theoretically, after a protracted seawater burial, the changes showed by the archaeological ceramic artefacts could be synergistically related to several different causes. For example, the extent of alteration could be correlated to the original composition of the ceramic paste (mineralogy and bulk chemistry) as well as its intrinsic textural features (packing, size and distribution of the temper aplastic grains, size distribution of pore spaces, etc.). The physical and chemical characteristics of the aquatic medium (temperature, pH, Eh, salinity, etc.), the composition and texture of the sea floor sediments, or even interaction with living organisms could also have significant effects.

Alteration processes of ceramic artefacts deriving from submarine excavation sites should involve the dissolution and/or the precipitation of a number of mineralogical phases and consequently the leaching and/or addition of chemical elements from the corresponding ceramic paste. Theoretically, this could significantly perturbate any "provenance" study concerning the same ceramic samples, based on a quantitative analytical approach and aimed to ascertain the trade routes from the place of production to the consumption centres. At the same time, seawater burial entails various matters that expressly concern the restoration (salt removal, cleaning, consolidation) and the musealization of the most relevant ceramic remains coming from the archaeological excavation. This latter issue is of relevant interest considering that the present deficiency of knowledge involving specific restoration procedures could have a clear consequence on the management of the Underwater Cultural Heritage (Montana et al., 2013; Belfiore et al., 2014). With this respect, it is important to mention that the UNESCO Convention on the Protection of the Underwater Cultural Heritage (adopted by the UNESCO General Conference on the 2nd of November 2001) was quite recently acknowledged by the Italian Parliament (on the 8th of April 2010 has come into force in Italy through the law number 157 on October 23rd 2009).

This study is presenting the preliminary results of a wider research project, funded by the Italian Ministry of Education, University and Research (MIUR), dealing with the analytical characterization and the restoration of ceramic

finds recovered from underwater archaeological excavations. In particular, the present paper deals with the first application of an innovative experimental approach specifically designed for appraising any compositional alteration originated after the protracted contact between ceramic and seawater. The experimental methodology used in this research consisted of the manufacture of ceramic test-pieces (briquettes and cylinders) in order to purposely reproduce compositional and textural characteristics generally showed by archaeological transport amphorae more frequently found in the shipwrecks recovered in the coastal areas of western Mediterranean. Experimental ceramic pastes were produced using different clays and sands with individual mixing and tempering procedures. Specifically, a "calcareous clay" (CaO > 5% wt) or a "non-calcareous" clay (CaO < 5% wt) were mixed with volcanic or sedimentary sands, even using various relative proportions of temper. Raw materials were previously characterized in terms of mineralogical and chemical composition by using, respectively, X-ray powder diffraction (XRPD) and X-ray fluorescence spectrometry (XRF). The ceramic test-pieces, carefully analysed by XRF after firing at 800 and 950 °C under oxidising conditions, were successively placed into different underwater environments both natural and laboratory-simulated. Briquettes were fixed into custom-made holders and placed in open seabed environment under monitored oxidizing and reducing conditions by an available dockside located in north-western Sicily. Moreover, customized glass containers were

designed for working under continuous supply of seawater to prevent evaporation and filled with different bottom sediments in order to produce reducing or oxidizing microenvironments below the water-sediment interface. Cylinder shaped test-pieces were placed in the sediment of both the tanks. Weekly monitoring of temperature, salinity, conductivity, pH, Eh, dissolved oxygen was carried out in both the above-described experimental settings. Comparative XRF analyses were performed on the ceramic test-pieces after 3 months of exposure in order to check whether the proposed experimental approach worked adequately.

Analytical methods

X-ray powder diffraction (XRPD) was conducted on raw materials (sands and clays) using a Philips X'Pert diffractometer with CuKα radiation (operating conditions: 40 kV and 40 mA, 2°-60° 2θ scan range, graphite monochromator, 2° 2θ min^{-1} scan rate and 2s time constant). Concerning clayey raw materials, both whole samples and oriented preparations of the clay-sized fraction (< 2μm) were analysed. Clay fractions were pre-treated with $MgCl_2 \cdot 6H_2O$ (5 mg in a solution of 350 ml) before being analysed in air-dried, ethylene glycol, 180 °C and 600 °C treated states for the identification of clay phyllosilicates. Experimental parameters were adequately optimised for quantification of any clay minerals present (2°-30° 2θ scan range, CuKα radiation, graphite monochromator, 1° 2θ min^{-1} scan rate and 2 s time constant). All diffractograms obtained were semi-quantitatively

evaluated (relative abundances expressed in %) employing the intensity ratio method originally proposed by Shaw et al. (1971) and modified by Laviano, (1987). Prior to semi-quantitative analysis, the experimental XRPD patterns were subjected to a deconvolution algorithm-based process using the software program Profile Fit 1.0.

For X-ray fluorescence analysis (XRF), approximately 2 g of homogenized sample (starting from a total quantity of 10 g of sample), after powdering by an automatic agate balls mill, was pressed at around 20 MPa onto a base of boric acid by a hydraulic press in order to obtain a circular powder pellet 4 cm in diameter. Sample powders have previously been mixed in a 2 ml of 3% water solution of Mowiol N50-98 (Polyvinyl Alcohol). Sample analyses were then carried out using a Rigaku ZSX Primus wavelength dispersive X-ray fluorescence spectrometer, equipped with four diffracting crystals: LiF (200), LiF (220), PET (002) and TAP (100). A Rh anode tube routinely running at 4 kW was used for major and trace element analysis, with up to 52 USGS and NBS standard reference materials employed (40 silicate rocks and 12 carbonate rocks). Fifteen elements were analyzed: Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe (given as oxides, weight %) and Cr, V, Cu, Zn, Rb, Sr, Y, Zr, Ba, Co, Pb, Ce, Nb, La and Ni (ppm). The average relative standard deviations evaluated (RSD) after seven runs of the SRMs IAEA/Soil-7, IAEA/SL-1 and NIST/BC-679 were reported (as % for major and trace elements) for the following elements: $SiO_2 = 2$; $TiO_2 = 8$, $Al_2O_3 = 1$, $Fe_2O_3 = 2$, $MnO = 9$, MgO

$= 2$, $CaO = 3$, $Na_2O = 1$, $K_2O = 10$, $P_2O_5 = 4$, $Cr = 7$, $V = 6$, $Cu = 10$, $Zn = 5$, $Rb = 19$, $Sr = 5$, $Y = 18$, $Zr = 28$, $Ba = 1$, $Co = 7$, $Ce = 12$, $Nb = 10$, $La = 5$ and $Ni = 4$. Analysis of each element was fully corrected for line interference and matrix effects from all other analysed elements. The results were then normalized on a dry-weight basis; details regarding the correction of instrumental drift and the matrix effect, as well as procedures carried out in the construction of calibration lines are described elsewhere (Hein et al., 2002). Chemical analyses concerning major and minor elements were additionally replicated by an accredited laboratory (Activation Laboratories Ltd.), as well as the concentration of two trace elements (Cr and V) by Fusion-XRF technique. The fusion disk was made by mixing a 0.5 g equivalent of the roasted sample with 6.5 g of a combination of lithium metaborate and lithium tetraborate with lithium bromide as a releasing agent. Samples were fused in Pt crucibles using an automated crucible fluxer and automatically poured into Pt molds for casting. Samples were analyzed on a Panalytical Axios Advanced wavelength dispersive XRF.

Weekly monitoring of the most important physico-chemical parameters was carried out in the two tested experimental settings, also depending on adverse weather conditions. In particular, temperature, pH, total dissolved solids (TDS), salinity, redox potential (ORP) and conductivity, were measured. Measurements were performed by means of a Handheld Multiparameter Instrument YSI 556 MPS (Multiprobe System). Periodic calibration of all

the sensors, except temperature, was performed in order to assure high performances of the measurements. Specific solutions (conductivity) and buffer solutions (pH and Eh) were used: a 80 mS/cm conductivity standard for seawater (HI 7034 by Hanna Instruments), three pH buffer solutions (4, 7 and 10 by Hanna Instruments) and a Redox Buffer Solution (by Hamilton Bonaduz AG) certified by NIST.

Raw materials and manufacture of ceramic test-pieces

Experimental ceramic test-pieces (briquettes and cylinders) were prepared in order to be fired under oxidizing atmosphere with predefined values of maximum temperature (800 and 950 °C). Two types of clay both already well studied and collected from outcrops located in western Sicily (Figure 1A) have been selected for this purpose (Table 1).
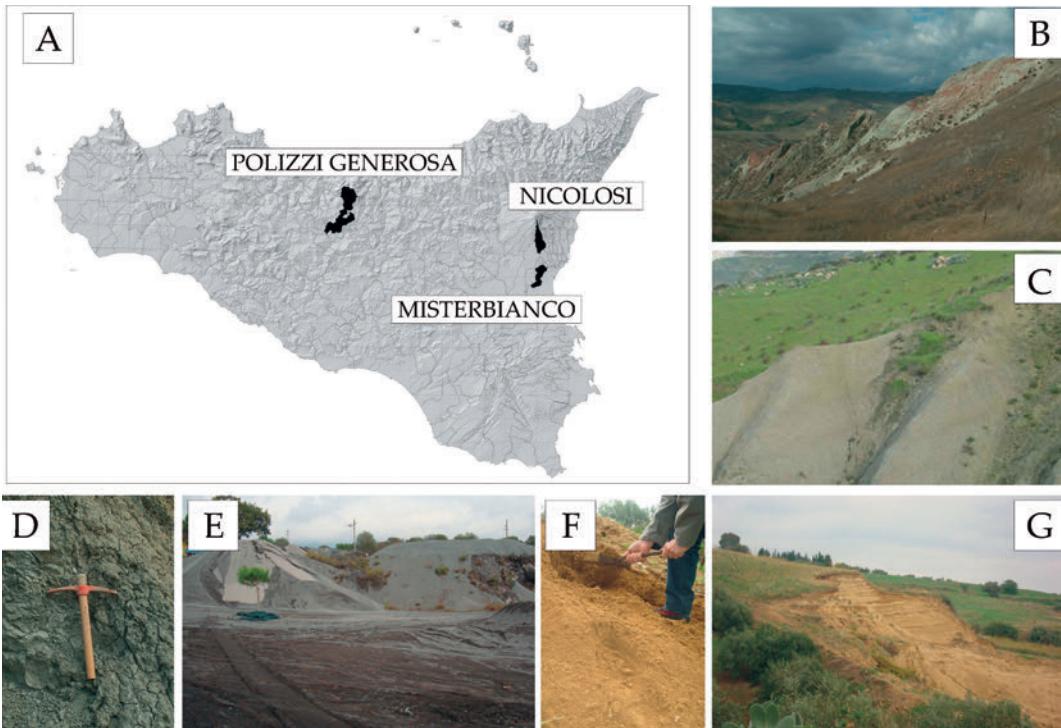
Figure 1. (A) Schematic map with the location of raw materials sampling points (clays and sands); view of the considered clayey outcrops: Terravecchia Formation (B) and Argille Varicolori Formation (C, D); artificial sand quarry on the basaltic lava flow close to Nicolosi at the slope of the Mount Etna volcano (E); silico-calcareous natural sand exploited from the Middle Pleistocene fluvial-marine deposits in the surrounding of Misterbianco (F, G).

Table 1. Summary of the main compositional and textural characteristics concerning the raw materials (sands and clays) used for manufacturing the experimental ceramic test-pieces.

Raw material	Formations/Units	Sampling point	Grain size	Mineralogy
Silico-calcareous sand (S)	Sand and gravel of "Villaggio S. Giorgio" (CT)	Quarry "Villaggio S. Giorgio" (CT)	Medium sand	Qtz (+++), Cal (++), Kfs (+), Plg (+)
Volcanic sand (V)	Etna deposits	Quarry "La Rosa & Magrì" (CT)	Coarse-medium sand	Plg (+++), Aug (++), Ol (+), Ti-Mag (+), Hem (+)
Non-calcareous clay (NC)	"Argille Varicolori fm"	*Contrada Pantaleo* (Castellana Sicula)	Silty clay	Ill (+++), Mnt (++), Kln (+), Chl (+) Qtz (+), Cal (tr), Kfs (tr)
Calcareous clay (C)	"Terravecchia fm"	*Contrada Guglia* (Polizzi Generosa)	Silty clay	Ill (+++), Mnt (++), Kln (++), Chl (+) Qtz (+), Cal (+), Kfs (tr)

Oxide (%wt)	SiO_2	TiO_2	Al_2O_3	P_2O_5	Fe_2O_3	MgO	MnO	CaO	Na_2O	K_2O
Non-calcareous clay (NC)	58.6	1.2	23.3	0.3	9.7	1.9	0.1	1.7	0.7	2.4
Calcareous clay (C)	56.6	1.0	20.3	0.1	8.0	2.6	0.1	7.8	0.7	2.9

Qtz = quartz; Cal = calcite; Kfs = K-feldspar; Plg = Plagioclase; Ol = olivine; Aug = augite; Hem = hematite; Ti-Mag = titaniferous magnetite; Ill = illite; Chl = chlorite; Kln = kaolinite; Mnt = montmorillonite; +++ = prevalent; ++ = common; + = subordinate; tr = trace.

The first clayey raw material, according to the definition of Maniatis and Tite (1975), can be classified as "calcareous clay" (CaO > 5% wt). It belongs to the *Terravecchia Formation* (Upper Tortonian-Lower Messinian) whose employ for pottery production has been widely attested in Sicily since the 7th century BC (Montana et al., 2011a; Montana et al., 2011b; Montana et al., 2012). Specifically, the clay used for the manufacture of the ceramic test-pieces was collected in the area of the Madonie Mountains (Figure 1B), in the vicinity of the village of Polizzi Generosa, around 100 km far from Palermo. The corresponding mineralogical and bulk chemical compositions together with grain-size distribution and general information concerning the sampling points are schematically resumed in Table 1. Basically, it turned out to be an illitic clayey-silt, where illite and illite-smectite mixed layers overcome kaolinite and chlorite, with a medium-low content of calcareous microfauna (mostly benthic foraminifera and ostracods) and fine/very fine detritic quartz grains (0.04-0.2 mm). Conversely, the second clayey raw material can be classified as "non-calcareous

clay", with a CaO concentration even lower than 2% wt (Table 1). It was collected in the same territory of the already described calcareous clayey material (Contrada Pantaleo at Polizzi Generosa) from the *Argille Varicolori* Formation of Cretaceous-Eocene age (Figure 1 C,D). It can be classified like a silty clay having a very low sand content, once again characterized by abundant illite and illite-smectite mixed layers. Detritic quartz grains have been found to constitute the coarse silt fraction and the finer sand grains (Table 1).

Two different typologies of sand were considered for tempering and therefore mixed in distinct proportions with the above described clayey materials. The first one is represented by a natural silico-calcareous sand exploited from the Middle Pleistocene fluvial-marine deposits cropping out in the surrounding of the village of Misterbianco at the northern edge of the Plain of Catania, around 10 km far from the city of Catania (Figure 1 E,F). This sand is mainly composed of quartz grains (ranging generally

from 0.2 to 1.0 mm in size), calcareous bivalve shells and gastropods, indicative of a shallow marine environment (Francaviglia, 1961; Wezel, 1967; Kieffer, 1971) (Table 1). The second type of sand used in the experimental tempering was artificially obtained by crushing and sieving a basaltic rock collected from a recent stone quarry located at the slope of the Mount Etna volcano, not far from the village of Nicolosi, around 16 km far from Catania (Figure 1G). This basalt (currently exploited from an eruptive lava flow dated back to the 1886) shows a Porphyritic Index between 20 and 30. Phenocrystals are represented by plagioclase and clinopyroxene (augite) in similar proportions (the former being slightly prevalent), followed by subordinate quantities of olivine and titanomagnetite (Table 1). The groundmass is composed of microlites of plagioclase (predominant), augite, olivine and rare titanomagnetite (Romano and Sturiale, 1982; Viccaro and Cristofolini, 2008).

The ceramic test-pieces were accomplished by the manufacture of 6 different experimental

Table 2. List of the six experimental ceramic pastes purposely manufactured and distinguishable by specific compositional and/or textural characteristics: relative abundance of CaO (weight %) in the clayey groundmass; relative abundance (packing) and mineralogical composition of temper; firing temperatures.

Pastes	Firing Temperature (°C)	Packing (% volume)	Sand Temper Composition	Clay Composition
I	800 °C	5%	Volcanic (V)	Non-calcareous (NC)
II	800 °C	25%	Volcanic (V)	Non-calcareous (NC)
III	800 °C	5%	Silico-calcareous (S)	Calcareous (C)
IV	800 °C	25%	Silico-calcareous (S)	Calcareous (C)
V	950 °C	5%	Silico-calcareous (S)	Calcareous (C)
VI	950 °C	25%	Silico-calcareous (S)	Calcareous (C)

Figure 2. Manufacture of ceramic test-pieces: (A) example of experimental paste at the "green state"; (B) manufacturing experimental briquettes by means of customized wooden-framed mould; (C) ceramic briquettes during the air dry phase; (D) ceramic cylinders during the air dry phase.

pastes distinguishable by the specific characteristics resumed in Table 2. Raw materials (clays and sand temper) have been worked and mixed by a professional potter with awareness and for several hours in order to obtain a sufficiently well homogenised paste (Figure 2A). Briquettes were handmade using a customized wooden-framed mould with length = 11 cm, width = 6 cm and thickness = 0,8 cm (Figure 2 B,C). Cylinders were prepared with an extruded equipment having a diameter = 2 cm and height = 20 cm (Figure 2D). Both the kinds of test-pieces were reproduced in the number of 150 and left to dry at room temperature for two

weeks. The experimental pastes categorized as Paste I and Paste II were realized by mixing the non-calcareous clay with the volcanic sand temper. In particular, Paste I is characterized by a relatively lower packing (5% volume) with respect to Paste II (25% volume). They were both fired at 800 °C (time of permanence under T max. = 3 hours). The experimental pastes categorized as Paste III and Paste IV were realized by mixing the calcareous clay with the silico-calcareous sand temper. Paste III is characterized by a relatively lower packing (5% volume) with respect to Paste IV (25% volume). They were both fired at 800 °C (time of

permanence under T max. = 3 hours). The experimental pastes, categorized as Paste V and Paste VI, were realized by mixing the calcareous clay with the silico-calcareous sand temper. Paste V is characterized by a relatively lower packing (5% volume) with respect to Paste VI (25% volume). They were both fired at 950 °C (time of permanence under T max. = 3 hours) for achieving a relatively higher level of sintering of the groundmass.

Experimental equipment and settings

The experimental equipment involved the manufacture of customized holders for maintaining the ceramic test-pieces (briquettes) fixed into the open sea bottom and, at the same time, the assembly of a confined system having negligible loss due to evaporation and guarantying also the continuous renovation of the seawater.

The custom-made holders were made by using Ertacetal® an acetal copolymer. This material was chosen for its specific characteristics: excellent workability, low water absorption (0.25-0.45%), satisfactory acid resistance, suitable melting temperature (165 °C), favourable mechanical properties in terms of tensile and compressive stress. Eight Ertacetal® plates were shaped being around 50 cm long and 20 cm wide with a thickness of 1 cm. Up to 6 rectangular compartments (110x50 mm) were made for housing the ceramic briquettes corresponding to the six experimental pastes previously described (Figure 3A). Both the sides of any single compartment were left open in order to allow a complete contact with seawater.

The two parts of the plate were fastened by means of eight stainless steel bolt-nuts and also four holes at the corners were made for fixing the plates at the sea floor in the selected microenvironments. The Ertacetal® plates were placed in open sea-bed environment under monitored oxidizing or reducing conditions by the Italian CNR-IAMC dockside at Torretta Granitola (Mazara del Vallo) in north-western Sicily (Figure 4). A series of four plates after being fixed to an equivalent number of suitably made concrete anchors was positioned in the part of the dockside relatively more exposed to the open sea, lying at around 4 meters below sea level. This apparatus, placed at a distance of around 40 cm from the bottom sediment, was designed to assure the plates to be constantly in contact with acceptably oxygenated water as well as to be appropriately arranged against the strongest surface sea streams originated after storms specially during the winter season (Figure 3 B,C). Another series of four plates, on the contrary, was placed in a shelter area of the dockside where the finest sediments mixed with algae fragments are naturally deposited, as a result originating permanent reducing conditions even around 50 cm over the sea floor (at around 2 meters below sea level). The plates were nailed at the bottom sediments by means of stainless steel rivets (40 cm long) and their position was signalled by floating balls (Figure 3 D,E).

In order to obtain a confined system under a continuous seawater flow two customized glass containers were designed having the following dimensions: length = 50 cm; width = 40 cm; height = 70 cm; glass thickness = 8 mm. Both
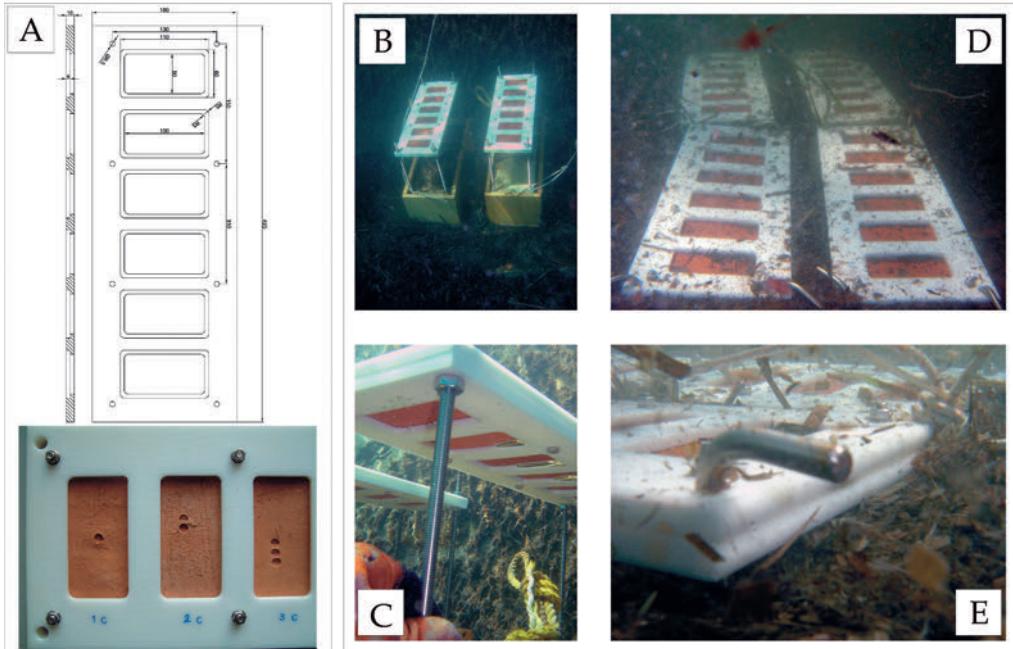
Figure 3. (A) Design of the custom-made Ertacetal® holders and detail showing their partitions; (B, C) view of the concrete anchors and the Ertacetal® holders positioned in the oxidising environment along the western dockside; (D, E) Ertacetal® holders fixed by means of stainless steel rivets at the bottom sediments of the reducing environment in the eastern side of the harbour.

the containers were plugged with a Plexiglas' removable hard top. A bilge pump with independent power supply assured a continuous input flux of seawater of around 6.5 litres/minute shared for the two tanks (around 3.2 litres/minute each). Both the tanks were designed with an overflow tap in order to maintain a constant water level. The project sketch together with some images of the whole arrangement during its assemblage are showed in Figure 5 A,B. Both the tanks were filled with differently sized bottom sands up to 25-30 cm in height in order to produce oxidizing or, on the contrary, reducing microenvironments below the water-sediment interface. In particular, the first glass container was filled with medium to very coarse calcareous sand while the other was filled with a significantly finer and relatively more siliceous sediment (Table 3). Moreover, in this latter a layer of foliage belonging to the *Posidonia oceanica* was placed at approximately 10 cm of depth in the sediment in order to sooner obtain reducing conditions after its decomposition. The cylinder shaped test-pieces, corresponding to the six described experimental pastes, were placed in the sediment of both the tanks, following the illustrated scheme (Figure 6 A,B).
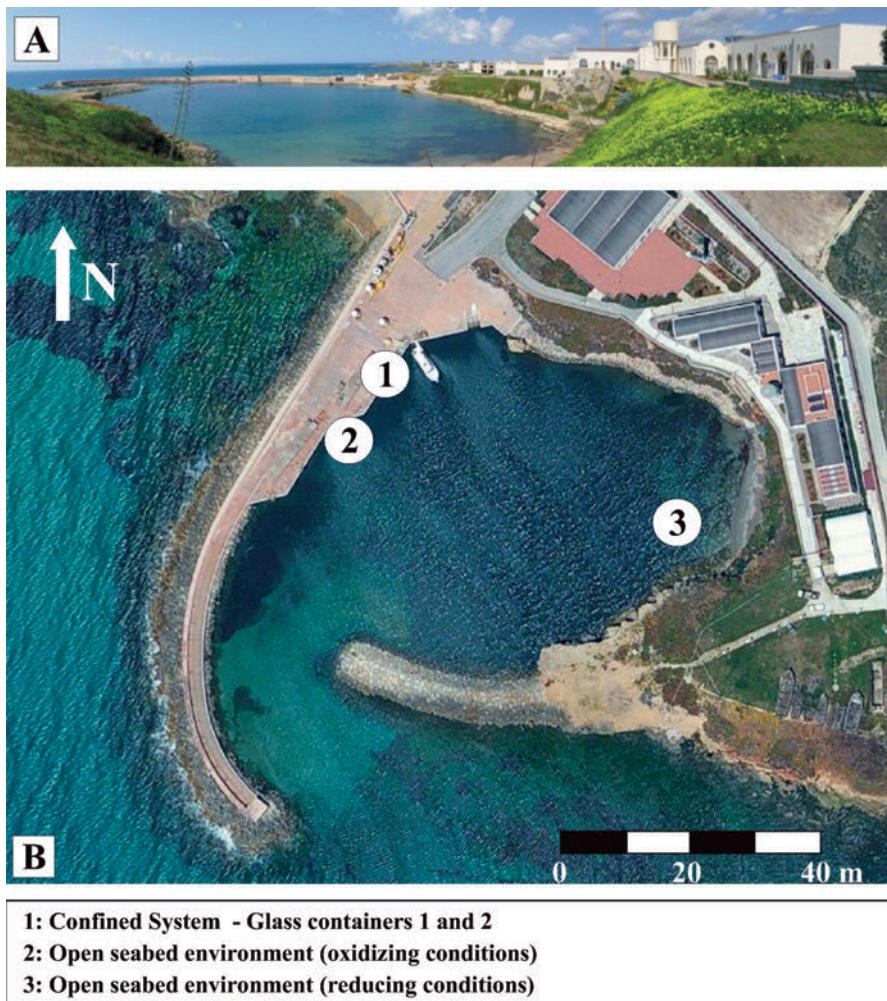
Figure 4. (A) CNR-IAMC harbour at Torretta Granitola (Mazara del Vallo, north-western Sicily); (B) aerial view of the experiment's location.

Results and discussion

Seawater monitoring for chemical-physical parameters

Seawater is a quite concentrated solution of different salts. Since the major constituents of the dissolved solids in the sea have a remarkably constant composition, seawater is a uniform and unique solution regardless of its total ionic strength (Huber et al., 2000). Seawater is therefore well buffered with respect to changes of pH (activity of the hydrogen ion) and Eh

(oxidation / reduction or redox potential). The concentrations of the major species in general vary only within a limited range being governed by oceanographic, geologic, atmospheric and biological factors. Consequently, the chemical homogeneity of the dissolved ions appear in constant ratios to one another.

As already mentioned, a weekly monitoring of the most important physico-chemical parameters was planned and carried out in the above-described experimental settings. Table 3 resumes the values of the measured parameters (temperature, pH, conductivity, salinity, total dissolved solids or TDS, redox potential or ORP)

during the first stage of the proposed experimental settings, that is to say three months from March 2012 to May 2012. Wind directions and speed (km/h) recorded in the area in the same period were also reported in Table 3.

Fluctuations of seawater temperature within the considered monitoring period were generally small between both the open sea experimental settings, being slightly colder in case of the oxidizing microenvironment, around -0.5 °C in average, with respect to the reducing one (Table 3 and Figure 7A). This result can be explained considering that the oxidizing environment is directly exposed to the entrance of the harbour
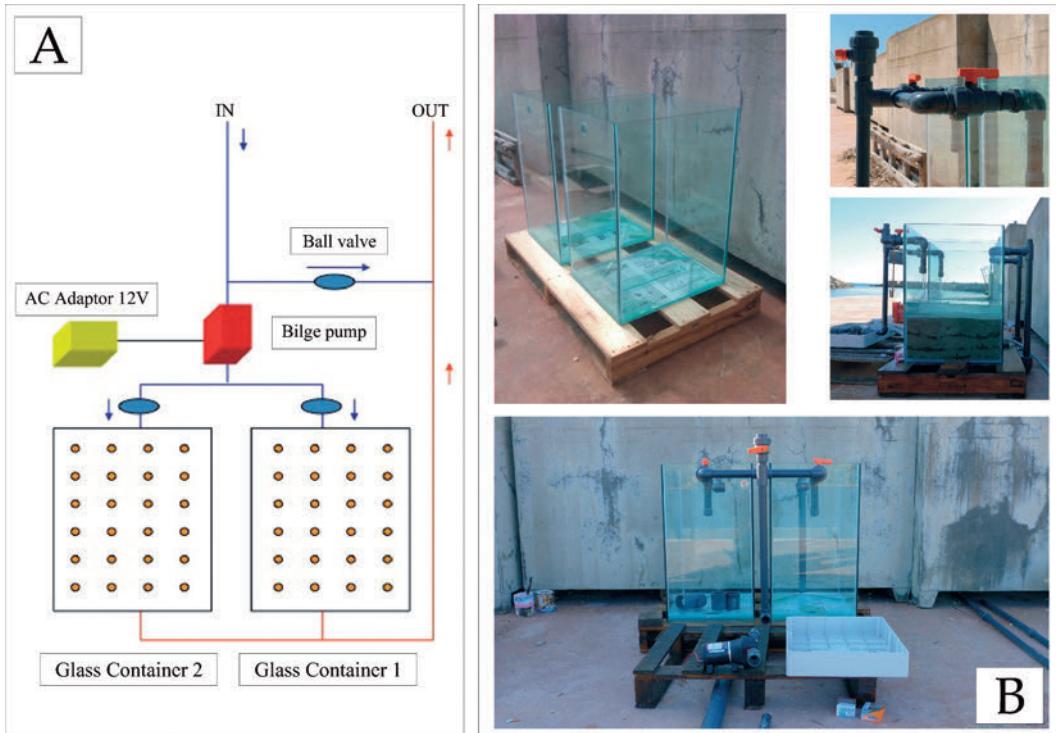

Figure 5. (A) Sketch of the experimental equipment for producing the "confined system"; (B) pictures taken during the assemblage.

Table 3. Chemical-physical data concerning seawater monitoring in the experimental settings during the first stage (3 months), together with wind direction and speed in the same period.

Site of Measurement	Date D/M/Y	Seawater Temp. °C	pH	TDS g/L	Salinity ‰	ORP mV	Cond mS/cm	Wind Speed km/h	Wind Direction
	16/03/12	16.8	8.2	36.6	37.5	230.6	56.4	39.2	S-SE
	28/03/12	15.7	8.1	35.9	36.6	169.4	55.2	27.0	S-SE
	05/04/12	17.3	8.1	37.1	38.0	78.4	56.8	62.6	S-SE
	12/04/12	15.7	8.0	36.2	37.0	204.2	55.7	51.9	SW
Oxidising open sea bed environment	19/04/12	15.9	8.0	35.7	36.4	179.0	54.9	51.9	NW
	26/04/12	17.6	8.1	35.6	36.4	51.5	54.8	35.2	SE
	04/05/12	17.1	8.1	36.4	37.2	85.6	56.0	22.2	N
	11/05/12	18.1	8.2	36.2	37.0	133.9	55.7	24.1	NE
	18/05/12	16.8	8.1	36.3	37.2	100.6	55.9	33.3	NW
	25/05/12	16.2	8.1	36.7	37.6	124.3	56.5	24.1	NW
	31/05/12	18.6	8.1	36.8	37.7	83.6	56.6	24.1	NE
	16/03/12	15.8	8.0	37.0	37.9	234.5	56.9	39.2	S-SE
	28/03/12	19.0	8.1	37.0	38.0	116.3	57.0	27.0	S-SE
	05/04/12	20.3	8.1	37.1	37.9	149.9	56.9	62.6	S-SE
	12/04/12	20.5	8.1	35.9	36.7	208.2	55.4	51.9	SW
Glass Container 1 (prevalent medium-coarse sand)	19/04/12	18.6	8.0	36.1	36.9	189.6	55.6	51.9	NW
	26/04/12	20.7	8.1	35.7	36.4	195.5	54.8	35.2	SE
	04/05/12	19.2	8.1	35.8	36.4	147.0	55.1	22.2	N
	11/05/12	20.0	8.1	36.2	37.0	219.2	55.6	24.1	NE
	18/05/12	19.3	8.1	36.5	37.4	131.3	56.2	33.3	NW
	25/05/12	18.1	8.1	36.6	37.5	164.1	56.3	24.1	NW
	31/05/12	20.6	8.1	36.6	37.5	114.8	56.2	24.1	NE

of Torretta Granitola (Figure 4) and therefore more subjected to cold water flows. As expected, wider temperature differences were recorded between the open sea experimental settings and the glass tanks, these latter showing a temperature of around 2.5 °C greater in average. To be noted that the temperatures measured in the "reducing tank" were averagely 0.6 °C greater than the ones of the "oxidizing tank"

(Table 3 and Figure 7A). In this case the difference can be justified taking into account a relatively more advantageous exposition to the sunlight.

The pH, by and large, results considerably stable in all of the monitored experimental settings (open and confined), with values ranging from a minimum of 7.98 (reducing open sea microenvironment) to a maximum of 8.20

Table 3. ...Continued

Site of Measurement	Date D/M/Y	Seawater Temp. °C	pH	TDS g/L	Salinity ‰	ORP mV	Cond mS/cm	Wind Speed km/h	Wind Direction
Reducing open sea bed environment	28/03/12	16.0	8.1	37.0	37.9	-59.4	56.9	27.0	S-SE
	05/04/12	17.9	8.0	37.2	38.1	-23.9	57.0	62.6	S-SE
	12/04/12	16.8	8.0	35.7	36.5	205.2	55.0	51.9	SW
	19/04/12	16.1	8.0	36.1	36.9	64.7	55.6	51.9	NW
	26/04/12	18.0	8.1	35.9	36.7	29.9	55.3	35.2	SE
	04/05/12	18.0	8.1	36.4	37.2	71.9	55.9	22.2	N
	11/05/12	18.3	8.1	36.3	37.1	-15.2	55.8	24.1	NE
	18/05/12	17.1	8.1	36.8	37.6	-12.8	56.5	33.3	NW
	25/05/12	16.5	8.1	36.8	37.7	-12.0	56.6	24.1	NW
	31/05/12	19.1	8.1	36.8	37.8	-15.0	56.7	24.1	NE
Glass Container 2 (prevalent fine sand)	16/03/12	16.3	8.0	36.0	36.8	195.8	55.4	39.2	S-SE
	28/03/12	19.9	8.1	37.1	38.1	109.9	57.1	27.0	S-SE
	05/04/12	21.2	8.0	36.9	37.8	191.6	56.7	62.6	S-SE
	12/04/12	21.5	8.1	35.9	36.7	232.1	55.3	51.9	SW
	19/04/12	19.9	8.1	36.2	37.0	204.6	55.7	51.9	NW
	26/04/12	21.0	8.1	35.8	36.6	187.7	55.1	35.2	SE
	04/05/12	19.5	8.1	36.4	37.3	128.9	56.0	22.2	N
	11/05/12	20.2	8.1	36.1	36.9	202.9	55.6	24.1	NE
	18/05/12	19.8	8.1	36.5	37.4	125.9	56.2	33.3	NW
	25/05/12	18.3	8.1	36.6	37.5	158.0	56.3	24.1	NW
	31/05/12	21.3	8.1	36.1	36.9	105.3	55.5	24.1	NE

(oxidizing open sea microenvironment), with an average value equal to 8.09. This behaviour is reasonably understandable considering the buffer action played by the bicarbonate and carbonate ions (Table 3). The highest pH values, recorded in the open oxidizing environment, might be likely correlated to the occurring biological processes (photosynthesis and respiration) which influence the concentration of dissolved carbon dioxide and consequently affect the pH value.

Conductivity, salinity and TDS values did not show any significant variation between the monitored environments (Table 3). Conductivity, that is to say the capacity of a solution to conduct an electric current, provides a rough indication of the total number of ions; it is related to the TDS and salinity.

As long established, the redox potential (Eh or ORP) of seawater is primarily determined by the concentration of dissolved oxygen or dissolved
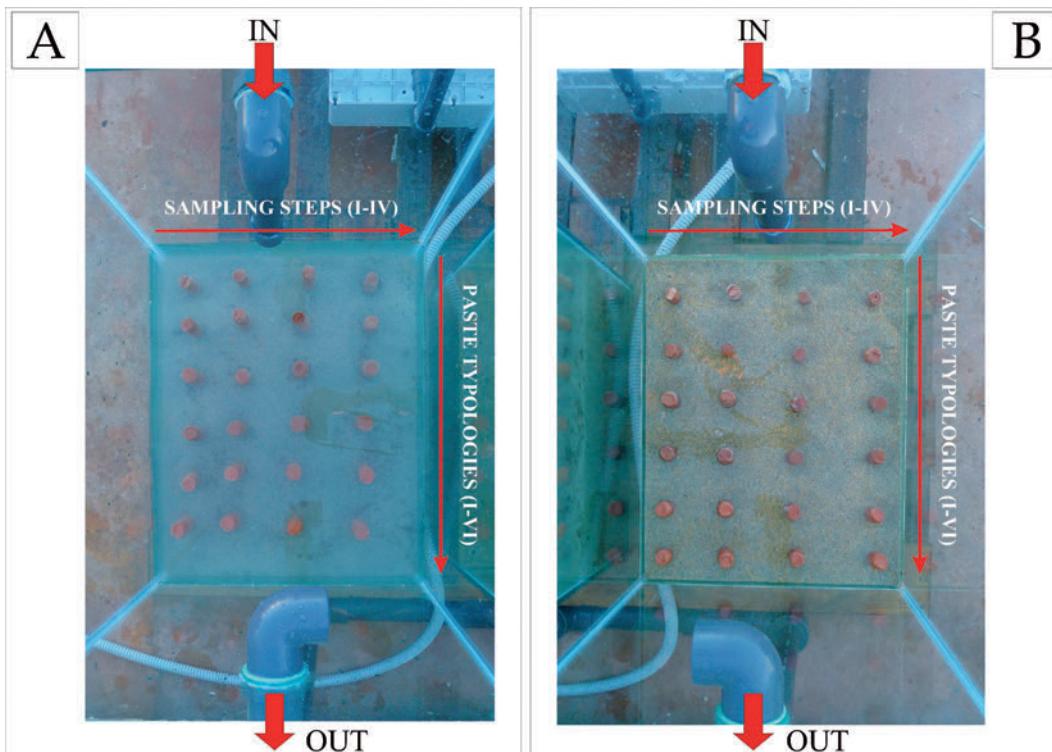
Figure 6. Immersion of the ceramic test-pieces at the beginning of the experiment: (A) glass container 2 and (B) glass container 1.

hydrogen sulphide (Edgington et al., 1967). In general, positive redox potentials correspond to the presence of dissolved oxygen, whereas negative values indicate a reducing medium such as the one existing in the presence of dissolved hydrogen sulphide. The oxygen in seawater may come from the atmosphere or be generated in photosynthetic processes. It is consumed by respiration (biochemical) and chemical reactions. The possible chemical reactions include oxidation of organic matter and the oxidation of hydrogen sulphide or other dissolved inorganic substances. The redox

potential of seawater normally falls within the range from +400 to -150 mV. The progression from positive to negative Eh values might also roughly correspond to increases in depth. Going to consider the experimental settings some differences can be appreciated between confined (glass tanks) and open microenvironments. The Eh values recorded for both "oxidizing" and "reducing" glass tanks showed a very similar trend of variation during the monitored range of time (Figure 7B). This conformity, a part of some negligible differences, was tested also in terms of absolute Eh values which ranged from a
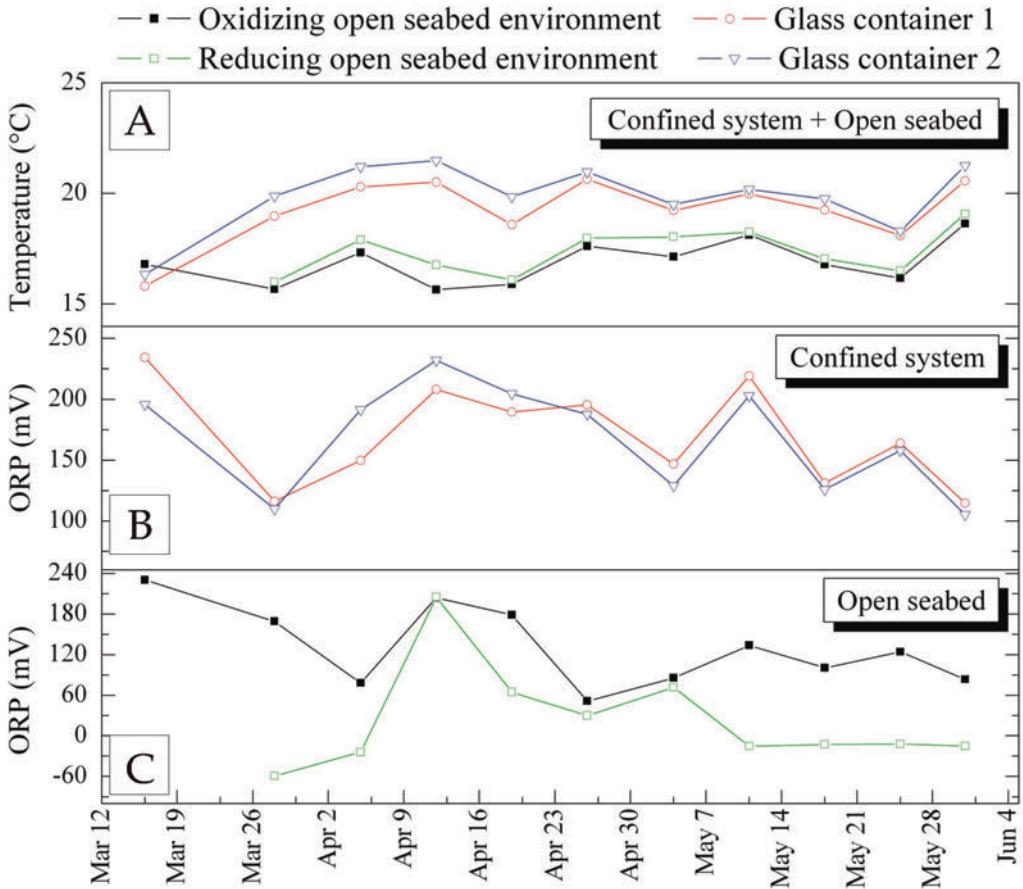
Figure 7. (A) Variation of seawater temperature within the first three months of monitoring in the considered experimental settings; (B) variation of redox potential (ORP) in the confined system; (C) variation of redox potential (ORP) in the open seabed environments.

minimum of +115 mV to a maximum of +234 mV in the oxidising tank and from +105 mV to +232 mV in the reducing tank (Table 3). This result suggests that in the confined microenvironments the redox potential measured in seawater is chiefly conditioned by the atmospheric oxygen rather than the chemical reactions occurring at the interface between

seawater and the different sediments filling the tanks. On the contrary, the two open sea settings showed a markedly different behaviour (Figure 7C). Considerably lower redox potential values were registered in the open seabed reducing environment from a minimum of -59 mV to a maximum of +205 mV, while in the oxidizing open setting it varied from +52 mV to 231 mV

(Table 3). To be underlined that in the reducing open seabed setting the most part of the Eh values are negative with the only exception of some measurements which were performed during or immediately after strong breeze conditions with wind speed exceeding 39 km/h and wave height up to 3-4 meters (Table 3).

XRF analyses

XRF analyses were performed on the ceramic test-pieces before and after 3 months of immersion into seawater considering both the described settings: open sea-bed environment under monitored oxidizing or reducing conditions and confined systems under a continuous seawater flow. To be underlined that in this preliminary paper, specially focused on the application of the whole experimental equipment, the following categories of ceramic test-pieces were chemically tested: a) briquettes placed in open sea-bed environment (both oxidizing and reducing conditions); b) cylinders from both the glass containers (confined systems) limited to the portion above the bottom sediment.

It is apparent that with reference to the aims of the paper the accurate measurement of the earliest chemical composition of the considered experimental pastes turns out to be of central significance. For this reason the XRF analyses of each single experimental paste, according to the procedure previously described, were repeated several times on a satisfactory number of sub-specimens (fragments of around 10 g of weight collected from randomly selected briquettes and cylinders after the firing process)

in order to ascertain the "within-paste" chemical variability. For the same purpose, the XRF analyses concerning major and minor elements as well as a couple of the measured trace elements (Cr and V) were additionally replicated by an accredited laboratory (Activation Laboratories Ltd).

The chemical characteristics of the considered experimental pastes before the start of the experimental settings are resumed in Table 4, where the corresponding mean values and standard deviations are reported.

With reference to the major and minor constituents it can be firstly stated that all the experimental ceramic pastes showed low values of standard deviation thus indicating a very good compositional homogeneity (adequately low "within-paste" chemical variability). This result can be considered a consequence of the appropriateness of the procedures followed during the steps of mixing and tempering (pastes manufacture). Also the replicates by XRF made following the method of lithium tetraborate fusion producing a glass disk (by the Activation Laboratories Ltd) showed a satisfactorily low level of variability and, at the same time, a very good correspondence with the results obtained by the classic XRF performed on pressed powder pellets on the corresponding experimental ceramic pastes. Furthermore, the bulk compositions of the considered ceramic pastes (Table 4) clearly reflect the nature of temper grains (volcanic or sedimentary) and/or their relative abundance (% packing) as well as the composition of the finer particles constituting the groundmass (being either "non calcareous" for pastes I and II or

Table 4. Chemical composition of the six considered ceramic pastes measured after experimental firing obtained by XRF (pressed powder pellets and alkaline fusion).

Oxides (wt%) Powder Pellets XRF	Paste I [σ] (n = 11)	Paste II [σ] (n = 11)	Paste III [σ] (n = 11)	Paste IV [σ] (n = 11)	Paste V [σ] (n = 11)	Paste VI [σ] (n = 11)
SiO_2	59.9 [0.4]	57.0 [0.6]	65.1 [0.9]	68.5 [1.5]	65.4 [0.7]	68.8 [1.1]
Al_2O_3	22.2 [0.0]	21.6 [0.3]	13.6 [0.4]	11.6 [0.6]	13.7 [0.4]	11.7 [0.5]
Fe_2O_3	8.2 [0.0]	8.7 [0.1]	5.7 [0.1]	5.3 [0.1]	5.9 [0.1]	5.2 [0.1]
MnO	0.1 [0.0]	0.2 [0.0]	0.1 [0.0]	0.1 [0. 0]	0.1 [0.0]	0.1 [0.0]
MgO	3.0 [0.2]	3.3 [0.1]	2.8 [0.1]	2.4 [0.3]	2.8 [0.1]	2.3 [0.2]
CaO	2.3 [0.0]	4.3 [0.1]	8.4 [0.3]	8.6 [0.6]	8.1 [0.1]	8.3 [0.3]
Na_2O	0.9 [0.4]	1.6 [0.0]	1.1 [0.0]	0.9 [0.1]	1.0 [0.0]	1.0 [0.0]
K_2O	2.0 [0.0]	1.9 [0.0]	2.2 [0.0]	2.0 [0.1]	2.2 [0.0]	2.0 [0.1]
TiO_2	1.2 [0.0]	1.3 [0.0]	0.7 [0.0]	0.6 [0.0]	0.7 [0.0]	0.6 [0.0]
P_2O_5	0.2 [0.0]	0.3 [0.0]	0.2 [0.0]	0.1 [0.0]	0.2 [0.0]	0.1 [0.0]
Trace Element (ppm)	Paste I [σ] (n = 11)	Paste II [σ] (n = 11)	Paste III [σ] (n = 11)	Paste IV [σ] (n = 11)	Paste V [σ] (n = 11)	Paste VI [σ] (n = 11)
V	269 [6]	246 [7]	98 [3]	82 [6]	88 [7]	79 [7]
Cu	78 [6]	91 [3]	38 [2]	38 [1]	38 [3]	33 [1]
Zn	132 [2]	148 [5]	98 [1]	93 [2]	103 [2]	98 [16]
Rb	92 [2]	70 [1]	93 [1]	84 [1]	91 [1]	82 [0]
Sr	289 [9]	565 [4]	237 [13]	226 [11]	236 [10]	227 [17]
Y	26 [1]	23 [0]	28 [0]	25 [1]	28 [1]	25 [0]
Zr	179 [6]	244 [8]	202 [5]	202 [4]	210 [9]	205 [9]
Ba	299 [18]	465 [22]	324 [10]	344 [11]	338 [11]	347 [15]
Co	25 [2]	24 [2]	17 [1]	17 [1]	17 [1]	17 [2]
Cr	188 [21]	142 [20]	89 [15]	85 [13]	86 [14]	90 [18]
Ce	89 [3]	95 [1]	71 [1]	63 [1]	75 [1]	65 [1]
Nb	20 [3]	32 [1]	15 [0]	13 [1]	15 [1]	14 [0]
La	46 [3]	50 [3]	36 [4]	32 [2]	38 [3]	33 [4]
Ni	48 [7]	39 [4]	28 [6]	26 [6]	29 [6]	28 [5]
Oxides (wt%) Fusion XRF	Paste I [σ] (n = 6)	Paste II [σ] (n = 6)	Paste III [σ] (n = 6)	Paste IV [σ] (n = 6)	Paste V [σ] (n = 6)	Paste VI [σ] (n = 6)
SiO_2	59.2 [0.4]	56.6 [0.6]	65.8 [0.1]	68.6 [0.2]	65.8 [0.1]	68.9 [0.2]
Al_2O_3	22.6 [0.3]	21.5 [0.1]	13.5 [0.0]	11.9 [0.2]	13.4 [0.1]	11.7 [0.2]
Fe_2O_3	8.4 [0.1]	8.7 [0.2]	5.6 [0.0]	5.1 [0.0]	5.7 [0.1]	5.0 [0.1]
MnO	0.1 [0.0]	0.2 [0.0]	0.1 [0.0]	0.1 [0.1]	0.1 [0.0]	0.1 [0.0]
MgO	2.9 [0.1]	3.3 [0.1]	2.7 [0.0]	2.3 [0.0]	2.7 [0.0]	2.3 [0.0]
CaO	2.4 [0.1]	4.5 [0.3]	8.2 [0.0]	8.4 [0.0]	8.2 [0.0]	8.3 [0.2]
Na_2O	0.8 [0.0]	1.7 [0.2]	1.0 [0.0]	0.9 [0.0]	1.0 [0.0]	0.9 [0.0]
K_2O	2.0 [0.0]	2.0 [0.0]	2.3 [0.0]	2.0 [0.0]	2.2 [0.0]	2,0 [0.0]
TiO_2	1.2 [0.0]	1.3 [0.0]	0.7 [0.0]	0.6 [0.0]	0.7 [0.0]	0.6 [0.0]
P_2O_5	0.3 [0.0]	0.3 [0.0]	0.2 [0.0]	0.1 [0.0]	0.2 [0.0]	0.1 [0.0]
Trace Element (ppm)	Paste I [σ] (n = 6)	Paste II [σ] (n = 6)	Paste III [σ] (n = 6)	Paste IV [σ] (n = 6)	Paste V [σ] (n = 6)	Paste VI [σ] (n = 6)
V	264 [2]	252 [3]	109 [3]	95 [2]	114 [1]	98 [2]
Cr	197 [8]	150 [14]	82 [4]	72 [4]	85 [5]	75 [8]

"calcareous" for pastes III, IV, V and VI. In contrast, noteworthy dissimilarity concerning the bulk chemistry of the studied experimental ceramic pastes have not been observed as consequence of the different firing temperatures (800 and 950 °C). Therefore, pastes I and II, being characterized by volcanic (basaltic rock fragments and single minerals) temper mixed with non-calcareous clay and both fired at 800 °C showed somewhat dissimilar concentrations of SiO_2, MgO, Fe_2O_3, CaO and Na_2O. Apart of SiO_2 that seems to be correlated to the groundmass/temper ratio all of the other oxides were more abundant in paste II which was manufactured using a relatively higher temper packing with respect to paste I (25% versus 5%). In fact, the rather higher mean concentrations of MgO and total Fe_2O_3 could be likely linked to the increasing frequency of mafic minerals (both olivine and clinopyroxene), while CaO and Na_2O to the abundance of plagioclase in the experimental paste II. Similar considerations can be made for the experimental ceramic pastes III, IV, V and VI, which were manufactured by adding variable quantities of silico-calcareous sand (respectively: pastes III and V 5%; pastes IV and VI 25%) and fired at different temperatures (pastes III and IV at 800 °C while pastes V and VI at 950 °C). Indeed, the differences of bulk chemical composition seem to be correlated to the relative abundance of sand temper: SiO_2 is visibly higher in pastes IV and VI (averagely 68.61 wt%) as a result of a larger occurrence of quartz grains; on the other hand Al_2O_3, total Fe_2O_3, K_2O and TiO_2 are somewhat more concentrated in pastes III and V, giving evidence of a comparatively greater

influence of the mica flakes and the clay minerals composing the groundmass (both silt-sized and < 2 micron particles). To be underlined that, within the same group of experimental ceramic pastes (III, IV, V and VI) the concentration of CaO does not significantly differ with the variation of the content of sand temper, thus suggesting that the calcareous microfossils are basically concentrated in the medium-coarse silt fraction (0.02-0.06 mm).

Concerning the trace elements, the "within-paste" chemical variability resulted in general to be reasonably good. Standard deviations were recorded to be noticeably below 10% for the majority of the measured elements (Table 4), with the highest variability (even if reasonably tolerable) showed by chromium, nickel and lanthanum. The replicates by XRF made on lithium tetraborate fusion beads and testing only two of the measured trace elements (Cr and V) showed adequately low values of standard deviation and also a more than acceptable correspondence with the results obtained by XRF analyses on pressed powder pellets, as previously recognized for major elements (Table 4). Considering the individual differences between the "non-calcareous" experimental ceramic pastes tempered with volcanic sand in terms of trace elements, paste II (packing = 25%) diverges from paste I (packing = 5%) because of its relatively higher concentration of Cu, Zn, Sr, Zr, Ba and Nb, which can be correlated with a major amount of temper rock fragments and minerals. On the contrary, paste I resulted to be averagely characterized by moderately richer concentration of V and Rb which might reflect

the higher abundance of clay minerals. The individual differences in the concentration of trace elements are comparatively less significant in case of the experimental pastes tempered with silico-calcareous sand (pastes III, IV, V and VI). In particular only faintly greater abundance of V, Rb, Ce and La seems to distinguish pastes III and V (packing = 5%) from pastes IV and VI (packing = 25%) once again reflecting the prevalence of fine silty and/or clayey particles over sand granules.

XRF analyses on pressed powder pellets were performed on the experimental briquettes and cylinders after the first experimental step (3 months of exposure to seawater). It is evident that 3 months might be considered a small range of time to significantly monitor the extent of variation in the bulk chemistry of the experimental ceramic pastes deriving from the interaction with the "marine environment". Nonetheless, as previously stated, this first analytical step of measurements was completed in order to appreciate if any form of alteration of the chemical composition of the experimental ceramic pastes may take place after a short marine burial as well and, in general, for testing the efficiency of the whole experimental apparatus.

The results of XRF analyses (pressed powder pellets) carried out on the experimental briquettes after 3 months of exposure in the open sea-bed environment under oxidizing or reducing conditions, are reported in Table 5. These values were compared with the $\pm 3\sigma$ values (99.7 confidence interval) obtained from the series of analysis made on all the

corresponding experimental ceramic pastes before the immersion into seawater (additional data are given in Electronic Supplementary Material, ESM 1). Concerning major and trace constituents, only a few changes respect to the initial composition can be noticed. The experimental ceramic paste I (tempered with volcanic sand 5% volume) showed small changes of SiO_2, Al_2O_3, K_2O, TiO_2, P_2O_5 concentrations with respect to the $\pm 3\sigma$ values, from around 1% to 9% weight compared with the initial composition. At the same time, a major enrichment was recorded only for the Na_2O content up to 36% weight (Figure 8A). To be underlined that the same trend in terms of elements and relative quantities was approximately observed for both the oxidizing and reducing burial environments. The experimental ceramic paste II (tempered with volcanic sand 25% volume) seems to have reacted in a slightly different way if compared with paste I. In fact, together with very small variations of SiO_2, Al_2O_3 and TiO_2 compared with the $\pm 3\sigma$ values, it showed not negligible enrichments of MgO, CaO and P_2O_5 over the $+3\sigma$ limit (up to around 17% weight in relation to the initial composition). Once again a noteworthy Na_2O enrichment was measured up to the 54% weight (Figure 8A). To be noted that a similar trend was recorded another time in both the experimental burial environments, not considering the very small depletion of SiO_2 below the -3σ limit which was documented only in the reducing setting. It is interesting to underline that, even if an unambiguous Na_2O enrichment was measured in both pastes I and II,

Table 5. Chemical composition of the ceramic briquettes after 3 months of exposure in the open seabed environment under oxidizing and reducing conditions (XRF on pressed powder pellets).

AFTER THREE MONTHS

Briquettes from oxidizing open sea bed environment					
Oxides (wt%)	OX B-I-23-3	OX B-II-25-3	OX B-III-18-3	OX B-IV-22-3	OX B-V-18-3	OX B-VI-21-3
SiO_2	59.1	56.9	66.8	69.5	66.9	69.8
Al_2O_3	23.1	20.1	13.5	11.5	13.4	11.9
Fe_2O_3	8.1	8.2	5.1	4.7	5.3	4.7
MnO	0.1	0.2	0.1	0.1	0.1	0.1
MgO	2.7	3.9	2.5	2.8	2.1	2.0
CaO	2.3	5.0	7.4	7.2	7.8	7.6
Na_2O	1.0	2.1	1.6	1.6	1.4	1.2
K_2O	2.1	1.9	2.3	2.0	2.2	1.9
TiO_2	1.2	1.4	0.7	0.6	0.7	0.6
P_2O_5	0.2	0.3	0.2	0.1	0.2	0.2
Trace Elements (ppm)	OX B-I-23-3	OX B-II-25-3	OX B-III-18-3	OX B-IV-22-3	OX B-V-18-3	OX B-VI-21-3
V	284	272	118	99	112	109
Cu	70	91	41	32	35	39
Zn	125	135	104	90	99	87
Rb	98	62	85	76	85	79
Sr	299	610	248	264	291	312
Y	23	23	27	25	27	24
Zr	179	268	194	192	188	185
Ba	247	476	325	320	350	362
Co	50	43	30	32	34	39
Cr	204	143	89	69	75	84
Ce	93	95	72	69	64	66
Nb	21	39	14	13	14	13
La	47	48	37	35	33	34
Ni	99	83	63	55	63	59

OX = oxidising conditions and RD = reducing conditions; B = briquette; I, II, III, IV, V, VI = type of paste; first number = number of a specific test-pieces chosen from a total of 150 briquettes; second number = time of immersion.

the former showed relatively lower values in oxidizing and reducing conditions as well. This result might be interpreted as consequence of a relatively greater intergranular porosity developed in paste II due to the larger quantity of sand temper compared to paste I. In terms of trace elements both pastes I and II, after three months of contact with seawater (Table 5), showed slight changes of V, Zn, Rb, Sr and Zr, together with more evident as well as conspicuous enrichments of Co and Ni, up to more than two times respect to the initial

Table 5. ...Continued

AFTER THREE MONTHS

Briquettes from reducing open sea bed environment					
Oxides (wt%)	RD B-I-21-3	RD B-II-21-3	RD B-III-21-3	RD B-IV-21-3	RD B-V-17-3	RD B-VI-25-3
SiO_2	59.6	54.6	67.5	69.4	66.7	72.6
Al_2O_3	22.7	21.8	13.2	11.7	13.5	10.6
Fe_2O_3	8.1	8.8	5.0	4.7	5.3	4.4
MnO	0.1	0.2	0.1	0.1	0.1	0.1
MgO	2.6	3.8	2.6	2.8	2.3	1.6
CaO	2.3	4.9	6.9	7.0	7.8	6.9
Na_2O	1.1	2.4	1.7	1.6	1.4	1.4
K_2O	2.1	1.9	2.2	2.0	2.2	1.7
TiO_2	1.2	1.4	0.7	0.6	0.7	0.6
P_2O_5	0.2	0.3	0.2	0.2	0.2	0.1
Trace Elements (ppm)	RD B-I-21-3	RD B-II-21-3	RD B-III-21-3	RD B-IV-21-3	RD B-V-17-3	RD B-VI-25-3
V	295	245	117	102	110	108
Cu	75	70	27	38	30	26
Zn	125	123	93	96	96	83
Rb	99	64	84	75	86	76
Sr	296	573	261	257	264	307
Y	22	23	28	25	28	24
Zr	174	273	199	215	204	202
Ba	226	461	314	364	337	359
Co	54	43	32	31	31	47
Cr	207	153	85	88	86	83
Ce	73	99	68	74	67	66
Nb	20	38	14	13	15	13
La	48	52	35	38	34	34
Ni	85	71	54	48	54	51

OX = oxidising conditions and RD = reducing conditions; B = briquette; I, II, III, IV, V, VI = type of paste; first number = number of a specific test-pieces chosen from a total of 150 briquettes; second number = time of immersion.

concentration. This seemingly odd result might be considered an effect of local sea pollution, even though it is worth noting that surface water of the Mediterranean Sea is known to be characterised, respect to nutrient-depleted open ocean, by elevated concentrations of some trace metals like Ni (Spivack et al., 1983; Boyle et al., 1985). Concerning the four "calcareous" experimental pastes III, IV, V and VI tempered with quartz-bearing sand and fired at two different temperatures, they showed all similar trends of variation of their bulk chemical
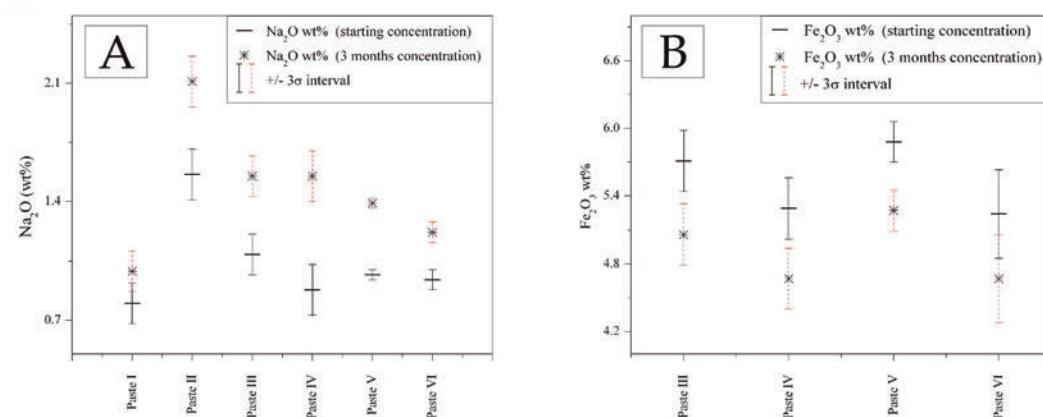
Figure 8. (A) Enrichment in Na_2O (wt%) concerning all the experimental ceramic pastes; (B) depletion of Fe_2O_3 concerning the four "calcareous" experimental pastes III, IV, V and VI.

composition, not depending on the burial environment (oxidizing or reducing), temper abundance (5% or 25% volume) and firing temperature (800 or 950 °C). A depletion of Fe_2O_3 below the -3σ limit, up to 16% weight compared with the initial composition (Figure 8B). At the same time, significant enrichments of Na_2O over the +3σ limit were detected, ranging from about 29% weight in paste VI (oxidizing setting), up to 76% weight in paste IV (both oxidizing and reducing settings). Moreover, significant depletions under the -3σ limit concerning MgO and CaO were pointed out for the "calcareous" pastes III, V, VI (MgO up to 30% and CaO up to 18% weight compared with the initial compositions), being in particular observed in the reducing experimental setting. As well known, both calcium and magnesium are employed in biomineralization of a wide variety of marine biota. Magnesium often substitutes for Ca in the calcite skeletons of

marine invertebrates (Borszcz et al., 2013), such as the calcareous Serpulidae worms that were copiously recognized in the surface of the experimental briquettes even after 3 months immersion (to be underlined that the calcareous concretions were removed from the surface of the samples before analysing them). In terms of trace elements' concentrations, the "calcareous" quartz-tempered experimental briquettes resulted to behave similarly to the "non calcareous" ones, being characterized by minor changes of V, Zn, Rb, Sr and Zr and, once more, high enrichments over the +3σ limit of Co and Ni (respectively up to the 176 % and 125% compared with the initial compositions). The most relevant variations concerning major and trace elements after the three months sampling step for each experimental paste, are summarized in Figure 9.

The results of XRF analyses (pressed powder pellets) carried out on the cylinders from both the previously described glass containers

BRIQUETTES FROM OXIDIZING OPEN SEA BED ENVIRONMENT

PASTE I	PASTE II	PASTE III	PASTE IV	PASTE V	PASTE VI
↑ Al₂O₃, K₂O, P₂O₅ ↓ SiO₂, TiO₂ ↑↑ Na₂O ↓ Zn ↑↑↑ Co, Ni	↑ TiO₂ ↓ Al₂O₃, Fe₂O₃ ↑↑ MgO, CaO, P₂O₅ ↑↑↑ Na₂O ↑ V, Sr ↓↓ Rb ↑↑↑ Co, Ni	↓↓ Fe₂O₃, CaO ↑↑↑ Na₂O ↑ Zn ↑↑ V ↑↑↑ Co, Ni	↓↓ Fe₂O₃ ↑↑↑ Na₂O ↓ Rb ↑↑ Sr ↑↑↑ Co, Ni	↑ TiO₂ ↓↓ Fe₂O₃, MgO ↑↑↑ Na₂O ↓ Rb ↑↑ V, Sr ↑↑↑ Co, Ni	↑ TiO₂ ↓↓ Fe₂O₃ ↑↑↑ Na₂O ↓ Rb ↑↑ V, Sr ↑↑↑ Co, Ni

BRIQUETTES FROM REDUCING OPEN SEA BED ENVIRONMENT

PASTE I	PASTE II	PASTE III	PASTE IV	PASTE V	PASTE VI
↑ Al₂O₃, K₂O, P₂O₅ ↓ TiO₂ ↑↑↑ Na₂O ↑ V, Rb ↓ Zn ↑↑↑ Co, Ni	↓ SiO₂ ↑ TiO₂ ↑↑ MgO, CaO, P₂O₅ ↑↑↑ Na₂O ↓ Rb ↑ Zr ↓↓ Zn ↑↑↑ Co, Ni	↓↓ Fe₂O₃, CaO ↑↑↑ Na₂O ↓ Rb ↑↑ V ↓↓ Zn ↑↑↑ Co, Ni	↓↓ Fe₂O₃ ↑↑↑ Na₂O ↑↑ V ↓↓ Rb ↑ Zr ↑↑↑ Co, Ni	↑ TiO₂ ↓↓ MgO, Fe₂O₃ ↑↑↑ Na₂O ↓ Zn, Rb ↑↑ V ↑↑↑ Co, Ni	↑ SiO₂ ↓↓ Fe₂O₃, MgO, CaO, K₂O ↑↑↑ Na₂O ↓ Rb ↑↑ V, Sr ↑↑↑ Co, Ni

CYLINDERS FROM GLASS CONTAINER 1 (PREVALENT MEDIUM-COARSE SAND)

PASTE I	PASTE II	PASTE III	PASTE IV	PASTE V	PASTE VI
↑ Al₂O₃ ↓ SiO₂, TiO₂ ↑↑ Na₂O, P₂O₅ ↑ V ↓ Zn ↑↑↑ Co, Ni	↓ SiO₂ ↑ TiO₂ ↑↑ CaO ↑↑↑ Na₂O ↓ Rb ↑ Sr ↑↑ V ↓↓ Zn ↑↑↑ Co, Ni	↑ SiO₂ ↓↓ Fe₂O₃, CaO ↑↑ Na₂O ↑↑↑ MgO ↓ Rb ↓ Zr ↑↑ V ↑↑↑ Co, Ni	↓↓ Fe₂O₃ ↑↑↑ Na₂O ↓ Rb ↓↓ Zr ↑↑ Sr ↑↑↑ Co, Ni	↑ TiO₂ ↓ Fe₂O₃ ↓↓ MgO ↑↑↑ Na₂O ↓ Rb ↑↑ V ↑↑↑ Co, Ni	↓ CaO ↓↓ Fe₂O₃, K₂O ↑↑ Na₂O ↓↓↓ MgO ↓ Rb ↑↑ Sr ↑↑↑ Co, Ni

CYLINDERS FROM GLASS CONTAINER 2 (PREVALENT FINE SAND)

PASTE I	PASTE II	PASTE III	PASTE IV	PASTE V	PASTE VI
↑ Al₂O₃, K₂O, P₂O₅ ↓ SiO₂, TiO₂ ↑↑ Na₂O ↓ Zn ↑↑ V ↑↑↑ Co, Ni	↓ SiO₂ ↑ TiO₂ ↑↑ MgO, CaO, P₂O₅ ↑↑↑ Na₂O ↓ Rb ↑ Sr ↓↓ Zn ↑↑ Ba ↑↑↑ Co, Ni	↓ Fe₂O₃ ↓↓ MgO ↑↑ Na₂O ↓ Rb ↑↑↑ Co, Ni	↓↓ Fe₂O₃ ↑↑↑ Na₂O ↓ Rb ↑↑ Sr ↑↑↑ Co, Ni	↑ TiO₂ ↓ Fe₂O₃ ↓↓ MgO ↑↑↑ Na₂O ↓ Rb ↑↑ V ↑↑↑ Co, Ni	↑ Na₂O ↓↓ Fe₂O₃, MgO, K₂O ↓ Rb ↑↑ V, Sr ↑↑↑ Co, Ni

Legend: ↑ and/or ↓ = variations < 10%; ; ↑↑ and/or ↓↓ = variations between 10% and 30%; ; ↑↑↑ and/or ↓↓↓ = variations >30%

Figure 9. Summary of the variations in major and trace elements after three months for each experimental ceramic paste.

(confined systems) are shown in Table 6. The analysis was in the interim limited to the portion above the bottom sediment (cylinders were cut at the water-sediment interface before analysing them). As made for the briquettes placed into the open sea settings, the results, in order to highlight the compositional variations, were again compared with the ± 3σ values obtained from the analytical series made on the matching ceramic pastes before the beginning of the experiment (additional data are given in Electronic Supplementary Material, ESM 2). It is interesting to note that trends quite similar to the ones already described for the briquettes

Table 6. Chemical composition of the ceramic cylinders from both the "confined system" (glass containers 1 and 2) after 3 months of immersion (XRF on pressed powder pellets). Legend:

AFTER 3 MONTHS

Cylinders from glass container 1 (prevalent medium-coarse sand)

Oxides (wt%)	OX C-I-5-3E	OX C-II-5-3E	OX C-III-4-3E	OX C-IV-15-3E	OX C-V-4-3E	OX C-VI-6-3E
SiO_2	59.1	54.6	68.4	70.6	66.8	72.1
Al_2O_3	23.0	21.7	12.9	11.5	13.6	10.7
Fe_2O_3	8.2	8.9	5.1	4.6	5.4	4.7
MnO	0.1	0.2	0.1	0.1	0.1	0.1
MgO	2.8	3.7	1.8	1.8	2.0	1.4
CaO	2.3	4.9	7.4	7.5	7.8	7.5
Na_2O	1.0	2.5	1.3	1.3	1.3	1.1
K_2O	2.1	1.9	2.2	1.9	2.2	1.8
TiO_2	1.2	1.4	0.7	0.6	0.7	0.6
P_2O_5	0.2	0.3	0.2	0.2	0.2	0.1

Trace Elements (ppm)	OX C-I-5-3E	OX C-II-5-3E	OX C-III-4-3E	OX C-IV-15-3E	OX C-V-4-3E	OX C-VI-6-3E
V	291	287	115	98	112	97
Cu	72	94	43	30	39	40
Zn	122	130	100	87	99	97
Rb	97	63	89	78	86	79
Sr	301	606	262	268	256	284
Y	22	23	26	23	27	24
Zr	171	237	186	177	193	180
Ba	245	495	332	348	343	367
Co	50	57	32	36	36	42
Cr	199	145	87	75	76	83
Ce	83	90	67	68	60	62
Nb	16	39	14	12	14	13
La	43	47	34	35	31	32
Ni	68	55	43	37	43	40

OX = oxidising conditions and RD = reducing conditions; C = cylinder; I, II, III, IV, V, VI = type of paste; first number = number of a specific test-pieces chosen from a total of 150 briquettes; second number = time of immersion; E = emerged portion of the cylinder (above the bottom sediment filling the thank).

were equally identified for major and trace elements. Indeed, the samples representative of pastes I and II ("non-calcareous" and tempered with volcanic sand) showed the same tendency in both the glass containers, with minor variations of SiO_2, Al_2O_3, K_2O and TiO_2. Besides CaO (only for paste II) and P_2O_5 showed not negligible enrichments over the $+3\sigma$ limit (up to around 17% weight in relation to the initial composition). On the other hand, like already pointed out for the experimental briquettes, noteworthy Na_2O enrichment over the $+3\sigma$ limit

Table 6. ...Continued

<div align="center">AFTER 3 MONTHS</div>

Cylinders from glass container 2 (prevalent fine sand)					
Oxides (wt%) RD C-I-1-3E	RD C-II-1-3E	RD C-III-1-3E	RD C-IV-1-3E	RD C-V-1-3E	RD C-VI-1-3E
SiO_2 59.4	54.4	67.5	70.3	66.3	71.9
Al_2O_3 22.8	21.7	13.2	11.3	13.7	10.9
Fe_2O_3 8.2	9.0	5.2	4.6	5.4	4.5
MnO 0.1	0.2	0.1	0.1	0.1	0.1
MgO 2.7	3.8	2.0	1.8	2.1	1.5
CaO 2.3	4.9	7.7	7.9	8.0	7.6
Na_2O 1.0	2.5	1.3	1.3	1.4	1.0
K_2O 2.1	1.9	2.2	1.9	2.2	1.8
TiO_2 1.2	1.4	0.7	0.6	0.7	0.6
P_2O_5 0.2	0.3	0.2	0.1	0.2	0.1
Trace Elements (ppm) RD C-I-1-3E	RD C-II-1-3E	RD C-III-1-3E	RD C-IV-1-3E	RD C-V-1-3E	RD C-VI-1-3E
V 300	243	103	100	117	107
Cu 71	91	36	39	40	38
Zn 121	130	94	93	100	90
Rb 96	63	88	80	85	79
Sr 297	591	259	282	256	288
Y 23	22	26	23	28	24
Zr 175	252	190	197	207	195
Ba 238	511	297	351	343	351
Co 44	48	26	30	36	41
Cr 203	151	88	84	89	86
Ce 76	94	69	72	65	68
Nb 23	39	14	13	16	14
La 49	55	35	37	33	35
Ni 68	56	44	36	42	41

OX = oxidising conditions and RD = reducing conditions; C = cylinder; I, II, III, IV, V, VI = type of paste; first number = number of a specific test-pieces chosen from a total of 150 briquettes; second number = time of immersion; E = emerged portion of the cylinder (above the bottom sediment filling the thank).

were recorded (27% and 59% weight relating to the initial concentration respectively for paste I and paste II). Therefore, in the "non calcareous" experimental ceramic paste tempered with volcanic sand the abundance of Na_2O deriving from the permanence into the seawater setting was confirmed to be strongly dependent on the relative abundance (packing) of sand temper, which might likely influence the amount of open pore spaces. On the other hand, like in the case of briquettes placed in the open sea-bed settings, the experimental cylinders made with the

"calcareous" pastes (III, IV, V and VI) resulted to be again characterized by a not negligible reduction of Fe_2O_3 concentration under the -3σ limit in both the two considered glass containers, ranging from 9% to 15% weight compared with the initial composition. The depletion in the original concentration of Fe_2O_3 seems to be not related to the diverse temper packing and/or to the dissimilar firing temperatures. Such a decrease of Fe contents may be due to the Fe-leaching, which would occur at ceramic-seawater interface, being iron an essential micro-nutrient for algae growth (e.g. Visser et al., 2003; Censi et al., 2010). For all of the considered "calcareous" pastes, Na_2O enrichments over the $+3\sigma$ limit were also observed (up to 44% weight), being comparatively higher for pastes IV and V with respect to pastes III and VI. Therefore, as regards the "calcareous pastes", the increasing of precipitated NaCl in pore spaces seems to be not always depending on the amount of sand tempering as showed by the "non calcareous" ones and, on the contrary, correlated to firing temperature only for paste V (temper packing = 5% and firing temperature 950 °C). This effect might be correlated to the extent of sintering of the groundmass and the development of secondary porosity due to the complete decomposition of calcareous microfossils during firing. Going to consider the trace elements, as also observed for the briquettes, paste I and II showed somewhat change of abundance with respect to the $\pm 3\sigma$ values in case of V, Zn, Rb, Sr, and Ba, compared to the initial compositions. Concentration of trace elements of the

experimental pastes tempered with silica-calcareous sand (pastes III, IV, V and VI) showed mostly moderate variation with respect to the $\pm 3\sigma$ values of V, Rb and Sr. Finally, it is still evident for all the considered ceramic pastes (I, II, III, IV, V, VI) the considerable enrichments of Co (up to more than two times respect to the initial concentration) and Ni (up to 54% respect to the initial concentration), therefore confirming the effect of the interaction between experimental ceramic test-pieces and metal polluted seawater (Boyle et al., 1985). A synopsis of the main variations of chemical composition concerning the studied experimental pastes is given in Figure 9.

Conclusive remarks

This paper illustrates an operative model, feasible in a relatively short time, aimed to understand the mechanisms of interaction between seawater and ceramic artefacts. The proposed experimental approach is thus placed in the mark of the specific framework of the physico-chemical variation affecting the ceramic artefacts that resided in the marine environment for a long time, in function of their different compositional and textural characteristics. The work mainly focuses on the variations of chemical composition in ceramic artefacts, which are induced by alteration and/or contamination processes. A further purpose concerns the consequent implications that such variations have on the treatment of the chemical data with the final aim to identify the production area of the recovered pottery (complementing the

archaeological hypothesis based on the typological and stylistic classification). The research, in the following actions, is also going to appraise the aspects connected to the restoration treatments of the ceramic findings from submarine burial environments, selecting the most adequate materials and procedures.

The analytical results, even though preliminary, provided encouraging evidence that the proposed experimental apparatus is efficiently working. In fact, despite the restricted time of exposure to seawater, several outcomes (more or less expected) were pointed out in terms of variation of bulk chemical composition, being correlate to quality and/or quantity of temper and, in a relatively fewer degree, also to firing temperatures (only for "calcareous" experimental pastes). For some major constituents (specially Na_2O and Fe_2O_3) not negligible alterations (enrichments and/or depletions) compared to the initial bulk chemical composition of the experimental ceramic test-pieces (briquettes and cylinders) were established. Trace elements resulted, in general, to be less involved at this point of the experiment if weighted against the major elements. The exception concerning the remarkable enrichment of Co and Ni was interpreted as an effect of the interaction between the ceramic substrates and the composition of seawater in the area of the Strait of Sicily. The observed decrease of Fe contents may be explained with Fe-leaching, which would occur at solid-seawater interface, by also considering that iron is an essential micro-nutrient for algae and phytoplankton growth; therefore, Fe-containing material may play an important role in iron bio-availability in a seawater environment.

To be underlined that, at this first sampling phase (three months), no significant differences were found between the "oxidizing" and the "reducing" experimental settings, both in open sea-bottom conditions and confined systems under a continuous seawater flow. Moreover, the data obtained from the settings placed in the natural environment seem to be acceptably comparable with the ones from the simulated confined systems, giving confirmation that the proposed experimental apparatus is efficiently working.

The experiment is going to continue for 18 months and further three sampling steps have been planned (6, 12 and 18 months) in order to obtain a more representative picture of the mechanisms of interaction between seawater and ceramic artefacts in a typical Mediterranean coastal environment.

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