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Did copper actually arrive in the Aeolian Islands in the fourth millennium BC? The evidence from a small but iconic fragment of vitreous material thought to be copper slag

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Abstract

A singular fragment of 'copper slag' from Lipari thought until recently to be the key artefactual evidence for the arrival of the copper metallurgy in the Aeolian Islands, Sicily, in the 4th millennium BC has now been reappraised, based on scientific analysis with the Scanning Electron Microscope (SEM-EDS). The results and comparative data sets point to the fragment being vitrified fuel ash (VFA). Preliminary experiments using local plant ash heated to high temperature in a laboratory furnace in the presence of SiO₂-rich (but not necessarily quartz-rich) beach sand from the island of Stromboli, resulted in sintering but no fusion; this necessitates the closer scrutiny of the sourcing of the raw materials and heating conditions. However, it is suggested that the process is not associated with any attempt to melt or smelt copper.

Keywords: *early metallurgy, Diana-Spatarella, Italy, p-XRF, SEM-EDS*

Introduction

The first appearance of metals in Italy is ascribed to the Neolithic and is evident in contexts dated to the second half of the 5th millennium- first half of 4th millennium BC (Fig. 1). Metallurgy is thought to have been introduced to Northern Italy from the north as a result of the close connection and exchange network with the Munchshofen culture of Lower Bavaria and Austria (Pessina and Tinè 2008, 132). Objects (mainly awls) have been discovered in Northern and Central Italy in (a) Chassey levels in Northern Italy dated to the middle Neolithic, (b) VBQ (*Vaso a Bocca Quadrata*) levels, a middle Neolithic phase in northern Italy characterized by square-mouth pots, and (c) late Ripoli levels dated to middle-late Neolithic. Ripoli contexts occur in a large area of Central Italy and show close connections with other Neolithic cultures like those at Serra D'Alto (Southern Italy), Danilo (on the Dalmatian coast), Lagozza-Chassey (Northern Italy and France) and finally at Diana (Southern Italy). Ripoli pottery is fine and painted with red and brown geometric motifs organized in panels and, mainly in the latest phases, decorated with cordons, dots, circles and series of incised lines.

In North Italy the archaeological traces of the earliest evidence of metal production are at the sites of Mezzocorona-Borgonuovo and Acquaviva di Besenello

(Trento province) and Botteghino of Parma (Emilia Romagna) in Chassey levels (metal 'drops' in association with slag) (De Marinis and Pedrotti 1994; Pessina and Tinè 2008, 132); in Liguria, at Monte Loreto, there are indications that copper extraction began around 3500 cal. BC (Maggi 2002; Maggi and Pearce 2005). In Central Italy and on the Adriatic coast at Santa Maria in Selva e Fossacesia in Abruzzo, the presence of some copper fragments has been reported; in Southern Italy, in a late Serra d'Alto context of Mattinelle di Malvezzi, a copper object has been found in a burial inside a stone cist (Pessina and Tinè 2008, 134).

Evidence of metal manufacturing (slags and crucibles) is primarily concentrated in the metals-rich areas bordering the Tyrrhenian Sea: in Tuscany in late Ripoli (Final Neolithic) contexts at Neto-via Verga, Podere Pietrino, Orti Bottegone where there are crucibles and copper awls (Sarti and Volante 2002; Pessina and Tinè 2008, 134) and in Cagliari, Sardinia, in Ozieri contexts, at the sites of Anghelu Ruju, Cuccuru S'Arriu and Su Coddu di Selargius, some smelting slag of copper and silver has been recovered (Lo Schiavo 1989). Finally in the Aeolian Islands, at the Acropolis of Lipari (Figs. 2a, b) a single fragment of 'slag' has been found (Figs. 3a, b). This paper focuses on the technical examination of this find, currently on display in the Archaeological Museum at

Lipari (MA no. 8993), and asks the question whether copper metallurgy did actually arrive on the Aeolian islands in the 4th millennium BC.

In the Aeolian Islands, the Final Neolithic (4000-3400 BC) is represented by the Diana culture from a large settlement on the homonymous plain to the north of the town of Lipari; the Diana culture is characterized by a distinctive pottery made of a glossy red slip and with tubular handles (Bernabò Brea and Cavalier 1980). The same pottery has been found in Sicily and on the mainland and is thought to reflect the intensive exploitation of the Liparian obsidian sources across the Tyrrhenian Sea. The Diana-Spatarella represents the first phase of the Chalcolithic (3400-3000 BC). The pottery from this phase is made up of vessels with truncated cone surfaces of brown colour and decorated with rows of zig-zag under the edge of the inner surface of the rim. There are currently four settlements in the archipelago known for their Diana-Spatarella phase. Two are on the island of Lipari and include (a) the settlement on the coastal hill of the Acropolis (Bernabò Brea and Cavalier 1980), and (b) the settlement at Monte-Spatarella, an inland plateau rising to c. 150-230m above sea level (Cavalier 1979; Martinelli 2001). The third settlement is on the island of Salina, at Serro Brigadiere, 50-55m above sea level (Bernabò Brea, Cavalier 1995). Finally, the fourth settlement is at San Vincenzo, on the island of Stromboli on the slopes of the volcano (Cavalier 1981; Levi *et al.* 2011, 2014).

The important archaeological excavations of the Acropolis of Lipari (Fig. 2b), a lava dome rising vertically above the sea, were conducted during the 1950s (Bernabò Brea and Cavalier 1980). The research uncovered about 10m of stratigraphy spanning the Neolithic, Eneolithic, Bronze Age, Greek and Roman periods, to the present. In the Acropolis, the Diana-Spatarella phase was manifested in trench AP, cuts 10 and 11, at a depth of approximately 2m below present ground level and has been dated with C-14 on the basis of charcoal to 5000 ± 200 BP or 3050 BC (MASCA 4060-3640 BC, Bernabò Brea and Cavalier 1980, 839-844; Martinelli and Procelli 2011, 118). However, according to more recent investigations in the Archipelago and in Sicily, this single radiocarbon date, obtained from the 1952 excavation (sample R-180, Bernabò Brea and Cavalier 1989, 840-841), appears not fully reliable. Within these layers a blueish-green glassy fragment (Figs. 3a,b) was recovered and interpreted as 'slag of copper' (Bernabò Brea and Cavalier 1980, 337). In the excavation report there is no description of any associated structures or areas of heating. The authors simply mention '*some shapeless items*' collected in the layer associated with cuts 10-11. Since today there is no evidence for any additional fragments of '*shapeless items*' stored in the Lipari Museum's collections, it is likely that MA no. 8993 from cut 10, published in Bernabò Brea and Cavalier (1980, 339), is the only relevant find which was interpreted as slag.

Following the publication of the results of the excavations at the Acropolis, this unique find became the critical evidence for arguing in favour of the introduction of copper metallurgy on the Aeolian Islands in the Early Chalcolithic, and furthermore for the insertion of Lipari within the network of commercial routes for the procurement of metals (Cocchi Genick 1994, 269) at the beginning of the Bronze Age. None of the other three settlements belonging to the same Diana-Spatarella phase have revealed evidence for metal objects nor indeed associated copper processing waste (Cavalier 1979; Cavalier 1981; Bernabò Brea and Cavalier 1995; Martinelli 2001).

Methodology

This paper presents the first technical characterization of this small, but iconic fragment. The fragment measures c. 10cm (long axis) and is c. 2cm thick. It has a 'top' vitreous surface of pale green-blue colour with grey white accretions adhering to the surface (Fig. 3a). The opposite ('bottom') surface appears sintered and with a patches of ferruginous areas. It is likely that both ferruginous and non-ferruginous areas are of the same composition but not exposed to the same temperature and redox conditions. There is abundant evidence of white grains of 'sand', originally thought to be quartz but no quartz grains were observed in the sections analysed (see discussion below). Two sets of analyses were carried out: first, a non-destructive analysis with a portable X-Ray Fluorescence analyser (p-XRF) (Niton XL3t using the TestAllGeo calibration) was carried out at the Lipari Museum; second, invasive analysis on two small fragments (554.1 and 554.2), which were removed from the object at the spot indicated by the arrows in Figs. 3a, b, was carried out with the Scanning Electron Microscope with Energy Dispersive Analyser (SEM-EDS) in the SEM facility of Earth Sciences, University of Glasgow. We focus here on the results of the SEM-EDS analyses since they provide an insight into the structure of the fragment, rather than simply on its surface chemical composition (as analysed by the p-XRF). The two samples were mounted in metallographic resin, ground, polished and carbon coated prior to analysis.

Results

Images of the polished sections were taken at high magnification (see Figs. 4a, b). They reveal a highly vesicular structure and a fused matrix rather than one which cooled from the molten state. The observed porosity emanates from the burning of organic material. Following photography, three sets of analyses were undertaken: (a) area analyses over the entire surface of each sample, reflecting 'bulk' chemical composition; (b) spot analyses on the semi-fused matrix; and (c) spot analysis on individual grains. Area analyses (Table 1a) reveal a highly siliceous material consisting of aluminium silicates ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio c. 5) and about 10-15% of combined oxides (Na_2O , CaO , K_2O , and FeO). Spot analyses on the matrix revealed a similar composition.

There are numerous inclusions which are predominantly iron rich, as shown in Table 1b, but also iron aluminium silicates and on one occasion barium sulphate. There was no evidence of pure quartz grains or indeed of any metallic inclusions within the sections analysed. Trace elements like Mn, Ba, V, Cr and S were below detection limits unless specified.

Discussion

The results presented above preclude the identification of this fragment of vitreous material as metallurgical slag. Instead it is suggested that it resembles a vitrified fuel ash (VFA). VFA is a light, frothy, highly siliceous vesicular material with a predominantly glassy surface giving the appearance of having been fused and/or melted. There are many types of VFAs and they can derive from a number of very diverse processes, as for example from the burning of coal in the context of 19th century cast iron-making furnaces; they can also originate from more 'primitive' technologies like the burning of kelp (seaweed) for the production of raw materials for glass and soap manufactories, as was the case in the 18th century (Clow 1952).

In the course of our research into this fragment we suggested that the Lipari VFA bears many similarities with VFAs found within Bronze Age cremation contexts in Northern Scotland (see Fig. 5b) (Photos-Jones *et al.* 2007). These materials recovered from within burial cists in association with small fragments of human bone are formed in the course of the cremation; they were recovered from the funerary pyre and buried within the cist. They were found to derive from the reaction of plant (usually seaweed) ash in the presence of (human) bone and a source of silica, normally the local quartz-rich sand. In comparing the Lipari VFA and the Scottish VFA, called in Orcadian dialect 'cramp' (Figs. 5a, b), we note the same extent of porosity and inclusion of unreacted mineral grains. What is completely absent from the Lipari VFA is the presence of bone.

To test this hypothesis, seaweed (*poseidonia oceanica*) from the shores of the island of Stromboli was collected together with other marine plants, such as *cystoseira*, and *crithnum maritimum*, both native to the island. All three were burnt to ash and each was subsequently analysed with the p-XRF together with samples of Stromboli beach sand. The compositions (Table 2) reveal that the plants are rich in calcium and potassium, while the beach sand is rich in iron and titanium. Some trace elements in the plant ashes are interesting and perhaps merit further investigation in their potential association with local 'pollution', either man-made or derived from the volcano. For example, there are high contents of arsenic in the *cystoseira* and lead in the *poseidonia*, phosphorus in the *crithnum* and sulphur in all three plant species. Beach sands are iron and titanium-rich reflecting the composition of some of the inclusions analysed in the Lipari VFA.

A mixture of Stromboli beach sand and *poseidonia oceanica* was subsequently heated in at 1000°C in a laboratory furnace for one hour, but there was no evidence of vitrification, only the production of a sintered mass forming at the bottom of a glass crucible (see Fig. 6) and resembling the 'bottom' surface of the Lipari VFA. We note that the high contents of titanium and iron in Stromboli beach sand and the high calcium content of the Stromboli plant ash do not correlate well with the low concentrations of the same elements in the Lipari VFA, although iron-rich unreacted mineral grains were indeed observed.

In summary, based on the examination of 554.1 and 554.2, we can conclude that object MA 8993 in the Archaeological Museum on Lipari is most certainly not a copper smelting or melting slag, on account of the absence of non-ferrous metallic inclusions and/or the usual iron silicate phases normally associated with copper slag. Instead, it resembles a slag-like vitreous material or vitrified fuel ash (VFA). Further experimental work and under varying laboratory conditions is required to establish the nature of the raw materials that made up this object; a single simulation experiment carried out here for the purpose of checking the plant ash+beach sand hypothesis shows that, for example, no calcium-rich marine plants were used for the Lipari VFA. Therefore we suggest that this object is treated as a 'unique' fragment until such time as evidence for similar materials is forthcoming, either from the Aeolian Islands or beyond.

On the evidence presented above, we can suggest that metallurgy did not arrive on the Aeolian Islands at this early date. It may be that self-sufficiency in the procurement of a 'cutting edge' via the exploitation and exchange of the valuable local obsidian source did not necessitate experimentation with or use of new materials like metals. We therefore conclude that early metallurgy in Italy appears to be concentrated in the metals-rich areas of the Central and North Tyrrhenian area and did not include the Aeolian Islands.

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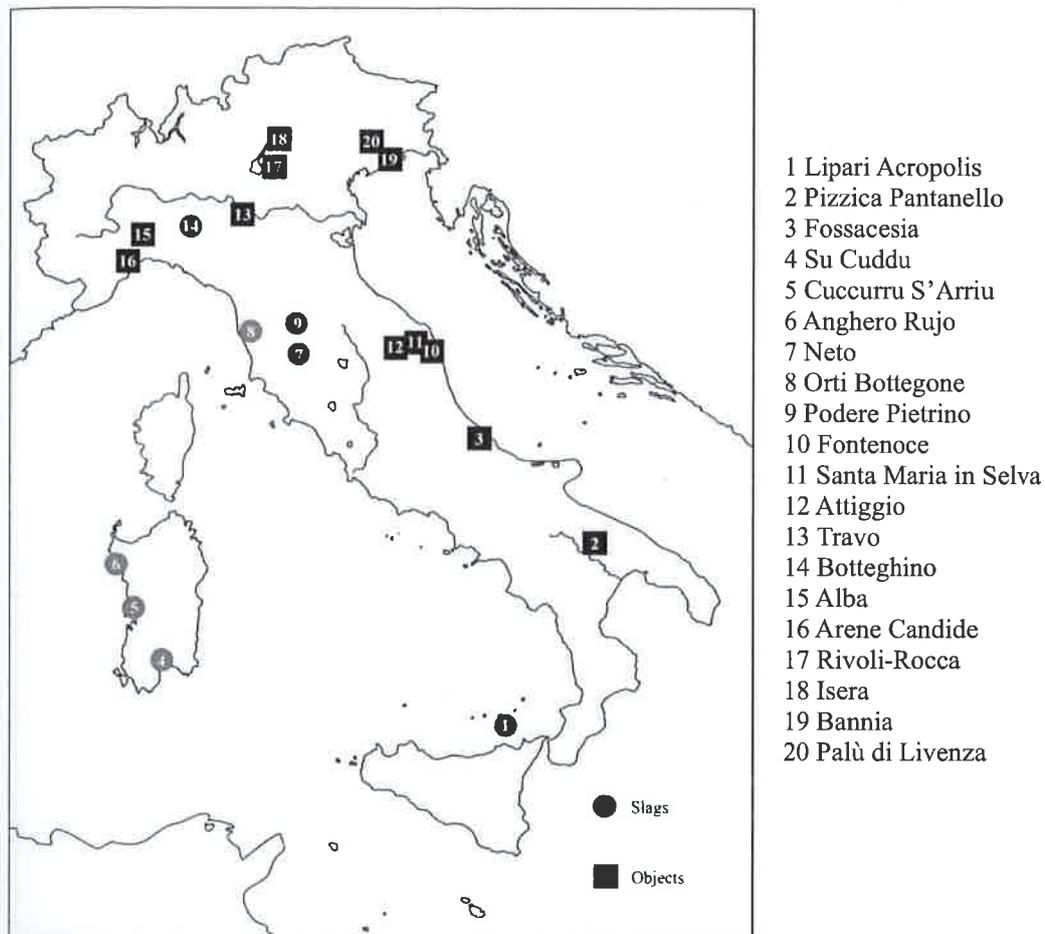


Fig. 1. Distribution of main sites across Italy with evidence of early copper artefacts and metallurgical waste (adapted from A. Di Renzoni from Pessina and Tinè 2008, fig. 14).

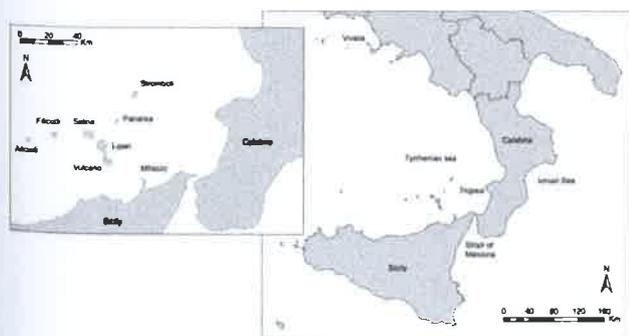


Fig. 2a. Location map of the Aeolian Islands.



Fig. 2b. The Acropolis of Lipari, Lipari (ME).



Figs. 3a and 3b. Fragment referred to as 'slag of copper' (MA no. 8993), consisting of a 'top' vitreous surface of pale green colour with light grey surface accretions and a 'bottom' sintered surface with patches of ferruginous areas. Two small fragments (about 1.5 cm) were removed for analysis (see arrow), incorporating sections of the sintered surface, but not the ferruginous area.

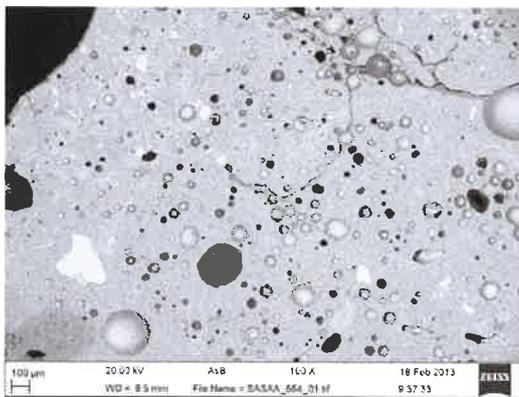


Fig. 4a. Scanning electron microscope image of sample 554.1. Bar = 100 microns.

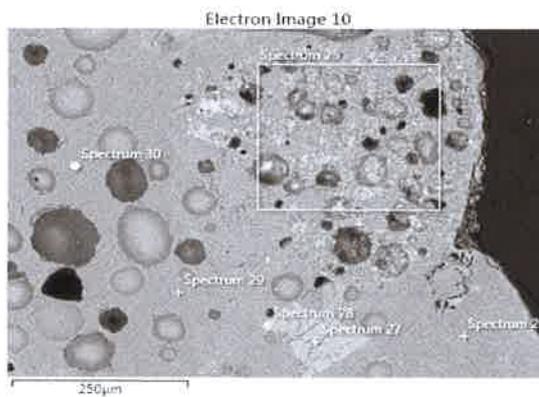


Fig. 4b. BS-SEM-EDAX image of sample 554.2 showing spot and area analyses.

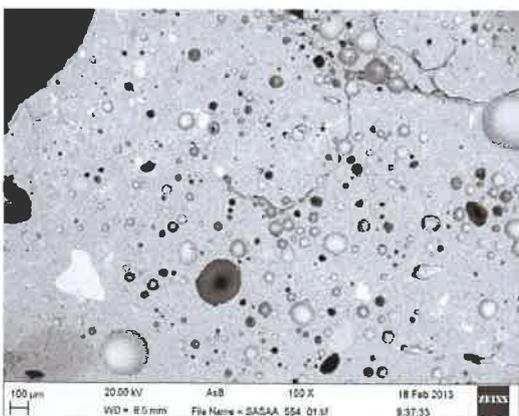


Fig. 5a. SEM-EDAX image of sample 554.1 showing ferruginous inclusions – white – in a highly vesicular matrix.

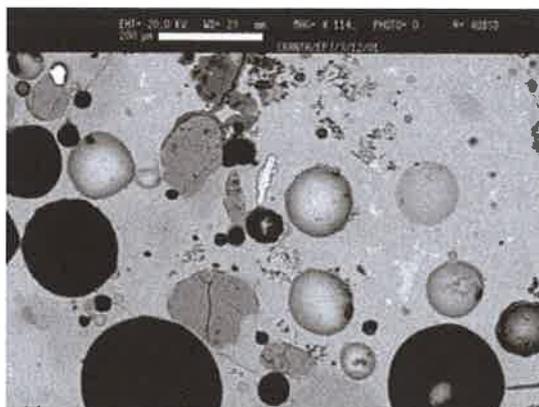


Fig. 5b. SEM-EDAX image of a sample of Scottish VFA showing high degree of porosity (round black holes) and unreacted grains of quartz (dark grey and fractured) (after Photos-Jones et al. 2007, fig. 9).

spectrum number	sample	SiO ₂	Al ₂ O ₃	FeO	K ₂ O	MgO	Na ₂ O	TiO ₂	CaO	Mn	Ba	S	V	Sb	Cr
6	554.1	75.3	14	2.3	5.4	bdl	4.5	bdl	1.8	bdl	bdl	bdl	bdl	bdl	bdl
14		75.7	14	2.1	5.4	bdl	5.6	bdl	1.8	bdl	bdl	bdl	bdl	bdl	bdl
15		74.6	14.5	2.3	5.3	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
mean		75.2	14.2	2.2	5.4	bdl	5	bdl	1.8	bdl	bdl	bdl	bdl	bdl	bdl
2	554.2	74.9	14	2.1	6	bdl	4.3	bdl	1.4	bdl	bdl	bdl	bdl	bdl	bdl
3		75.1	13.8	2.1	6.5	bdl	3.1	bdl	1.5	bdl	bdl	bdl	bdl	bdl	bdl
5		75.1	13.6	2.2	6	bdl	5.8	bdl	1.5	bdl	bdl	bdl	bdl	bdl	bdl
25		58	19.7	9.5	4.9	1	5.4	1.2	3.5	bdl	bdl	bdl	bdl	bdl	bdl
mean		75	13.8	2.1	6.2	bdl	4.4	bdl	1.5	bdl	bdl	bdl	bdl	bdl	bdl

Table 1a. Area analyses – mean of three areas per sample – giving the composition expressed as element oxides in weight %. Bdl is below detection limit. Areas analysed vary in size. See, for example, Fig. 4b for spectrum 25.

spectrum number	sample	SiO ₂	Al ₂ O ₃	FeO	K ₂ O	MgO	Na ₂ O	TiO ₂	CaO	Mn	Ba	S	V	Sb	Cr
7	554.1	0.6	0	76.4	bdl	5	bdl	8.5	bdl	bdl	bdl	bdl	bdl	bdl	bdl
8		1.9	0	0	bdl	bdl	bdl	bdl	bdl	bdl	60.8	14.5	bdl	bdl	bdl
10		33.4	8.1	48.4	2.2	bdl	4.9	4.8	bdl	bdl	bdl	bdl	bdl	bdl	bdl
12		0	4.2	81.2	0	2	bdl	8.5	bdl	bdl	bdl	bdl	bdl	bdl	bdl
16		2.4	7.6	72.9	0.1	bdl	bdl	6.5	0.3	bdl	bdl	bdl	bdl	bdl	bdl
17		1.1	7.6	72.7	bdl	6.6	bdl	7.5	0.3	0.6	bdl	bdl	bdl	bdl	bdl
27	554.2	53.9	2.3	10.7	bdl	15.3	bdl	0.5	22.1	0.3	bdl	bdl	bdl	1.1	bdl
28		1.3	2.8	94.7	0.2	2.7	bdl	9	bdl	bdl	bdl	bdl	1	bdl	bdl

Table 1b. Spot analyses on iron-rich, barium-rich and other inclusions; weight % element oxides. Bdl below detection limit.



Fig. 6. Sintered mass produced in the laboratory from the reaction of marine plant ash and Stromboli beach sand.

	SiO ₂	CaO	K ₂ O	Al ₂ O ₃			
Cystoseira	7.4	16.3	10.8	4.3			
Poseidonia	9.2	14.3	7.9	6.2			
Crithnum	7.7	25.2	10	5			
Beach 'sand'	37	9.3	1.7	14.7			
	Sr	Rb	Pb	As	Zn	Bi	P
Cystoseira	36340	125	17	1249	5430	122	3885
Poseidonia	6439	71	73	29	198	57	5076
Crithnum	8647	86	bdl	bdl	206	14	20484
Beach 'sand'	393	20	bdl	9	68	11	bdl
	Cu	Cr	V	Ti	Mn	S	Ba
Cystoseira	26	bdl	140	617	86		230
Poseidonia	87	bdl	198	1090	360	45533	bdl
Crithnum	86	85	137	1081	89	33258	bdl
Beach 'sand'	52	281	394	2970	1907	bdl	823

Table 2. p-XRF analyses of major oxides of plant ash deriving from the three marine plant species and also Stromboli beach sand. Major oxides are in %; minor and trace elements are in ppm.