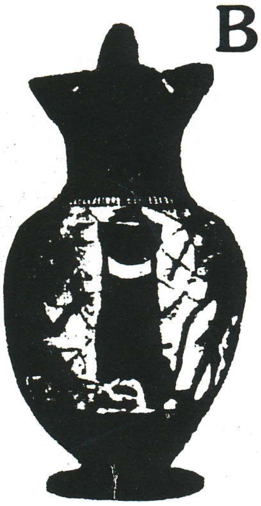
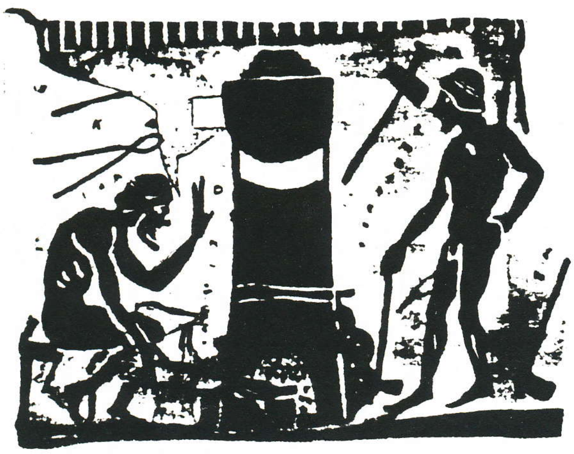
BRITISH SCHOOL AT ATHENS 1886-1986

ASPECTS OF ANCIENT MINING AND METALLURGY ACTA OF A BRITISH SCHOOL AT ATHENS CENTENARY CONFERENCE AT BANGOR, 1986





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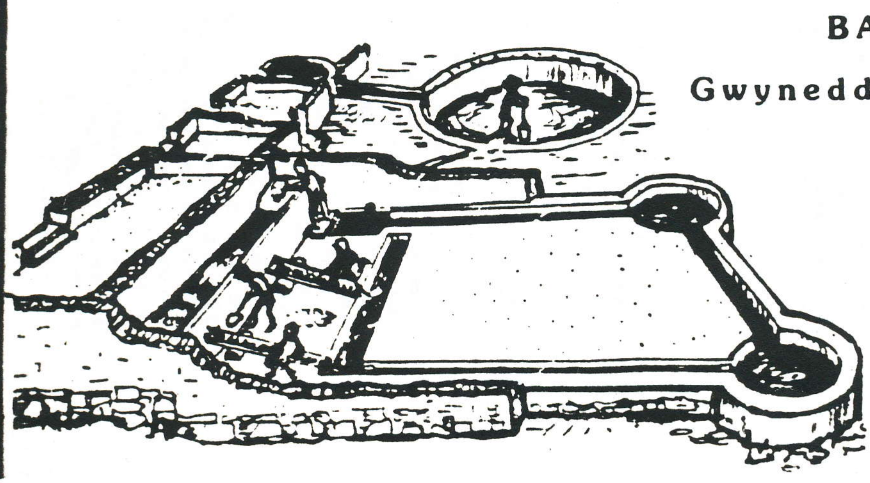

the east coast of Kythnos in the EC II period. The copper was mined on cape Tsoulis near a possible coastal settlement at Ayios Ioannis. It was then transported uphill to the head of the valley at Skouries where it was smelted in small clay furnaces that were contained in large round stone-built structures. This evidence is supported by the lead isotope analysis of copper from the mine and furnaces; the samples match and also fall in the same field as the Kythnos Hoard of copper tools (GALE/STOS-GALE 1984, 267-8). This hoard has been dated on typological ground to the EC II period (RENFREW 1967, 7-9). Our work on Kythnos supports this date and adds further concrete evidence to the hypothesis of a period of great wealth and 'internationalism' in the Early Bronze II Aegean (RENFREW 1972, 451-455). This is a period during which the Early Cycladic civilization seems to have flourished. EC art was at its highest quality, as shown by the numerous examples of marble Folded-Arm-Figurines, most of which were manufactured during this period. This is also the greatest period of EC metallurgy, as shown by metal tools and weapons found in tombs and settlements throughout the islands (Ibid., 308-338). There is evidence for contemporary mining in Siphnos and at Thorikos, near Lavrion, where a Cycladic influence may be seen in the pottery (SPITAELS 1984). Much of the islanders' wealth may have come from trading, and copper mining must have also contributed.

The report given here is of a preliminary nature but we believe that the general indications are correct. There remain specific problems, such as the availability of sufficient fuel to achieve the high temperatures needed for smelting, but there is no doubt that copper mining and smelting was undertaken in Kythnos in the EC period. Many contemporary Cycladic copper objects were made of Kythnian copper, as the lead isotope analysis has shown. We think that the operations at Skouries and Tsoulis belong to a single chapter in early metallurgy.

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THE POSSIBILITY OF SMELTING NICKEL-RICH LATERITIC IRON ORES IN THE HELLENISTIC SETTLEMENT OF PETRES, N.W. GREECE

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Abstract

This paper describes the scientific examination of iron slag and objects from Petres, a recently-excavated Hellenistic settlement (3rd cent. B.C.) in W. Macedonia. Emphasis is placed on investigating the likely smelting at the site of nickel-rich lateritic iron ores, in addition to the more common hematite ores. Evidence to that extent has been provided by the presence of nickel in iron prills in slag from Petres. The results of chemical and metallographic investigation showed that in fact all but one of the examined iron objects found at Petres contained no nickel, from which it must be deduced that the local smiths did not know how to work Ni-rich iron. Experimental smelts of lateritic ores from Central Greece were undertaken to elucidate questions arising from the archaeological evidence.

Introduction

Recent years have seen an awakening of interest in early extractive iron metallurgy in Greece (ROSTOCKER/GEBHARD; BACKE-FORSBERG/RISBERG; PHOTOS/FILIPPAKIS/SALTER). In particular, there has been a trend towards integrating effort in relating iron ore, slag and artefact; for example, Photos et al have characterised slag on the island of Thasos, resulting from the smelting of Ti-rich magnetite sands (PHOTOS/KOUKOULI-CHRYSANTHAKI/GIALOGLOU). The presence of Ti acts as a potentially valuable indicator of ore type in the slag inclusions of iron artefacts. The present study is concerned with the experimental smelting of nickel-rich iron laterites, the ease with which iron can be extracted from them and the distribution of nickel in the bloom, the iron mass obtained from the furnace before hot forging. The site of Petres, a recently-excavated Hellenistic settlement, has offered an excellent focus of attention since, in addition to the considerable evidence for iron working, Ni was discovered in some of the iron slag. It was suggested that the nearby lateritic deposits were possibly exploited on the site, doubtless in addition to the more common hematite ores.[1] This is important since it is usually difficult to establish whether a nickel-rich artefact has been the product of laterite smelting, unless the artefact, the slag and the ore co-exist on the same site, as is probably the case at Petres. Besides presenting the chemical and metallographic analyses of some slag and iron artefacts, this paper briefly describes the results of experiments in smelting laterites. (Early extractive iron metallurgy in Greece is the subject of the doctoral dissertation of one of us (E.Ph). The thesis mainly concerns the experimental smelting of iron ores from Central Greece, Ti-rich magnetite sands and hematites from Macedonia. The results of these experiments will be published in the near future.)

Petres

In the summer of 1982 a Hellenistic settlement was located on a trapezoidal mound 1.5 km. NW of the modern village of Petres, 35 km. SE of Florina in W. Macedonia (ADAM-VELENI). The settlement belonged geographically to the NW section of Eordaia, a canton of Upper Macedonia in the Hellenistic and Roman periods. It is a strongly fortified settlement (**FIG. 1**) covering approximately 200,000 sq. m. The settlement architecture followed the natural slope and must have faced east onto the valley of Amyntaion and the lake of Petres. Excavation has been carried out on the S slope (area A in Fig. 1) and continued on the top of the mound (area B in Fig. 1). Both areas revealed a number of rooms in what would have been two-storied houses. It has been difficult to establish the limits of each house since no road system has yet been identified. The stratigraphy of the site suggests that the town was built in two phases. The first dates to the end of the 3rd. century BC when it was probably founded by a Macedonian king between the reigns of Antigonus Gonatas and Philip V. The second phase lasted to the middle of the 1st century BC when the settlement was destroyed by fire. The destruction of Petres and other towns in Lyncus and Eordaia, districts in Upper Macedonia, in the middle of the 1st cent. B.C. is attributed by some scholars to the burning by the retreating legions of Domitius, one of Julius Caesar's generals (KERAMOPOULOS).

Archaeological evidence obtained from four seasons of excavation suggests that Petres was not merely an agricultural settlement but rather an urban centre, whose prosperity depended on the revenues provided not only from cultivation of the fertile Amyntaion plain but also from its position as a trading post, given its proximity to the Via Egnatia. Around 130 BC this important road passed at a distance of only 2 km. from the settlement.

Petres is also important because of the extensive evidence of iron working and iron making on the site. The evidence consists of a large quantity of slag, the waste product of smelting and/or smithing operations, as well as a large variety of iron artefacts in a relatively good state of preservation. A total of approximately 70 kg of slags have been recovered from the site between 1982 and 1985, most of it found in a number of rooms under the destruction layer and occasionally as part of the wall fabric. About 50 kg were retrieved from the top of the mound (SE corner, area B, Fig. 1) in a room that was probably a metallurgical workshop. The slag size ranges between 2.5-10 cm. The weight of the larger (10-15cm) pieces (plano-convex smithing hearth bottoms) does not exceed 1.5 kg. In general the slag is very porous and in a rather poor state of preservation. A hoard

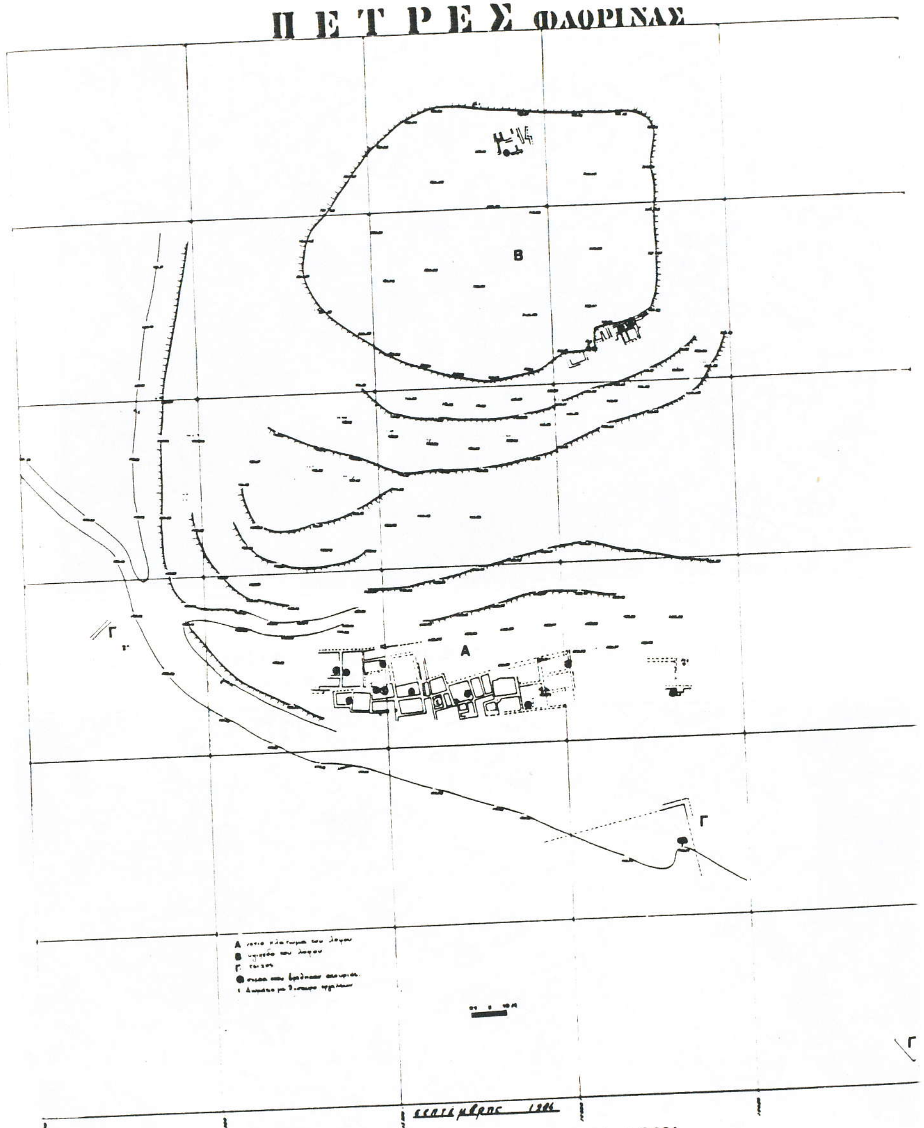

FIG. 1 Plan of Petres (nr. Florina) - September 1984.
Area A: south plateau of the mound. Area B: flat top of the mound
Area C: (= Γ): wall. ●: locations where slag was found

of iron objects was found in a pithos jar in room 1 (area A in Fig. 1) containing agricultural and domestic tools, weapons, strigils, lead weights and a few bronze and silver objects. The iron objects analysed here come from this hoard.

<u>Material evidence and scientific investigation</u>

Slag was analysed with the Electron Probe Microanalyser (EPMA) attached to energy dispersive analysis facilities. A beam of electrons (1 micron square) is focused on a particular area of interest, and this spot is analysed quantitatively for all elements heavier than sodium. Microprobe analysis is particularly helpful since it allows the investigator to examine the composition of mineralogical phases in slags and slag inclusions in metal artefacts, thus providing a very powerful tool in iron-ore type provenance studies.

Mineralogically, the Petres slag consists of dendrites of wustite in a silicate matrix (**FIG. 2**). The matrix is not always glassy but may comprise a fine eutectic of wustite and anorthite/fayalite (Ca,Al-rich/Fe-rich silicates respectively). The slag microstructure is hardly uniform and areas of calcium-rich fayalite needles are incorporated in an anorthitic matrix. Analysis of the most common phases (i.e. wustite and matrix) are given in Table 1. The matrix is rich in aluminium, calcium, silica and iron. It is evident that manganese was included in trace amounts in the ore. The composition of the two phases does not reveal any trace elements characteristic of a particular ore body and suggests that hematites (including small amounts of Mn) were used. From these analyses it is impossible to establish whether the slags are smelting or smithing. The plano-convex bottoms are probably smithing, but the rest of the slag pieces cannot be classified as such with any degree of certainty.

Occasionally, metallic grains of iron were found to be trapped in the slag. EPMA analysis revealed that some of the prills contained nickel (Fl-Petr. 2: 91.75% Fe, 3.45% Ni) and in one instance (Petres-Acr) a prill has the composition of 97.36% Ni and 4.49% Fe. In the absence of other elements like copper, arsenic or lead, characteristic of non-ferrous ores, it is suggested that these slags were the product of the smelting of lateritic iron ores or the smithing of nickel-rich iron blooms.

Table 2 given a summary of the objects sampled, their typology, chemical analysis with EPMA and metallographic observations relating to their structure. EPMA does not measure carbon, the essential element in steel, so its presence and content has to be deduced from the metallography. Chemical analyses with the EPMA revealed that the main trace element in most of the iron objects is copper.

In general, there is little or no correlation between the type of object and the metallographic structure (Table 2). The varying degree of carburization reflects the original bloom rather than extensive or intentional carburization during

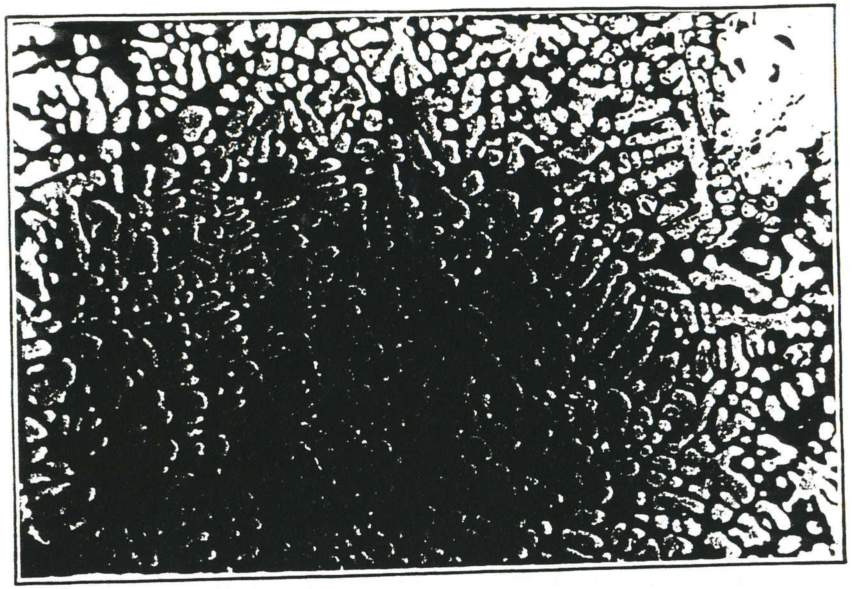

FIG. 2 Petres slag: dendrites of wustite in glassy silicate matrix, x 303

FIG. 3 Petro. 6: ? bloom with 2.25% Ni in Fe, x 606

Table 1

	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO
Matrix									
Fl-Petr1	0.56	11.48	38.14	2.98	7.28	10.33	0.36	1.64	26.58
Fl-Petr2	0.51	11.21	35.51	0.82	2.16	13.61	0.35	3.09	28.88
Petr1	nd	nd	nd	nd	nd	nd	nd	nd	
Petr2	0.00	19.75	28.49	0.00	4.81	25.32	0.46	0.00	17.14
Petr3	0.61	14.22	39.45	1.53	1.52	17.34	0.29	2.54	23.82
Petr.Acr	nd	nd	nd	nd	nd	nd	nd	nd	
Wustite									
Fl-Petr1	0.00	1.19	0.74	0.00	0.00	0.00	0.57	1.52	85.57
Fl-Petr2	0.64	0.76	1.18	0.00	0.00	0.36	0.89	2.34	89.32
Petr1	0.00	0.72	7.35	0.00	0.00	1.06	0.00	0.25	90.84
Petr2	0.73	0.92	0.38	0.00	0.00	0.58	0.55	94.33	
Petr3	0.00	0.00	0.42	0.00	0.00	0.13	0.00	1.13	90.89
Petr.Acr	0.00	0.38	0.54	0.00	0.00	0.24	0.53	1.88	90.74

Table 2

Sample	Typology	Fe	Cu	Ni	Metallography
Petro. 1	handle	98.49	0.34	0.00	Two areas: one is mostly ferritic but with cementite films at the grain boundaries. The other is medium C steel. The two areas are forge welded. Slag stringers are evident at the interface.
Petro. 2	hook	nd	nd	nd	corroded
Petro. 3	strigil	98.26	0.35	0.00	Structure of iron with less than .05% C. It is cooled slowly. Large ferrite grains. Black spots are probably carbonitrides, the result of fast cooling and then annealing between 200 and 700C
Petro. 4	handle	98.27	0.00	0.00	Iron with about .15%C. Fine ferrite grains with pockets of pearlite at the grain boundaries. Cooled moderately fast. HV(200)=196.
Petro. 5	nail	98.14	0.14	0.00	Ferrite grains with thin cementite films at the grain boundaries and as stringers. HV(200)=182.
Petro. 6	iron lump	95.94	0.00	2.25	Ferrite in matrix of pearlite. Widmanstatten structure. HV(200)=492,348,170
Petro. 7	clamp	98.36	0.00	0.00	Iron with about .15%C. Pearlite at the grain boundaries. HV(200)=185.

smithing. The object that is indeed of most interest to this report is Petro 6 (Table 2). It is a shapeless lump of iron about 5 cm. long and 2 cm. wide containing 2.25% Ni. This object is the only evidence, apart from the prills in the slag, that we have of the smelting of lateritic iron ores in Petres. It was found in the same hoard as the rest of the objects and seems that it was put aside as a difficult piece to work. The metallographic structure of the object is ferrite and pearlite in a widmanstatten structure (**FIG. 3**). It is estimated that the carbon content in the presence of 2.25% Ni is about 0.15-0.2% C.

What is the origin of the nickeliferrous iron in Petres? The known lateritic deposits closest to the site are in the regions around Kastoria and Edessa (59 km SW and 45 km NE of Petres respectively) (ALBADAKIS 1981). Naturally, these particular deposits are reported in the literature as economically viable by modern standards. It is assumed that given the laterization of the area the Petres smiths had access to smaller and much nearer ones. Analyses of ores from Kastoria gave the following compositions: 1% Ni, 0.08% Co, 32% Fe_2O_3, 40% SiO_2, 1.2% MgO, 2.5% Al_2O_3, 2% Cr_2O_3 and 0.7% CaO (ALBADAKIS 1981, 207). No appreciable MnO_2 is reported. However, MnO was found in the analysis of the Pétres slag. Thus, it is possible that other ores like limonites and hematites in which MnO_2 is commonly found were mixed with iron laterites.

<u>Smelting Experiments</u>

The distinctly limited evidence at Petres for nickel in iron, both in metallic prills in the slag and iron objects, called for a series of smelting experiments to establish, among other questions, the distribution of nickel in iron within a bloom and its associated slag. These were carried out in a shaft furnace (1.05m height, 25cm inner diam.) using iron laterites from the modern mine at Larymna in Boeotia. The average composition of these ores consists of 1-2% NiO, 2.5% Cr_2O_3, 65-70% Fe_2O_3, 0.5-3% CaO, 7-14% SiO_2, 10-14% Al_2O_3 and 1.5-2.5% MgO (ALBADAKIS 1974, 27). The microstructure of the slags produced in our experimental smeltings revealed chromium-rich phases in addition to wustite and a silicate matrix. These chromium-rich phases are crystalline (55% Cr_2O_3, 20% FeO and 20% Al_2O_3 + SiO_2) and are present in the slags produced from lateritic iron ores alone or mixed with hematites. As was shown in Table 1, these phases are absent from Petres slags which contained only wustite and the silicate matrix. This observation leads us to postulate that the Petres slags were most probably smithing unless, of course, the local smiths has access to chromium-poor lateritic iron ores. However, the first hypothesis may be the most likely.

That nickel, unlike chromium, will not partition in the slag is due to the position of the NiO in the free energy diagram (ROSENQVIST 482). This implies that chromium is the least reducible at 1250 C and thus will end up in the slag rather than the metal. Hence the inherent difficulty in locating evidence for the smelting of lateritic iron ores. Unless nickel-rich iron prills are found in the slag, there is no direct way of establishing whether lateritic deposits have been exploited. Ni-rich iron prills are themselves quite elusive. From the thirty prills analysed with the EPMA in one experimental slag sample, only two contained nickel. In addition, the nickel in the iron prills can vary immensely, as the composition of a prill in sample Petr-Acr discussed above has shown. The presence of nickel in Petro 6, its distribution being very uniform ranging from 2.1% to 2.3% Ni, suggests that it was a section from a bloom. The distribution of nickel in the experimental bloom is similarly uniform ranging from 3.2% to 3.7% Ni. Smithing of the experimental bloom proved difficult since when hammered hot on the anvil it became very brittle. Thus it is possible that the Petres smith had little experience in forging such a material as Petro 6 and so put it aside.

Conclusions

The evidence for Ni-rich metallic prills in a small number of iron slags from Petres and a shapeless mass of iron, probably a section of a bloom, suggest that nickel-rich lateritic iron ores may have been exploited at Petres in the Hellenistic period. Petres is particularly interesting since it provides the investigator with sufficient archaeological material to apply this unified approach towards ore, slag and artefact. This approach is essential when dealing with nickel-rich lateritic iron ores given the elusive nature of nickel in slag.

It is difficult to establish whether these particular ore deposits were intentionally sought after at Petres, but preliminary evidence suggests otherwise. The majority of the iron objects contained no nickel and the slags are probably of the smithing type. Preliminary smelting experiments showed that nickel in small iron prills can vary substantially and is not always present, confirming our observation of the scarcity of nickel-rich iron prills in the archaeological Petres slags. The brittleness of the experimental bloom containing 3% Ni and similar in composition to Petro 6 suggests that the local smiths were not experienced in the forging of nickel-rich iron with about 0.2% C.

FOOTNOTE

1. Early nickel-rich iron has been traditionally ascribed a meteoritic origin. G. Varoufakis showed that some Mycenean iron rings contained up to 10% Ni, but he did not conclude that their origin was necessarily meteoritic (see: The origin of the Mycenean and Geometric iron on the Greek mainland and the Aegean Islands; in Early Metallurgy in Cyprus 4000-500 B.C. J.D. Muhly, R. Maddin and V. Karageorghis, eds, Nicosia, 1982, 315-24). Petres iron can hardly be considered as such, given the relatively late date of the site and the presence of lateritic deposits in the vicinity.

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