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ARCHAEOMETALLURGY IN MESSINA: IRON SLAG FROM A DIG AT BLOCK P, LABORATORY ANALYSES AND INTERPRETATION

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ABSTRACT

The archaeological site in Via La Farina, Block P, in Messina, is unique in many ways, due also to the high quantity of samples of iron slag. The slag was examined to identify the production centres of such materials, and, after characterization, was compared to similar material, exclusively for product typology, from different archaeological sites in the province of Messina, situated in the Peloritani Mountains (Messina city, S. Marco d'Alunzio, Milazzo, Francavilla di Sicilia, Novara di Sicilia as well as the archaeological site of Halaesa, near Tusa). Mineralogical characterization of the phases carried out by X-ray diffractometry (XRD) and Rietveld data elaboration, morphological study of slag findings and a semi-quantitative analysis by scanning electronic microscope (SEM+EDX) were performed. A chemical investigation was carried out by electron probe micro analysis (EPMA), to determine major element,. Minor and trace elements were determined by LA-ICP-MS. All the examined slag is related to iron metallurgy, and, in the case of Via La Farina, there is firm archaeological evidence pinpointing to smelting activity.

KEYWORDS: iron slag, Messina, archaeometallurgy, XRD, EPMA, LA-ICP-MS

INTRODUCTION

The archaeological excavation carried out in Messina in compartments 90-91 of Block P, between 2003 and 2004 (Ingoglia 2007), revealed an extraordinary concentration of iron slag (fig. 1), inside a ditch (US 56) located in the western part of the area under investigation.

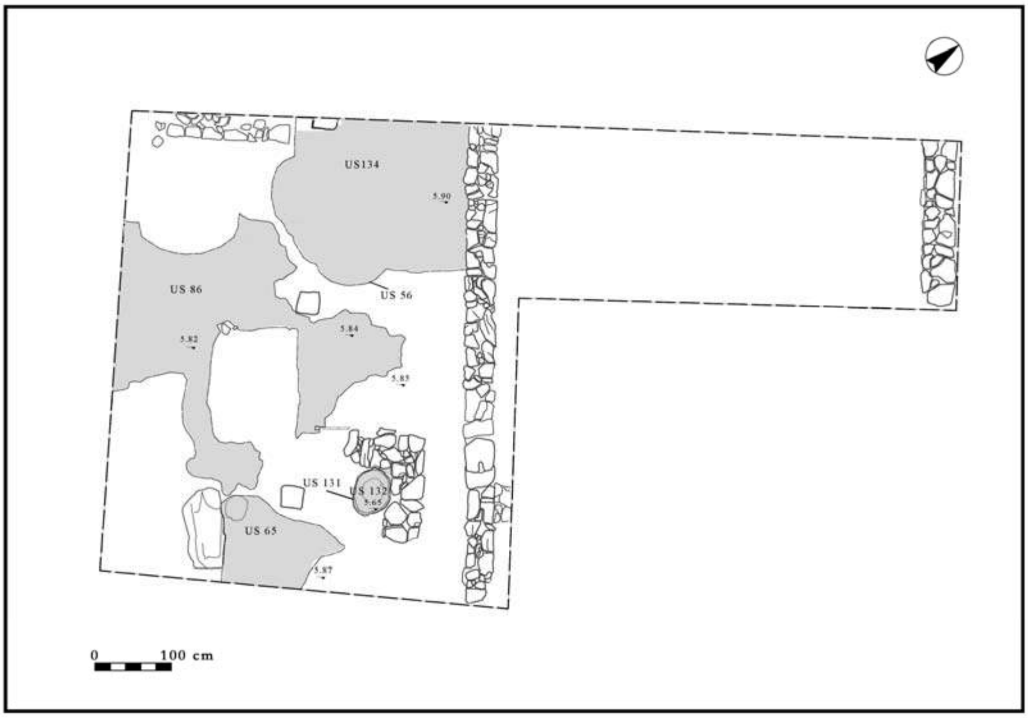

Fig. 1 General plan phase 3 of period 3

It is certain that the find consists of some waste products from iron works which were thrown into the hole, together with other observed material used as charge flux prepared for burning (shells, animal bones). The activity was probably linked to a furnace, the exact whereabouts of which is still unknown, but which was certainly not far from the area studied by our team of archaeologists. All the area surrounding the ditch is in fact full of clues which would indicate a metallurgical workshop, which, as we shall see, dating back to the 5th century BC, can be reasonably considered the most ancient excavated in Sicili (for other mineralogical, petrografic and chemical analyses on archaeological finds, ceramics, from Messina, Bacci et al. 2006)

Thinking that the potential information which could be gleaned from the slag might be of great use in better defining the area under investigation, and above all, in an attempt to reconstruct techniques and methods of metal production in Messina in the Classic Greek age, it was decided to undertake a study based on archaeometric analyses.

Some slag samples were analysed in order to determine the metal origin through observation of composition and chemical features. Given the archaeological context of origin, and being aware of the potential importance of a new discovery, an effort was made to understand the pyrometallurgical processes undergone by the metal, also taking into account evidence found in literature, which traditionally attributes particular metallurgical skills to the inhabitants of Calcide from Eubea, homeland of Zancle, the ancient name of Messina.

ARCHAEOLOGICAL DATA

Archaeological findings from the dig in the area investigated have allowed us to identify five distinct periods with activity, and two of abandonment, distributed over a time span from 7th cent. to the mid-4th century BC ca.

In particular, it was possible to determine that, during the third period (ca.480-450 B.C.), a siderurgical workshop was set up in the zone, from which some pieces were found in a waste ditch. Some work areas were also identified, but we have not been able to determine the exact nature of the work carried out, given the reduced size of the excavated area.

The stratigraphic archaeological investigation identified three phases of activity in the life of the workshop, in the same third period and all dateable, on the basis of pottery in the layers, to just before or around the mid-5th cent. BC. Excavation activities have been recorded in different Stratigraphic Units, further on identified as "US".

Two ditches relate to the first phase (US 164 and US 160), both excavated in a sand deposit (US 167) and linked by a channel (US 169). The finding, in ditch US 160, of two layers of filler material, superimposed and rich in iron slag, was vital in identifying the area as a workshop, and, in particular, in conferring a waste function to ditch US 160 (fig. 2).

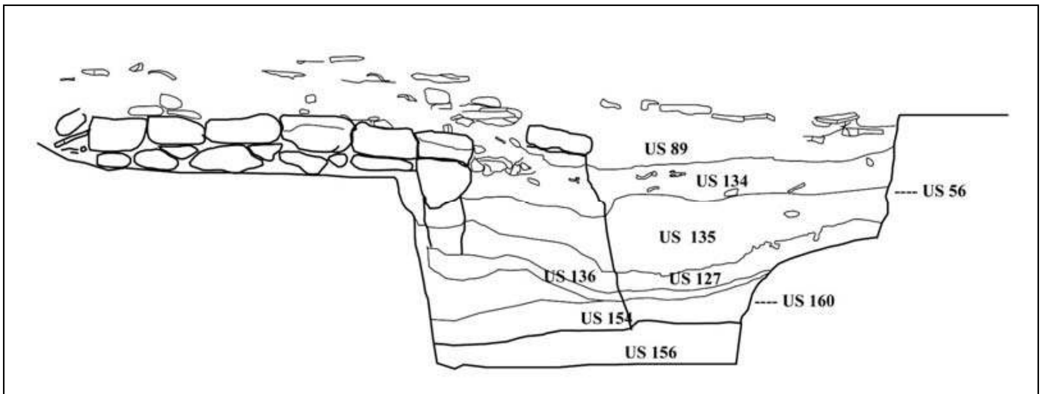

Fig. 2. West wall section of US 56 and US 160

The deepest landfill, US 154, consisted of dark, carbonaceous earth, with a lot of iron slag and a quantity of shells; it was covered by US 136, not as thick (ca. 8 cm), but rich in iron slag, which explains the reddish colour of the earth, and also with a very high quantity of shells on the surface. On the western side of the hole, there are two small layers of a lighter coloured, ferrous earth, US 159 and US 161, with no trace of any archaeological material.

Ditch US 164 was filled with silty sand, with very few archaeological findings (US 163) and the entire area was covered by a layer of sandy silt (US 156 that is, for color and composition, the same as US 157).

US 141, part of a wall, belongs to phase 2. The wall ran in an east-west direction and was covered, to the south, by tile fragments, which very probably marked a tank which can now be seen in US 156 (US 148) inside of which, the liquid, which ran in the terracotta channel US 146, cutting US 141 perpendicularly, most likely flowed.

Later, both ditches were filled with dark, silty earth, very rich in archaeological material (US 149 and US 166) dateable to around mid-5th cent. BC. All the area was sealed by a lighter-coloured heap of earth (US 127 is the same as US 129).

Phase 3 is distinguished by the finding of a workshop floor (US 86) made up of a bed of pebbles and iron slag, about cm 3.00/3.50 thick, over which lime was cast making the floor suitable for treading (see, fig. 1), and by a new waste ditch, bigger than the previous one, related to phase 1, below the said floor (US 56). The filling in the ditch is made up of a thick layer of black earth, rich in iron slag (11 crates were filled) representing the entire US 134. This covered a lighter-coloured layer (US 135) with a high quantity of punctiform, carbonaceous traces and pottery, often darkened only externally, mixed in with iron slag, but in much lower quantities compared to US 134. Both US 134 and 135 of phase 3 and US 136 of phase 1 contained many shells.

A small tank (US 131) also belongs to phase 3, found in the eastern part of the dig, with walls, fragmented in the upper part, covered with refractory clay (fig. 3). The function of the small tank is uncertain. It was filled with earth (US 132) with hardly any archaeological material, and a block of conglomerate, probably formed naturally. We were unable to ascertain if it could have been used in some way in the activity of the workshop.

(Caterina Ingoglia)

Fig.3. US 131

DESCRIPTION OF THE IRON SLAG ANALYSED: TYPOLOGICAL DISTINCTION

Some previous isolated works on ferriferous slag found in sites of north-eastern Sicily, have provided information on existing relationships between the various typologies of metalliferous slag found and metallogenesis in the Peloritani mountains. This is related, above all, to two distinct events which can both be found in low-medium grade metamorphites.

The first event refers to pre-metamorphic and pre- Hercynian "strata-bound", mineralized bodies, characterized by simple Fe, Pb and Zn sulphides: the second event is characterized by mineral bodies of distinct veins, linked to a hydrothermal system, and associated with local, late-Hercynian metamorphic events, represented principally by complex, Cu, Pb, Sb, As, and Bi sulphide mineralization.

The archaeological site in Via La Farina, in Messina, is unique in many ways, due also to the high quantity of samples of iron slag analysed. Most of the material was taken from stratigraphic unit US 134 (fig. 4) and, after characterization, was compared to similar material exclusively for product typology. The fact that the sites investigated related to a very wide time span – with metallurgical slag from different archaeological sites from the province of Messina, situated in the Peloritani Mountains (Messina city, S. Marco d'Alunzio, Milazzo, Francavilla di Sicilia, Novara di Sicilia as well as the archaeological site of Halaesa, near Tusa) - was also taken into account (Barone et al. 2005, Bonanno et al. 1998; Sabatino et al 2004; Triscari et al. 2006).

Fig. 4 Some of the exhamined iron slag from the Blok P site in Messina.

LABORATORY ANALYSES: METHODOLOGY

After a precise selection and preparation of samples, preliminary stereoscopic tests were carried out under the microscope. Slides were then prepared for a reflected polarized light metallographic test. Mineralogical characterization of the phases was carried out by X-ray diffractometry (XRD) and Rietveld method. Morphological study of slag findings and a semi-quantitative analysis were performed by scanning electronic microscope (SEM+EDX, Dept. of Earth Sciences, Univ. Messina). After the characterization study, a mineral - chemical investigation was carried out by electron probe micro analysis (EPMA), to determine major elements The instrument used (ARL-SEMQ c/o Univ. Modena) utilizes an internal software automatic correction that minimizes the effect of mobilization of light elements under the electronic beam: this has proved to be very usefull in vitreous material analyses (Triscari et al. 2006). Minor and trace elements were detected by Laser Ablations (LA-ICP-MS) (Dept. Earth Sciences, Univ. Perugia).

ANALYTICAL RESULTS

All samples from the investigated excavation examined in this study are fayalite-type slag, and are considered products of iron metallurgy in the first phase of ferriferous bloom production, with oxides, sulphides and/or carbonates as charge material. Fayalite crystals in elongated aggregates were found in the underlying silicate mass. Mineralogical data collected in this work are comparable to other data related to materials which are typical of a "technology of iron metallurgy production": chronologically they cannot be compared, in that they differ greatly in time periods. This technology remained unvaried over many centuries, changing only charge material from which metal was then extracted (Bonanno et al. 1998; Sabatino et al., 2004; Triscari et al 2001, 2002, 2005, 2006)

Reflected polarized light microscopy and X-ray diffractometry with the Rietveld method have shown metallic Fe, maghemite, wüstite and fayalite. The percentage of glass of all ferriferous slag examined was over 60% in every case. (see Table I)

A mineralogical characterization summary of the most significant slag is shown in the following table, where the slag from Via La Farina, Messina, Italy, is compared to similar material, by typology, but coming from chronologically different sites.

Morphological and semi-quantitative analyses with a scanning electronic microscope and energy dispersion microanalysis (SEM+EDX) identified both single olivine crystals (fayalite) (fig. 5), and the vitreous-based paste where the crystals were buried.

Having already obtained good information through physical-chemical analyses of the mineralogical phases, it was considered useful to chemically characterize the vitreous part of the slag, where significant chemical elements, useful for determining origin, were thought to be concentrated.

EPMA compared silica content with oxides from other elements present. In the following table, the average values of analyses carried out, both on metallic iron found in the slag and in the amorphous silicate phase, and finally, on only fayalite, are shown.

The Mg/Mn ratio identified in the slag in Via La Farina could be used as a determining factor for origin. Although temporally diverse, and coming from completely different excavations, if just the "ferriferous fayalite-type slag" typology is analysed, then this ratio could be used to identify different charge material amongst them – as, in fact, can be seen from the following discriminative diagrams (fig. 6). This is a current working hypothesis used in other works, when trying to confirm different origins amongst charge materials used.

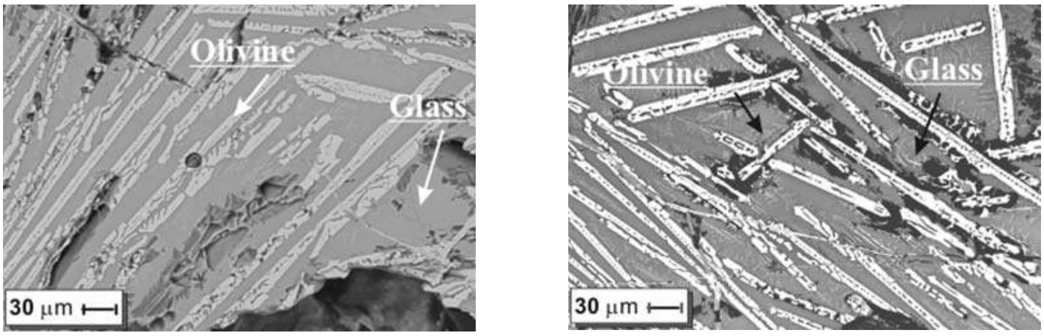

Fig. 5 SEM (BSE) images of irons slag. Fayalite elongated crystals are discernible in the vitreous groundmass.

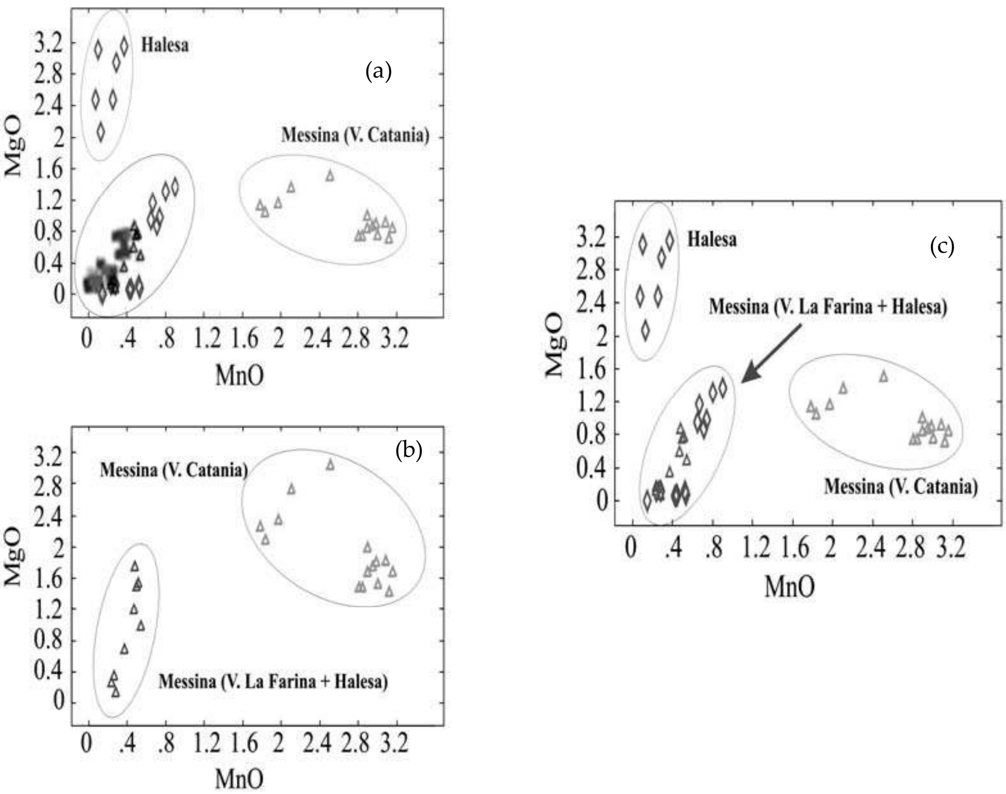

Fig. 6 Mg/Mn ratio in the examined samples compared with similar iron slag (in type, not in age). (a) all samples, within the lower left corner specimens from the Messina, together with the ones from Novara, S. Marco and Milazzo sites, (b) all Messina samples and Halesa archaeological site, (c) all Messina town samples (Block P Via La Farina and Via Catania).

Samples	Maghemite	Magnetite	Hematite	Fayalite	Quartz	Metallic Iron
Messina (La Farina 5)	X	X	X	X		
Messina (La Farina 11)		X		X		
Messina (La Farina 12)	X	X		X		
Halesa 1	X	X	X	X		
Halesa 2		X		X		
Halesa 4	X	X	X	X		
Halesa 5	X	X	X	X	X	
Milazzo 1		X		X	X	X
Milazzo 2	X	X		X		
Messina (Via Catania 1)	X			X		
Messina (Via Catania 2)	X			X		
Messina (Via Catania 3)	X		X		X	
Novara Sicilia 1	X	X		X		
Novara Sicilia 2	X	X	X	X		
S. Marco Alunzio	X	X	X	X		

TABLE I Qualitative mineralogical composition (by X-Ray diffraction and Rietveld elaboration) for main phases in the examined slag

% oxides	MnO	Fe_2O_3	NiO	Cu_2O	TiO_2	CaO	Sb_2O_3	K_2O	SiO_2	P_2O_5	Na_2O	MgO	As_2O_3	Al_2O_3	Total
Messina															
Iron metallic phase (aver. 10 analyses)	0.33	94.21	0.06	0.22	0.10	0.19	0.01	0.13	2.93	0.06	0.10	0.42	1.01	0.89	100.66
Amorphous silicate phase (aver. 14 analyses)	0.31	26.65	0.01	0.09	0.10	6.80	0.23	6.30	37.06	1.66	3.69	0.22	0.19	17.12	100.43
Fayalite (aver. 9 analyses)	0.88	58.10	0.02	0.02	0.05	2.17	0.03	1.28	30.64	0.43	0.77	2.37	0.54	3.52	100.82

Tab. II Chemical (EPMA) analysis of metallic iron, amorphous silicate phase and fayalite

DISCUSSION

On the basis of macroscopic tests and laboratory analyses, it can be concluded that the combined used of LA ICP-MS and EPMA techniques can provide significant data for the attribution of origin of slag by referring to charge material. In some cases, this material would seem to come, above all from surface enrichment of metallic sulphide hydrothermal vein systems. The discriminative diagrams, which highlight Mn as a significant element, could identify ferrous-manganiferous carbonates, (siderite-ankerite levels in the Peloritani mountains) as probable charge materials used, due to the levels found.

All the slag examined concerns iron metallurgy, and, in the case of Via La Farina, there is firm archaeological evidence traceable to smelting activity.

(Maurizio Triscari and Giuseppe Sabatino)

CONCLUSION

All the artefacts analysed are traceable to a waste ditch of work rejects from a reduction process which transformed iron ore into a metallic mass, carried out with a low flame, but of which there is no trace in the area surveyed. The reduction process involved the smelting of a part of the ore and not the iron itself, which remained inside, and which was to later undergo further metallurgical treatment.

To better eliminate impurities in the metal, organic residues might have been added to the charge. They would have been suitable for obtaining the calcium carbonate needed to lower the melting point, with the heat of the flame, and to favour the formation of slag in the furnace. During the archaeological excavation in Via La Farina, the finds, for this phase of the entire metal production process, which included the filling of the waste ditch with iron smelting slag, numerous deposits of unwanted shells (the presence of shell valve fragments in much of the slag was also significant), together with some calcinated animal bones (that is, which were subjected to high temperatures and therefore used exclusively as flux to improve the iron reduction process, e.g. Cima 1986, p. 186; Mele 1981), have thrown light on the level of technology reached in the city of Messana, around the mid-5th cent BC.

In general, the limited size of the archaeological area surveyed did not permit us to better interpret the ditches from phases 1 and 2 of the 3rd period, but rather, only study the simple clues related to activity carried out in this artisan workshop which produced iron slag deposited over many time periods, in two, superimposed waste ditches. Also, the small tank covered in refractory clay from phase 3 could be hypothetically connected to the workshop.

Archaeological data collected certify three different moments in the organization of the locations of siderurgical activity. For phase 1, we know of only a pit and a waste ditch; for phase 2, a wall covered with tile fragments and two probable tanks; and for phase 3, a floor and a new, bigger, waste ditch.

It would seem clear then, that the area in question might have been an artisan workshop for iron production, a workshop of a limited time, maybe connected to an extraordinary yet unknown event (a shipyard – building site?) which needed a supply of iron tools. However, the suggestion cannot be discarded of being, most likely, a simple western testimony - Messina was a Chalcidian- founded Greek settlement – on the metallurgical art which, in Greek literature, recognise Chalcidians. In effect, sources attribute the inhabitants of Chalcis of Euboea island, homeland of Zancle (the ancient name of Messina), with a particular skill in working metals (Callimacus, Fragment 701 Pfeiffer; Ephoros, Fragmenta Graecorum Historicorum, 70 F 134; Strabo, V, 4,5, 245 C; IX, 2,18,407 C; X, 1, 9, 447 C; Stephanus Byzantinus, sub voce "Aidepsos"; Eustathius, ad Dionysii Periegetae Orbis Descriptionem, 764; Theophrastus, History of Physics. V, 9,2) (Mele 1981). Moreover, the finds of workshops for iron production in Euboica western sites, in particular the isle of Pithecusa (Ischia) (which already in the 8th cent. BC was importing ore from the island of Elba), have been taken from historiographical literature as a confirmation, as well as, a very important economic aspect, of the siderurgical vocation of Greek Euboea, since archaic times (Ridgway 1974, p. 186; Buchner 1985; Mele 1981).

At this point, one may wonder if the find at Block P cannot be considered an additional contribution in putting forward again the issue of the role in the mining district of Messina (Fiumedinisi) (Scibona 1986; Baldanza-Triscari 1987, p. 15), in the various stages of the city of the Strait, given that this aspect may have contributed, along with the strategic position of the city, to the increased interest of the Chalcidians, at the time of founding the city, and later on by Hippocrates of Gela in ca. 490 BC. (Herodotus 6,23), and yet again, by Dionysius I of Siracusa, between the end of the 5th and the beginning of the 4th cent. BC (Diodorus Siculus 14,44,3;14,78,5-6).

(Caterina Ingoglia)

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In addition, a taxonomic determination was carried out on some shell samples from US 134 and an animal bone from US 136. The shell studies were carried out by Prof. Salvatore Giacobbe from the Department of Animal Biology and Marine Ecology, University of Messina, whom we thank. He recognised that all the shells found belong to the same species i.e. the bivalve Cerastoderma Edule. Further, we are grateful to Dott. G. Mangano, Department of Earth Sciences, University of Messina, who identified the bone from US 136 as an intact ox ulna, heavily calcinated by fire, from comparison with similar materials. We are grateful to the Editor and the anonymous referees for constructive comments. Last but not least we would like to thank Antonella Manganaro for the graphics and Trays for her help with the language.

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