

SOIL REHABILITATION IN THE MUNICIPALITY OF LAVRION ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΥΣ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ

LIFE Programme Contract No.: 93/GR/A14/GR/4576



Volume 1Β Τόμος 1Β

Appendix reports Εκθέσεις παραρτήματος



GEOCHEMICAL ATLAS OF THE LAVRION URBAN AREA FOR ENVIRONMENTAL PROTECTION AND PLANNING

ΓΕΩΧΗΜΙΚΟΣ ΑΤΛΑΣ ΤΗΣ ΑΣΤΙΚΗΣ ΠΕΡΙΟΧΗΣ ΤΟΥ ΛΑΥΡΙΟΥ ΓΙΑ ΠΕΡΙΒΑΛΛΟΝΤΙΚΗ ΠΡΟΣΤΑΣΙΑ ΚΑΙ ΣΧΕΔΙΑΣΜΟ

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Volume 1Β Τόμος 1Β

GEOCHEMICAL ATLAS OF THE LAVRION URBAN AREA FOR ENVIRONMENTAL PROTECTION AND PLANNING

APPENDIX REPORTS

Edited by

Alecos Demetriades

ΓΕΩΧΗΜΙΚΟΣ ΑΤΛΑΣ ΤΗΣ ΑΣΤΙΚΗΣ ΠΕΡΙΟΧΗΣ ΤΟΥ ΛΑΥΡΙΟΥ ΓΙΑ ΠΕΡΙΒΑΛΛΟΝΤΙΚΗ ΠΡΟΣΤΑΣΙΑ ΚΑΙ ΣΧΕΔΙΑΣΜΟ

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Appendix Report 1

MULTI-ELEMENT GEOCHEMICAL DESK STUDY OF GARDEN SOIL IN LAVRION

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1.1. INTRODUCTION

Available geochemical data on only As, Cd, Cu, Fe, Hg, Pb and Zn (Hadjigeorgiou-Stavrakis and Vergou-Vichou, 1992) were not considered as adequate for a sound decision on elements to be determined in the individual particle characterisation study (refer to Appendix Report 2 in this Volume, p.2.0-2.45), and the planned detailed assessment of environmental conditions in Lavrion (see Volumes 1, 1A & 2). Hence, a multi-element preliminary geochemical study was undertaken. For this purpose, fifty "garden soil" samples were selected from the archives and analysed by X-ray fluorescence (XRF) at the British Geological Survey (BGS) (Volume 1, Chapter 2B, Section 2B.2.1, p.33-35), and ten "garden soil" samples were digested by aqua-regia at the IGME Central Laboratory in Athens (Volume 1, Chapter 2B, Section 2B.2.4 p.39-40), and elements determined by Induced Coupled Plasma Atomic Emission Spectrometry (ICP-AES) at BGS. The elements determined by the different methods were:-

- XRF (28 elements): Ag, As, Ba, Bi, Ca, Ce, Co, Cr, Cu, Fe, La, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Sn, Sr, Th, Ti, U, V, W, Y, Zn & Zr, and
- ICP-AES (28 elements): AI, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sc, Si, Sr, V, Y, Zn and Zr.

Further, Cd results by atomic absorption spectrophotometry (AAS) following an aqua regia digestion, and Hg determination by the Scintrex_® HGG-3 Hg-atomic absorption spectrometer on the same suite of 50 samples were used (Volume 1, Chapter 2B, Section 2B.2.6, p.40-41) in the multi-element study by cluster and factor analyses.

In the following description of results 41 elements will be discussed, and the concentration of As, Cd, Cu, Fe, Hg, Pb and Zn in road and house dust (Hadjigeorgiou-Stavrakis and Vergou-Vichou, 1992) will also be referred to.

1.1.1. TERMINOLOGY

It is stressed that the term "soil" in the context of the Lavrion urban area is a misnomer in the majority of cases. The enormous amounts of metallurgical processing wastes, and their transportation by aerial, fluvial and anthropogenic means, has altered the chemical composition of even residual soil. Since, a considerable amount of the loose surface material is not residual or alluvial soil *sensu strictu*, but a mixture of soil and metallurgical processing wastes, the term "soil" or "garden soil" is used *sensu latu*. Consequently the term "overburden" is considered more appropriate in the case of Lavrion. Overburden is defined by Jackson (1997, p.457) as *"the loose soil, silt, sand, gravel, or other unconsolidated material overlying bedrock, either transported or formed in place"*. *"Garden soil"* is the sample collected by Hadjigeorgiou-Stavrakis and Vergou-Vichou (1992) during the first urban geochemical contamination study carried out in Lavrion. In this case, garden soil is a collective term, and is synonymous to overburden (refer to Volume 1, Chapter 6, Section 6.1, p.129).

"Contamination"/"pollutants" and "contamination"/"contaminants" are terms, which are apparently used as synonyms, and are not clearly defined in either *"Europe's Environment - The Dobříš Assessment"* (Stanners and Bourdeau, 1995), which was published by the European Environmental Agency, or the *"CARACAS"* reports (Ferguson *et al.*, 1998, 1999), the programme of *"Concerted Action on Risk Assessment for Contaminated Sites in the European Union".*

The Fourth Edition of the Glossary of Geology (Jackson, 1997) gives the following definitions:

- "Contamination [water]: The addition to water of any substance or property that changes the physical and/or chemical characteristics of the water and prevents the use or reduces its usability for ordinary purposes such as drinking, preparing foods, bathing, washing, recreation, and cooling. Sometimes arbitrarily defined differently from *contamination*, but generally considered as synonymous" (p.137).
- "**Contaminant**: (a) Any physical, chemical, biological, or radiological substance or matter that has an adverse effect on air, water, or rocks. (b) An undesirable substance in water, air, or rocks that is either not normally present or is an unusually high concentration of a naturally occurring substance. Syn: *pollutant*" (p.137).
- "Pollute: (a) To make physically impure or unclean. (b) Often considered as synonymous with "contaminate", but in some environmental regulations *pollute* represents a more advanced state of degradation. To pollute is to introduce any substance that alerts some aspect of the environment in a manner to make it unfit for a particular use" (p.500).
- "Pollution: Contamination [water]" (p.500).

The above definitions indicate clearly that the two terms are synonymous. However, Douben (1998) attempts to clear this ambiguity, *i.e.*,

"Pollution: 'the presence in the environment, or the introduction into it, of products of human activity which have harmful or objectionable effects'. The definition in the Dangerous Substances Directive 76/464/EEC pollution may be more practical; pollution is defined as 'the discharge by man, directly or indirectly, of substances or energy into the aquatic environment, the results of which are such as to cause hazards to human health, harm to living resources and to aquatic ecosystems, damage to amenities or interference with other legitimate uses of water'. This clearly distinguishes it from contamination in that some harmful effect can occur at the levels present, a notion eloquently articulated by Holdgate (1979)" (p.12).

Hence, according to Douben's review, *"pollution"* describes the discharge of substances at levels that can *definitely* cause harm to human health and damage to the environment. Whereas, *"contamination"* indicates that *some harmful effect* can occur at the levels present, meaning that the levels are not high enough to definitely cause harm. Since, there is still some doubt about the definitions given for "pollution/pollutant" and "contamination/contaminant", in the reports of the present project the latter terms will be preferably used.

A noteworthy point is that the above definitions do not mention "soil", which is just as important to life on earth as is water, and likewise vulnerable to contamination.

1.2. ELEMENT CONTENTS IN "GARDEN SOIL": A PRELIMINARY STUDY

Tables 1.1 to 1.5 should be consulted for they give information on the global abundance of trace elements in rocks, uncontaminated and contaminated soils. Lavrion garden soil data are included in Tables 1.1 to 1.3 to facilitate comparisons.

A relative enrichment/depletion index was calculated for all elements determined on the Lavrion garden soil samples (Table 1.2), in order to obtain a numerical value for contamination or depletion. The median or mean values of the global abundance of elements in soil were taken to represent the "soil clarke" values. The median values were used in most cases, since this is a more robust statistical parameter. The star (*) after the value in Table 1.2 indicates the cases where the mean was used. An enrichment range was calculated for sulphur, since this is the only element with neither a median or mean abundance. *Index values greater than unity indicate enrichment or contamination, and less than unity depletion*.

1.2.1. SILVER (Ag)

The range of silver in Lavrion garden soil varies from 5 to 56 ppm, with a median of 19 ppm, and a mean of 21.9 ppm. Normal soil normally has an average of about 0.1 ppm (Levinson, 1980). Lavrion garden soil is, therefore, enriched considerably in silver as is indicated by a relative enrichment or contamination index of 218.80 (Table 1.2).

1.2.2. ALUMINIUM (AI)

The range of aluminium in Lavrion garden soil varies from 8559 to 34739 ppm, with a median of 13203 ppm, and a mean of 15712 ppm. The 1140 Missouri soil samples have Al contents between 11000-79000 ppm, with a geometric mean of 41000 ppm (Tidball, 1984). Lavrion garden soil has apparently aluminium contents within the normal range of variation, but is slightly depleted as indicated by a depletion index of 0.32 (Table 1.2).

1.2.3. ARSENIC (As)

The range of arsenic in Lavrion garden soil varies from 650 to 14800 ppm, with a median of 1660 ppm, and a mean of 3202 ppm. Comparatively uncontaminated soil has values between 5 and 10 ppm As, with an overall mean of 11.3 ppm for 1193 global soil samples (Fergusson, 1990). Sandy soil, soil over granites, alluvial soil and chernozems have concentrations of 5.1, 3.6, 8.2 and 8.8 ppm respectively (Fergusson, 1990), whereas smelter contaminated soil has values greater than 110 ppm As (Mattigod and Page, 1983) (Table 1.3). Arsenic levels in Lavrion garden soil are indeed very high, which is also indicated by a contamination index of 221.33 (Table 1.2).

Lavrion road dust contents vary from 35 to 6100 ppm, with a median of 700 ppm. Road dust arsenic values quoted in the literature vary from 1.6-29.5 ppm (Fergusson, 1990) (Table 1.4), which are much lower than the Lavrion ones.

Lavrion house dust arsenic contents vary from 275 to 3820 ppm, with a median of 750 ppm. Fergusson (1990) quotes a house dust arsenic value of 15.8 ppm, which is much lower than the Lavrion ones.

Table 1.1. Average abundance of elements in the earth's crust, rocks, soil and Lavrion garden soil (global data from Levinson, 1974, Table 2.1, p.43-44, and Plant and Raiswell, 1983, Table 1.2, p.5-6). Note: All element concentrations in ppm, except Hg* in ppb. Elements from Al to Si were determined by ICP-AES (n=10).

Πίνακας 1.1. Μέση τιμή των στοιχείων στο φλοιό της γης, στα πετρώματα, στο έδαφος και στο κηπευτικό έδαφος του Λαυρίου. Σημ.: Όλες οι συγκεντρώσεις σε ppm, εκτός του Hg" σε ppb. Τα στοιχεία από Al έως Si προσδιορίστηκαν με ICP-AES.

ut l	Earth's	Ultramafic	Basalt	Grano-	Granite	Sandstone	Shale	Limestone	estone Global :		Lavrie	on "gardei	n soil" (n=	=50)
l me	crust			diorite					rang	ge	Median	Mean	Ran	ge
Ť									Min.	Max.	Weulan	Wearr	Min.	Max.
Ag	0.07	0.06	0.1	0.07	0.04	-	0.05	1	-	0.1	19	21.88	5	56
As	1.8	1	2	2	1.5	1	15	2.5	-	1.5	1660	3202	650	14800
Ва	425	2	250	500	600	-	700	100	100	3000	562.5	1318.14	199	9290
Bi	0.17	0.02	0.15		0.1	-	0.18	-	-	-	11	12.9	1	51
Ca	-	-	-	-	-	-	-	-	-	-	112450	118680	52300	224200
Cd	0.2	-	0.2	0.2	0.2	-	0.2	0.1	-	1	50.5	85.54	9	520
Ce	60	8	35	40	46	-	50	10	-	-	21	21.52	8	43
Co	25	150	50	10	1	0.3	20	4	1	40	10.5	11.32	1	25
Cr	100	2000	200	20	4	35	100	10	5	1000	139	147.78	28	391
Cu	55	10	100	30	10	-	50	15	2	100	249.5	526	84	2000
Fe	-	-	-	-	-	-	-	-	-	-	51700	76082	29100	233000
Hg*	80	-	80	80	80	30	500	50	-	30	193	267.03	37	575
La	30	3.3	10.5	36	25	-	20	6	-	-	16.5	16.54	8	27
Mn	950	1300	2200	1200	500	-	850	1100	-	850	2465	3477	1040	11990
Мо	1.5	0.3	1	1	2	0.2	3	1	-	2	7	8.84	1	54
Nb	20	15	20	20	20	-	-	-	-	-	6	5.64	2	12
Ni	75	2000	150	20	0.5	2	70	12	5	500	116.5	118.58	34	243
Pb	12.5	0.1	5	15	20	7	20	8	2	200	9360	11098.4	2120	28400
Rb	90	-	30	120	150	60	140	5	20	500	46	48.5	23	80
Sb	0.2	0.1	0.2	0.2	0.2	-	1	-	-	5	151	191.46	28	567
Sn	2	0.5	1	2	3	-	4	4	-	10	18.5	25.94	3	225
Sr	375	1	465	450	285	20	300	500	50	1000	133.5	147.32	74	376
Th	10	0.003	2.2	10	17	1.7	12	2	-	13	8	8.56	1	19
Ti	5700	3000	9000	8000	2300	1500	4600	400	-	5000	1445	1521	440	3230
U	2.7	0.001	0.6	3	4.8	0.45	4	2	-	1	3	3.51	0.5	10
V	135	50	250	100	20	20	130	15	20	500	55.5	55.48	22	129
w	1.5	0.5	1	2	2	1.6	2	0.5	-	-	27.5	33.1	2	79
Y	30	-	25	30	40	-	25	15	-	0.7	9.5	13.29	0.5	49
Zn	70	50	100	60	40	16	100	25	-	20	10000	21557	2100	121000
Zr	165	50	150	140	180	-	160	20	-	300	41	60.72	2	1056
AI	-	-	-	-	-	-	-	-	-	-	13202.5	15711.9	8559	34739
в	10	5	5	20	15	35	100	10	2	10	136	135	115	175
Ве	2.8	-	0.5	2	5	-	3	1	-	6	1	1.3	0.6	3
ĸ	-	-	-	-	-	-	-	-	-	-	2157	2603	950	6322
Li	20	-	10	25	30	15	60	20	5	200	11.5	11.1	3	21
Mg	-	-	-	-	-	-	-	-	-	-	7825	8653.2	6065	11707
Na	-	-	-	-	-	-	-	-	-	-	852	1409.2	492	6398
Р	-	-	-	-	-	-	-	-	-	-	1316	1803	973	4947
s	-	-	-	-	-	-	-	-	-	-	12690	18068.6	5068	44304
Sc	16	10	38	10	5	-	15	5	-	-	6.5	6	4	9
Si	-	-	-	-	-	-	-	-	-	-	1014	1037	880	1408

1.2.4. BORON (B)

The range of boron in Lavrion garden soil varies from 115 to 175 ppm, with a median of 136 ppm, and a mean of 135 ppm. Global soil has a median of 29 ppm (Rose *et al.*, 1979) and a mean of 12 ppm B (Levinson, 1974). Soil, depending on its derivation, has a range of boron values between 2-100 ppm (Levinson, 1980). The 1140 Missouri soil samples have B contents between <20-700 ppm, with a geometric mean of 31 ppm (Tidball, 1984). Lavrion garden soil is apparently enriched with respect to boron as is indicated by an enrichment index of 4.69 (Table 1.2).

Table 1.2. Element contents in soil from different parts of the World compared to Lavrion garden soil, and its enrichment/depletion index.

Note: All element concentrations in ppm, except Hg* in ppb. Elements from Al to Si were determined by ICP-AES (n=10). Missouri soil data from Tidball (1984).

Πίνακας 1.2. Συγκεντρώσεις των στοιχείων στο έδαφος από διάφορα μέρη της Υφηλίου συγκρινόμενες με αυτές του κηπευτικού εδάφους του Λαυρίου και ο δείκτης εμπλουτισμού/ανεπάρκειάς του. [Συγκεντρώσεις σε ppm].

Ħ		Levinson (1974, 1980)								Ro	ose et al.	(1979))	S	iegel (197	4)	Missou	ri soil (n=	1140)	Lavrio	on "gard	en soil" (n=50)	Enrichment/
ame	Mean	Ra	ange	Temp	erate	Ai	id	Trop	oical	Median	Mean	Rai	nge	Mean	Rar	ige	G-mean	Ran	ge	Median	Mean	Rar	nge	depletion
ă	weam	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	wicdian	wican	Min.	Max.	wican	Min.	Max.	0-mean	Min.	Max.	weatan	wear	Min.	Max.	Index
Ag	0.1	·		-	-	-	-	-	-	-		-	-	0.1	0.01	5	0.7	<0.7	3	19	21.88	5	56	218.8*
As	5	1	50	-	-	-	-	-	-	7.5	-	-	-	6	0.1	40	8.7	2.5	72	1660	3202	650	14800	221.33
Ba	500	50	3000	150	3000	10	1500	10	3000	300	-	-	-	500	100	3000	580	100	1500	562.5	1318.1	199	9290	1.88
Bi	-	· ·		-	-	-	-	-	-	-	0.8	-	-	-	-	-	-	-	-	11	12.9	1	51	16.13*
Ca	-	· ·		-	-	-	-	-	-	-	-	-	-	13700	7000	500000	3300	<700	56000	112450	118680	52300	224200	8.66*
Cd	1	·		-	-	-	-	-	-	-	-	0.1	0.5	0.06	0.01	0.7	<1	<1	11	50.5	85.54	9	520	1425.67*
Ce	5			-	-	-	-	-	-	-	-	-	-	-	-	-	115	<150	300	21	21.52	8	43	4.30
Co	10	1	40	1	45	10	100	1	50	10	-	-	-	8	1	40	10	<3	30	10.5	11.32	1	25	1.05
Cr	50	5	5 1000	7	300	200	500	150	300	43	-	-	-	100	5	3000	54	10	150	139	147.78	28	391	3.23
Cu	20	2	2 100		25	15	100	10	150	15	-	-	-	20	10	1000	13	5	150	249.5	526	84	2000	16.63
Fe	-	· ·		-	-	-	-	-	-	21000	-	-	-	38000	7000	550000	21100	4900	54000	51700	76082	29100	233000	2.46
Hg	30	· ·		-	-	-	-	-	-	56	-	-	-	30	10	300	39	<10	800	193	267.03	37	575	3.45
La	-	· ·		-	-	-	-	-	-	33	-	-	-	30	1	5000	41	<30	150	16.5	16.54	8	27	0.50
Mn	850	· ·		-	-	-	-	-	-	320	-	-	-	850	100	4000	740	15	3000	2465	3477	1040	11990	7.70
MO	2	· ·		1	5	2	5	1	5	-	2.5	-	-	2	0.2	5	<3	<3	15	1	8.84	1	54	3.54^
ND NI:	15			-	-	-	-	-	-	-	15	-	-	-	-	-	1.2	<10	15	440.5	5.04	2	12	0.38"
	30		000		20		50		40	17	-	-	-	40	10	1000	14	<0	70	0000	118.58	34	243	6.85
PD	20	4	200		40		20		20	17	-	-	-	10	2	200	20	10	7000	9360	11098	2120	28400	550.59
RD	20- 500	· ·		-	-	-	-	-	-	35	-	-	-	100	20	102	-	-	-	40	48.5	23	80 567	1.31
50	10	· ·		-	10	-	-	-		-	10	-	-	- 10	2	200	-15	- 15	-	10 5	25.04	20	207	35.73
011	E0 1000	· ·		2	10	3	50	3	20	- 67	10	-	-	200	50	1000	110	<15	50	10.0	20.94	74	220	2.59
Th	13	· ·		-	-					13	-	-		500	0.1	1000	0.6	20	21	100.0	9.56	1	10	0.62
ті	5000	· ·		-	-					15	-	-		5000	1000	10000	3300	1500	7000	1445	1521	440	3230	0.02
	1				-						1			1	000	00000	3.8	1 1	15	1443	3.51	440	J230 10	3.51
v	80	20	500	10	400	10	300	10	300	57				100	20	500	69	15	150	55.5	55.48	22	129	0.97
w	-			-	-	-		-		-	1	-	-	-	-		-	-	-	27.5	33.1	2	79	33.10
Y	-	Ι.		-	-		-	-		27		-	-	50	25	250	32	<10	70	9.5	13.29	0.5	49	0.35
Zn	50	10	300	10	600	10	900	10	400	36	-	-		50	10	300	49	18	640	10000	21557	2100	121000	277.78
Zr	300			-	-	-	-	-		270	-	-		300	60	2000	310	70	700	41	60.72	2	1056	0.15
AI	-			-	-	-	-	-		-	-		-	-	-	-	41000	11000	79000	13203	15712	8559	34739	0.32
в	12	2	2 100	2	145	25	190	1	3	29	-	-	-	-	-	-	31	<20	700	136	135	115	175	4.69
Be	6	.		-	-	-	-	-		-	-	0.5	4	-	-	-	0.8	<1	2	1	1.3	0.6	3	0.22
к	-			-	-	-	-	-		11000	-	-	-	-	-	-	14000	3300	37000	2157	2603	950	6322	0.000091
Li	30	5	200	-	30	-	30	-	30	22	-	-	-	-	-	-	22	7	47	11.5	11.1	3	21	0.52
Mg	-	.		-	-	-	-	-	-	-	-	-	-	-	-	-	2600	500	28000	7825	8653.2	6065	11707	3.01
Na	-	.		-	-	-	-	-	-	-	-	-	-	-	-	-	5300	700	12000	852	1409.2	492	6398	0.16
Р	-	.		-	-	-	-	-	-	300	-	-	-	-	-	-	590	<100	6100	1316	1803	973	4947	4.39
s	-	.		-	-	-	-	-	-	-	-	100	2000	-	-	-	-	-	-	12690	18069	5068	44304	22.15-50.68
Sc	-	.		-	-	-	-	-	-	-	-	-	-	7	10	25	7.6	<5	15	6.5	6	4	9	0.86
Si	-			-	-	-	-	-	-	-	-	-	-	-	-	-	35%	23%	43%	1014	1037	880	1408	0.003

Table 1.3. Concentration of elements in Lavrion garden soil compared to other smelter and mine contaminated soils.

Note: Elements from AI to Na were determined by ICP-AES (n=10). [All values in ppm].

Πίνακας 1.3. Συγκεντρώσεις των στοιχείων στο κηπευτικό έδαφος του Λαυρίου συγκρινόμενες με αυτές των ρυπασμένων εδαφών από άλλες μεταλλουργικές περιοχές. [Συγκεντρώσεις σε ppm].

		This	study				Matti	god and Page (1983)			U	niska (198	5)
nt	Love	ion (Aa Ph	Zn Ac cm	o/tor)	Pb smelter	Pb smelter	Zn s	melters	Contamii	nated soil	Proximate soil	Zinc plant	Smelting	Mining and
eme	Lavn	on (Ag-Fb	-211-45 5110	ener)	Missouri	Kellogg	Palr	merton	Top soil	Subsoil	Top soil		works	smelting
Ш	Modian	Moon	Ra	nge	(Total)	(Total)	(Total)	Range	100 301	500301	100 301			complex
	Weulan	wear	Minimum	Maximum	(0-7.6 cm)	(0-2 cm)	(A1 horizon)		(0-15 cm)	(15-30 cm)	(0-15 cm)			
As	1660.0	3202.0	650	14800	-	110	-	-	-	-	-	-	-	-
Ba	562.5	1318.1	199	9290	-	-	-	-	4960	2900	750	-	-	-
Ca	112450.0	118680.0	52300	224200	-	-	-	-	70900	93100	3600	-	-	-
Cd	50.5	85.5	9	520	-	140	1500	900-1500	578	423	29	0 - 80	0 - 14	0 - 3640
Cr	139.0	147.8	28	391	-	-	-	-	-	-	-	0 - 1600	3 - 3000	2 - 1980
Cu	249.5	526.0	84	2000	-	-	1200	600 - 1200	68	43	42	-	-	-
Fe	51700.0	76082.0	29100	233000	-	-	-	-	66700	35700	58000	-	-	-
Mn	2465.0	3477.0	1040	11990	-	-	-	-	2655	2305	5935	-	-	-
Мо	7.0	8.8	1	54	-	-	-	-	30	9	trace	-	-	-
Pb	9360.0	11098.4	2120	28400	22740	7900	1100	200 - 1100	8100	7230	1825	4 - 4560	4 - 2300	1 - 3640
Zn	10000.0	21557.0	2100	121000	4170	29000	80000	50000 - 80000	60200	44700	6700	-	-	-
Al	13202.5	15711.9	8559	34739	-	-	-	-	15100	15600	29900	-	-	-
к	2157.0	2603.0	950	6322	-	-	-	-	16100	24200	21100	-	-	-
Mg	7825.0	8653.2	6065	11707	-	-	-	-	17800	25600	4100	-	-	-
Na	852.0	1409.2	492	6398	-	-	-	-	521	581	2320	-	-	-

Table 1.4. Concentration of Pb, Cd, As, Sb and Hg in road and house dust (compare with Table 1.5 below).

(From Fergusson, 1990, Chapter 11:- Adventitious sources of the heavy elements: 407-428). All values in ppm except where indicated.

Πίνακας 1.4. Συγκεντρώσεις Pb, Cd, As, Sb και Hg στη σκόνη δρόμων και σπιτιών (σύγκρινε με Πίνακα 1.5).

Area / Element		Le	ad			Cadı	nium	
	Road	dust	House	e dust	Road	dust	House	e dust
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Rural	20	305	20	100	1.3	3		-
Suburban	50	500	20	500				-
Urban	77	19073	170	8097	1.7	336	0.6	336
Inner City	150	4530	-		-			-
Industrial areas	120	30100	-		6	1450		-
Around smelters	1041	6508	2800	103756	-		12	387
Mineralised areas	-	-	up to	1 - 2%	-		0.8	273
Arsenic (As)	1.2	29.5	8	23.4	-			-
Antimony (Sb)	1.6	15.8	1.8	30.6	-			-
Selenium (Se)	1	1	-		-			-
Mercury (Hg)	90	ppb	-		-			-

Table 1.5. Statistical parameters of the whole data sets and subsets for garden soil, road and house dust, Lavrion (from Hadjigeorgiou-Stavrakis and Vergou-Vichou, 1992).

All values in ppm except Hg in ppb.

Πίνακας 1.5. Στατιστικές παράμετροι ολόκληρου του αρχείου των δεδομένων και μέρους αυτών για το κηπευτικό έδαφος, τη σκόνη δρόμων και σπιτιών στο Λαύριο. Όλες οι συγκεντρώσεις σε ppm εκτός του Hg σε ppb.

			Garden	soil				Road	dust			House	dust	
lent	AAS d	ataset	AAS s	ubset	XRF st	ubset	AAS da	taset	AAS si	ıbset	AAS d	ataset	AAS si	ıbset
ler	(n=1	(53)	(n={	50)	(n=5	50)	(n=13	37)	(n=3	4)	(n=1	28)	(n=3	2)
<u> </u>	Median	С%	Median	C%	Median	С%	Median	C%	Median	C%	Median	C%	Median	C%
As	1120.0	110.7	1660.0	109.3	1494.0	93.7	700.0	88.2	1585.0	70.0	398.0	93.5	750.0	74.4
Cd	32.0	108.7	50.5	122.2	-	-	21.0	90.9	40.0	65.0	16.0	77.3	21.5	83.3
Cu	143.0	111.5	249.5	96.4	326.5	98.8	151.0	106.1	223.5	90.3	187.0	170.1	296.0	173.5
Fe	37400.0	61.1	51700.0	66.5	48150.0	54.8	29320.0	79.5	46970.0	69.2	20630.0	77.4	39330.0	61.7
Hg	117.0	102.3	193.0	75.4	-	-	98.0	22.3	88.5	22.3	88.0	55.3	79.0	82.0
Pb	6400.0	65.0	9360.0	61.7	8567.0	54.1	4540.0	102.6	6600.0	61.9	3220.0	70.5	4220.0	64.8
Zn	5720.0	113.3	10000.0	107.1	9325.5	107.5	4820.0	114.1	8980.0	91.4	3050.0	102.9	6020.0	82.8

1.2.5. BARIUM (Ba)

The range of barium in Lavrion garden soil varies from 199 to 9290 ppm, with a median of 562.5 ppm, and a mean of 1318 ppm. Uncontaminated soil, depending on its origin, has a range of values between 100 to 3000 ppm Ba, a mean of 500 ppm (Levinson, 1980), and a median of 300 ppm (Rose *et al.*, 1979). According to Mattigod and Page (1983) contaminated soil has values from 750 to 4960 ppm (Table 1.3). Lavrion garden soil has, however, much higher values, and is, therefore, definitely contaminated by barium, as is also indicated by a relative contamination index of 1.88 (Table 1.2).

1.2.6. BERYLLIUM (Be)

The range of beryllium in Lavrion garden soil varies from 0.6 to 3 ppm, with a median of 1 ppm, and mean of 1.3 ppm. Soil depending on its derivation has a range of beryllium values between 0.5-4 ppm (Rose *et al.*, 1979), and a mean of 6 ppm according to Levinson (1980). The 1140 Missouri soil samples have Be contents between <1-2 ppm, with a geometric mean of 0.8 ppm (Tidball, 1984). Lavrion garden soil appears, therefore, to be depleted with respect to Be as is shown by a depletion index of 0.22 (Table 1.2).

1.2.7. Візмитн (Ві)

The range of bismuth in Lavrion garden soil varies from 1 to 51 ppm, with a median of 11 ppm, and a mean of 12.9. Soil has mean bismuth value of 0.8 ppm (Rose *et al.*, 1979) or 0.2 ppm (Fergusson, 1990). Lavrion garden soil appears, therefore, to be enriched in bismuth, as is also indicated by a relative enrichment index of 16.13 (Table 1.2).

1.2.8. CADMIUM (Cd)

The range of cadmium in Lavrion garden soil varies from 9 to 520 ppm, with a median of 50.5 ppm, and a mean of 85.5 ppm. Soil free of contamination has values ranging from 0.1 to 1 ppm, and the mean value for 1642 soil samples from all over the world is 0.62 ppm (Fergusson, 1990). Smelter contaminated soil has cadmium values varying from <0.0x to 1500 ppm (Mattigod and Page, 1983; Uniska 1985) [Table 1.3]. Lavrion garden soil has definitely been contaminated by the smelting activities, as is shown by a contamination index of 1425.67 (Table 1.2).

Lavrion road dust cadmium contents vary from 2 to 165 ppm, with a median value of 21 ppm. Fergusson (1990) quotes cadmium road dust values from 6 to 1450 ppm in industrial areas (Table 1.4), which is a much wider range than the Lavrion one.

Lavrion house dust cadmium contents vary from 5 to 140 ppm, with a median value of 16 ppm. Fergusson (1990) mentions cadmium house dust values between 12 to 387 ppm around smelters (Table 1.4), which is again a much wider range than the Lavrion one.

1.2.9. CALCIUM (Ca)

The range of calcium in Lavrion garden soil varies from 52300 to 224200 ppm, with median of 112450 ppm, and a mean of 118680 ppm. Tidball (1984) from an investigation of 1140 soil samples from Missouri reported that the calcium varies from 700 to 56000 ppm, with a geometric mean of 3300 ppm. The lower calcium concentrations in Lavrion garden soil begins from the upper range of Missouri soil. According to Mattigod and Page (1983) soil contaminated by calcium has values from 3600 to 70900 ppm (Table 1.3). Lavrion garden soil has calcium contents much higher than these. It is, therefore, enriched with respect to calcium, with an enrichment index of 8.66 (Table 1.2). This enrichment may be due to the high calcium content of the parent rocks, *i.e.*, marble.

1.2.10. CERIUM (Ce)

The range of cerium in Lavrion garden soil varies from 8 to 43 ppm, with a median of 21 ppm, and a mean of 21.5 ppm. Soil has a mean of about 5 ppm Ce (Levinson, 1980). The 1140 Missouri soil samples have Ce contents between <150-300 ppm, with a geometric mean of 115 ppm (Tidball, 1984). Lavrion garden soil appears, therefore, to be enriched in Ce when compared to world soil statistics (relative enrichment index of 4.30, Table 1.2), and depleted with respect to Missouri soil.

1.2.11. COBALT (CO)

The range of cobalt in Lavrion garden soil varies from 1 to 25 ppm, with a median of 10.5 ppm, and a mean of 11.3 ppm. Soil, depending on its derivation, has a range of 1-40 ppm Co, a mean of 10 ppm (Levinson, 1980), and also a median of 10 ppm (Rose *et al.*, 1979). The dominant rock type in Lavrion is marble, which has a mean cobalt content of 4 ppm (Levinson, 1980). It appears, therefore, that Lavrion garden soil has slightly elevated cobalt contents, as is also indicated by the low relative enrichment index of 1.05 (Table 1.2).

1.2.12. CHROMIUM (Cr)

The range of chromium in Lavrion garden soil varies from 28 to 391 ppm, with a median of 139 ppm, and a mean of 147.8 ppm. Soil, depending on its derivation, has a range of 5-1000 ppm Cr, a mean of 50 ppm (Levinson, 1980), and a median of 43 ppm (Rose *et al.*, 1979). The dominant rock type in Lavrion is marble, which has a mean chromium content of 10 ppm (Levinson, 1980). According to Uninska (1985) contaminated soil around smelters has values ranging from <0.0x to 3000 ppm Cr (Table 1.3). Lavrion garden soil does not have such a wide range of Cr values, since this depends on the composition of the smelted ores. Nevertheless, it certainly has elevated chromium contents, as is shown by a relative enrichment index of 3.23 (Table 1.2).

1.2.13. COPPER (Cu)

The range of copper in Lavrion garden soil varies from 84 to 2000 ppm, with a median value of 249.5 ppm, and a mean of 526 ppm. Normal uncontaminated soil, depending on its derivation, has a range of values between 2-100 ppm Cu, a mean of 20 ppm (Levinson, 1974, 1980), and a median of 15 ppm (Rose *et al.*, 1979). Whereas, soil near smelters has copper contents, which vary from 600-1200 ppm (Mattigod and Page, 1983) (Table 1.3). The degree of copper contamination, caused by smelting activities on Lavrion garden soil can, therefore, be estimated, *i.e.*, the relative enrichment or contamination index for copper is 16.63 (Table 1.2).

Lavrion road dust copper contents vary from 45 to 1615 ppm, with a median value of 151 ppm.

Lavrion house dust copper contents vary from 30 to 5050 ppm, with a median value of 187.

1.2.14. IRON (Fe)

The range of iron in Lavrion garden soil varies from 29100 to 233000 ppm, with a median of 51700 ppm, and a mean of 76082 ppm. Uncontaminated soil has a median of 21000 ppm iron (Rose *et al.*, 1979) (Table 1.2), whereas smelter contaminated soil has values varying from 35700 to 66700 ppm (Mattigod and Page, 1983) (Table 1.3). Lavrion garden is apparently contaminated as indicated by a soil contamination index of 2.46 (Table 1.2).

Lavrion road dust iron contents vary from 10200 to 195400 ppm, with a median value of 29320 ppm.

Lavrion house dust iron contents vary from 6940 to 141500 ppm, with a median value of 20630 ppm.

1.2.15. MERCURY (Hg)

The range of mercury in Lavrion garden soil varies from 37 to 575 ppb, with a median of 193 ppb, and a mean of 267 ppb. Normal uncontaminated soil has a median value of about 56 ppb according to Rose *et al.* (1979), whereas Fergusson (1990) states that most soils have mercury values <100 ppb, with a range of 10-60 ppb; the mean value for 3049 soil samples from around the world is 98 ppb; Hg levels of up to 400 ppb are found in organic soils. Consequently, Lavrion garden soil is definitely contaminated with respect to Hg as is shown by a relative contamination index of 3.45 (Table 1.2).

Lavrion road dust mercury contents vary from 41 to 117 ppb, with a median of 98 ppb. Fergusson (1990) quotes a road dust value for mercury of 90 ppb (Table 1.4), which is very close to the Lavrion median.

Lavrion house dust mercury contents vary from 3 to 375 ppb, with a median of 88 ppb.

1.2.16. POTASSIUM (K)

The range of potassium in Lavrion garden soil varies from 950-11707 ppm, with a median of 2157 ppm, and a mean of 2603 ppm. Soil has a median potassium content of 11000 ppm (Rose *et al.*, 1979). The 1140 Missouri soil samples have K contents between 3300-37000 ppm, with a geometric mean of 14000 ppm (Tidball, 1984). Lavrion garden soil appears, therefore, to have potassium contents within the normal range of variation, but it is slightly depleted as indicated by a depletion index of 0.000091 (Table 1.2).

1.2.17. LANTHANUM (La)

The range of lanthanum in Lavrion garden soil varies from 8 to 27 ppm, with a median and a mean of 16.5 ppm. Soil has a median of 33 ppm La (Rose *et al.*, 1979). The 1140 Missouri soil samples have La contents between <30-150 ppm, and a geometric mean of 41 ppm (Tidball, 1984). Lavrion garden soil is, therefore, depleted in lanthanum, as is also indicated by a relative depletion index of 0.50 (Table 1.2).

1.2.18. LITHIUM (Li)

The range of lithium in Lavrion garden soil varies from 3 to 21 ppm, with a median of 11.5 ppm, and a mean of 11.1 ppm. Soil, depending on its derivation, has a range of lithium values between 5-200 ppm Li, a mean of 30 ppm (Levinson, 1980) and a median of 22 ppm. The 1140 Missouri soil samples have Li contents between 7-47 ppm, with a geometric mean of 22 ppm (Tidball, 1984). Lavrion garden soil appears, therefore, to be depleted with respect to Li as is indicated by a depletion index of 0.52 (Table 1.2).

1.2.19. MAGNESIUM (Mg)

The range of magnesium in Lavrion garden soil varies from 6065 to 11707 ppm, with a median of 7825 ppm, and a mean of 8653 ppm. The 1140 Missouri soil samples have Mg contents between 500-28000 ppm, with a geometric mean of 2600 ppm (Tidball, 1984). Lavrion garden soil appears, therefore, to have magnesium contents within the normal range of variation, but is slightly enriched as indicated by a relative enrichment index of 3.01 (Table 1.2).

1.2.20. MANGANESE (Mn)

The range of manganese in Lavrion garden soil varies from 1040 to 11990 ppm, with a median of 2465 ppm, and a mean of 3477 ppm. Uncontaminated soil has a median value of 320 ppm (Rose *et al.*, 1979), and a mean of 850 ppm Mn (Levinson, 1974), whereas smelter contaminated soil has values of 2305 to 5935 (Fergusson, 1990) (Table 1.3). Lavrion garden soil has a much wider range of values, and is apparently contaminated by manganese as indicated by the contamination index of 7.70.

1.2.21. MOLYBDENUM (MO)

The range of molybdenum in Lavrion garden soil varies from 1 to 54 ppm, with a median of 7 ppm, and a mean of 8.8 ppm. Uncontaminated soil has a mean of 2.5 ppm Mo (Rose *et al.*, 1979), whereas contaminated soil has values from 9 to 30 ppm Mo (Mattigod and Page, 1983) (Table 1.3). Lavrion garden soil appears, therefore, to be contaminated with respect to molybdenum, as is also indicated by a relative contamination index of 3.54 (Table 1.2).

1.2.22. Sodium (Na)

The range of sodium in Lavrion garden soil varies from 492 to 6398 ppm, with a median of 852 ppm, and a mean of 1409 ppm. The 1140 Missouri soil samples have Na contents between 700-12000 ppm, with a geometric mean of 5300 ppm (Tidball, 1984). The sodium content in Lavrion garden soil is in the lower range of Missouri soil, which is also indicated by a depletion index of 0.16 (Table 1.2).

1.2.23. NIOBIUM (Nb)

The range of niobium in Lavrion garden soil varies from 2 to 12 ppm, with a median of 6 ppm, and a mean of 5.6 ppm. Soil has a mean of 15 ppm (Rose *et al.*, 1979). The variation of niobium observed in the 1140 Missouri soil samples was from <10 to 15 ppm, with a geometric mean of 7.2 ppm (Tidball, 1984). Therefore, the niobium content in Lavrion garden soil appears to be within the normal range. The calculated index of 0.38 (Table 1.2) shows that there is a slight depletion of Lavrion garden soil with respect to niobium.

1.2.24. NICKEL (NI)

The range of nickel in Lavrion garden soil varies from 34 to 243 ppm, with a median of 116.5 ppm, and a mean of 118.6 ppm. Soil, depending on its derivation, has range of 5-500 ppm Ni, a mean of 3 0 ppm (Levinson, 1980), and a median of 17 ppm (Rose *et al.*, 1979). The dominant rock type in Lavrion is marble, which has a mean nickel content of 12 ppm (Levinson, 1980). It appears, therefore, that Lavrion garden soil has elevated nickel values, which is also shown by a relative enrichment index of 6.85 (Table 1.2).

1.2.25. LEAD (Pb)

The range of lead in Lavrion garden soil varies from 2120 to 28400 ppm, with a median of 9360 ppm and a mean of 11098. Normal uncontaminated soil has average figures around 10-20 ppm, and contaminated soil values >100 ppm Pb (Fergusson, 1990); organic soil tends to have higher lead levels than mineral soil, with mean concentrations in the order of 30 and 13 ppm respectively; smelter contaminated soil has values varying from 1 to 22740 ppm (Mattigod and Page, 1983; Uniska, 1985) (Table 1.3). Lead contamination of Lavrion garden soil is, therefore, enormous, with a contamination index of 550.59 (Table 1.2).

Lavrion road dust lead contents vary from 460 to 39200 ppm, with a median of 6540 ppm. This is, according to Fergusson's (1990) review, in the same order of magnitude for industrial areas, which have a range of values from 120 to 30100 ppm (Table 1.4), whereas around smelters the values vary from 1041-6508 ppm Pb.

Lavrion house dust lead contents vary from 610 to 19500 ppm, with a median of 3220 ppm. According to Fergusson (1990) house dust values around smelters vary from 2800 to 103756 ppm Pb (Table 1.4), figures which are indeed very high, and much higher than the Lavrion ones.

1.2.26. PHOSPHORUS (P)

The range of phosphorus in Lavrion garden soil varies from 973 to 4947 ppm, with a median of 1316 ppm, and a mean of 1803 ppm. Normal soil has a median of 300 ppm (Rose *et al.*, 1979). The 1140 Missouri soil samples have P contents between <100-6100 ppm, with a geometric mean of 590 ppm (Tidball, 1984). Lavrion garden soil appears, therefore, to be enriched with respect to P as is indicated by an enrichment index of 4.39 (Table 1.2).

1.2.27. Ruвidium (Rb)

The range of rubidium in Lavrion garden soil varies from 23 to 80 ppm, with a median of 46 ppm, and a mean of 48.5. Soil, depending on its derivation, has a range of 20-500 ppm Rb (Levinson, 1974), and a median of 35 ppm (Rose *et al.*, 1979). The dominant rock type is marble, which has a mean rubidium content of 5 ppm (Levinson, 1974). Lavrion garden soil has apparently elevated rubidium contents, as is also shown by a relative enrichment index of 1.31 (Table 1.2).

1.2.28. SULPHUR (S)

The range of sulphur in Lavrion garden soil varies from 5068 to 44304 ppm, with a median of 12690 ppm, and a mean of 18069 ppm. Soil, depending on its derivation, has a range of S values between 100-2000 ppm. Lavrion garden soil is enriched, therefore, with respect to S as is indicated by an enrichment index of 22.2-50.7 (Table 1.2).

1.2.29. ANTIMONY (Sb)

The range of antimony in Lavrion garden soil varies from 28 to 567 ppm, with a median of 151 ppm, and a mean of 191.5 ppm. Uncontaminated soil has values of 0.9 ppm or less according to Fergusson (1990), and a mean of 2 ppm (Rose *et al.*, 1979) or 5 ppm (Levinson, 1980). Lavrion garden soil is definitely contaminated, therefore, by antimony as indicated by the relative contamination index of 95.73 (Table 1.2).

1.2.30. SCANDIUM (Sc)

The range of scandium in Lavrion garden soil varies from 4 to 9 ppm, with a median of 6.5 ppm, and a mean of 6 ppm. Soil, depending on its derivation, has a range of scandium values between 10-25 ppm, with a mean of 7 ppm (Siegel, 1974). The 1140 Missouri soil samples have Sc contents between <5-15 ppm, with a geometric mean of 7.6 ppm (Tidball, 1984). Lavrion garden soil is depleted, therefore, with respect to scandium as indicated by a depletion index of 0.86 (Table 1.2).

1.2.31. SILICON (SI)

The range of silicon in Lavrion garden soil varies from 880 to 1408 ppm, with a median of 1014 ppm, and a mean of 1037 ppm. The 1140 Missouri soil samples have Si contents between 23-43%, with a geometric mean of 35% (Tidball, 1984). Lavrion garden soil is largely derived from carbonate rocks, which have very low silicon contents as indicated by a depletion index of 0.003 (Table 1.2).

1.2.32. TIN (Sn)

The range of tin in Lavrion garden soil varies from 3 to 225 ppm, with a median of 18.5 ppm, and a mean of 25.9. Soil has an average tin content of about 10 ppm (Rose *et al.*, 1979). Lavrion garden soil is enriched, therefore, with respect to tin, as is also indicated by a relative enrichment index of 2.59 (Table 1.2).

1.2.33. STRONTIUM (Sr)

The range of strontium in Lavrion garden soil varies from 74 to 376 ppm, with a median of 133.5 ppm, and a mean of 147.3 ppm. Soil, depending on its derivation, has a range of 50-1000 ppm Sr (Levinson, 1974), and a median of 67 ppm (Rose *et al.*, 1979). The dominant rock type in Lavrion is marble, which has a mean strontium content of 610 ppm (Rose *et al.*, 1979). If one considers the overall median value for soil, Lavrion garden soil has an elevated strontium content, which is also indicated by a relative enrichment index of 1.99 (Table 1.2).

1.2.34. THORIUM (Th)

The range of thorium in Lavrion garden soil varies from 1 to 19 ppm, with a median of 8 ppm, and a mean of 8.6 ppm. Soil has a mean of about 13 ppm Th (Rose *et al.*, 1979). The 1140 Missouri soil samples have Th contents between 3.2-21 ppm, with a geometric mean of 9.6 ppm (Tidball, 1984). Lavrion garden soil appears, therefore, to have thorium contents within the normal range of variation. The calculated index of 0.62 (Table 1.2) shows, however, that it is slightly depleted with respect to thorium.

1.2.35. TITANIUM (TI)

The range of titanium in Lavrion garden soil varies from 440 to 3230 ppm, with a median of 1445 ppm, and a mean of 1521. Tidball (1984) from an investigation of 1140 soil sample from Missouri reported that titanium varies from 1500 to 7000 ppm, with a geometric mean 3300 ppm. It appears, therefore, that titanium in Lavrion garden soil is within the normal range of values. The calculated index of 0.30 (Table 1.2) shows that it is in fact slightly depleted with respect to titanium.

1.2.36. URANIUM (U)

The range of uranium in Lavrion garden soil varies from 0.5 to 10 ppm, with a median of 3 ppm, and a mean of 3. Soil has a mean uranium content of about 1 ppm (Rose *et al.*, 1979). The 1140 Missouri soil samples have U contents between 1.1-15 ppm, with a geometric mean of 3.8 ppm (Tidball, 1984). Lavrion garden soil has apparently uranium contents within the normal range of variation, and is slightly enriched as indicated by a relative enrichment index of 3.51 (Table 1.2).

1.2.37. VANADIUM (V)

The range of vanadium in Lavrion garden soil varies from 22 to 129 ppm, with a median of 55.5 ppm, and a mean of 55.5. Soil, depending on its derivation, has a range of 20-500 ppm V (Levinson, 1980), and a median of 57 ppm (Rose *et al.*, 1979). It appears, therefore, that vanadium in Lavrion garden soil is within the normal range of values. The calculated index of 0.97 (Table 1.2) shows, however, a slight depletion. If the dominant rock type is considered, the marble, which has a mean vanadium content of 15 ppm (Levinson 1980), then Lavrion garden soil appears to have elevated vanadium values.

1.2.38. TUNGSTEN (W)

The range of tungsten in Lavrion garden soil varies from 2 to 79 ppm, with a median of 27.5 ppm, and a mean of 33.1 ppm. Soil has a mean tungsten content of about 1 ppm (Rose *et al.*, 1979). Lavrion garden soil is apparently enriched in tungsten, as is also indicated by a relative enrichment index of 33.10 (Table 1.2).

1.2.39. YTTRIUM (Y)

The range of yttrium in Lavrion garden soil varies from 0.5 to 49 ppm, with a median of 9.5 ppm, and a mean of 13.3 ppm. Soil has a median of 27 ppm (Rose *et al.*, 1979). The dominant rock type is marble, which has a mean yttrium content of 15 ppm (Levinson, 1974). Lavrion garden soil is depleted, therefore, with respect to yttrium, as is also shown by a relative depletion index of 0.35 (Table 1.2).

1.2.40. ZINC (Zn)

The range of zinc in Lavrion garden soil varies from 2100 to 121000 ppm, with a median of 10000 ppm and a mean of 21557 ppm. Uncontaminated soil, depending of its derivation, has a range of values of 10-300 ppm Zn, a mean of 50 ppm (Levinson, 1980), and a median of 36 ppm (Rose *et al.*, 1979). Smelter contaminated soil varies from 4170 to 80000 (Mattigod and Page, 1983). Lavrion garden soil is definitely contaminated, therefore, by zinc, as is also indicated by a relative contamination index of 277.78 (Table 1.2).

Lavrion road dust zinc contents vary from 600 to 51800 ppm, with a median of 4820 ppm.

Lavrion house dust zinc contents vary from 480 to 34200 ppm, with a median of 3050 ppm.

1.2.41. ZIRCONIUM (Zr)

The range of zirconium in Lavrion garden soil varies from 2 to 1056 ppm, with a median of 41 ppm, and a mean of 60.7 ppm. Soil has a median of 270 ppm (Rose *et al.*, 1979) and a mean of 300 ppm Zr (Levinson, 1974). The dominant rock type in Lavrion is marble, which has a mean zirconium content of 20 ppm. Although Lavrion garden soil appears to have elevated zirconium contents, the calculated index of 0.15 (Table 1.2) shows that it is slightly depleted.

1.3. CORRELATION AND CLUSTER ANALYSES

Spearman rank correlation matrices for the XRF/AAS and ICP-AES results are tabulated in Tables 1.6 and 1.8. However, such complicated correlation matrices cannot easily be interpreted. Hence, the results are presented in dendrographs (Figs. 1.1 & 1.3), a cluster analysis tool (McCammon, 1968, 1969, 1974; Obial, 1970; Obial and James, 1973; Labonté, 1989; Labonté and Goodarzi, 1987, 1990). It is stressed that the natural element correlation coefficients are masked by the contamination caused by

Table 1.6. Spearman rank correlation coefficients of XRF and AAS data on garden soil samples (n=50), Lavrion.

Πίνακας 1.6. Συντελεστές συσχέτισης τάξεων του Spearman των δεδομένων φασματομετρίας ακτίνων-Χ και ατομικής απορρόφησης των δειγμάτων εδάφους από κήπους σπιτιών (n=50) του Λαυρίου.

	Ca	Ti	Mn	Fe	V	Cr	Co	Ni	Cu	Zn	Rb	Sr	Zr	Nb	Мо	Ag	Sn	Sb	Ва	La	Ce	Pb	Th	U	As	W	Bi	Y	Cd	Hg
Са	1.00																													
Ti	-0.21	1.00																												
Mn	-0.44	-0.58	1.00																											
Fe	-0.60	-0.47	0.87	1.00																										
V	-0.24	-0.76	-0.44	-0.27	1.00																									
Cr	-0.12	-0.74	-0.56	-0.49	0.53	1.00																								
Co	-0.18	0.74	-0.53	-0.42	0.65	0.83	1.00																							
Ni	-0.11	0.54	-0.45	-0.41	0.45	0.89	0.75	1.00																						
Cu	-0.35	-0.70	0.84	0.87	-0.45	-0.64	-0.57	-0.50	1.00																					
Zn	-0.31	-0.74	0.84	0.80	-0.50	-0.70	-0.65	-0.49	0.92	1.00																				
Rb	-0.40	0.53	-0.23	-0.07	0.49	0.56	0.60	0.66	-0.20	-0.19	1.00																			
Sr	-0.02	-0.20	0.28	0.41	0.00	-0.33	-0.31	-0.46	0.39	0.31	-0.41	1.00																		
Zr	-0.23	0.66	-0.33	-0.24	0.44	0.61	0.56	0.37	-0.44	-0.57	0.25	-0.15	1.00																	
Nb	-0.27	0.73	-0.36	-0.23	0.74	0.49	0.57	0.35	-0.43	-0.44	0.47	-0.10	0.39	1.00																
Мо	-0.33	-0.45	0.65	0.59	-0.35	-0.47	-0.49	-0.37	0.63	0.65	-0.16	0.25	-0.45	-0.36	1.00															
Ag	-0.20	-0.66	0.61	0.56	-0.50	-0.61	-0.58	-0.35	0.75	0.86	-0.01	0.05	-0.67	-0.40	0.66	1.00														
Sn	-0.09	-0.54	0.57	0.65	-0.43	-0.42	-0.46	-0.35	0.71	0.62	-0.18	0.51	-0.33	-0.46	0.46	0.50	1.00													
Sb	-0.20	-0.68	0.61	0.56	-0.52	-0.59	-0.52	-0.30	0.75	0.86	0.05	0.00	-0.65	-0.43	0.59	0.96	0.48	1.00												
Ba	-0.30	-0.55	0.78	0.83	-0.40	-0.48	-0.51	-0.43	0.82	0.75	-0.24	0.56	-0.29	-0.40	0.61	0.52	0.77	0.50	1.00											
La	-0.63	0.13	0.47	0.58	0.31	-0.02	0.15	-0.01	0.40	0.33	0.32	0.28	0.21	0.29	0.28	0.17	0.22	0.14	0.42	1.00										
Ce	-0.56	0.53	0.00	0.11	0.54	0.32	0.52	0.20	-0.13	-0.17	0.42	0.15	0.35	0.51	-0.01	-0.28	-0.13	-0.26	-0.04	0.51	1.00									
Pb	-0.27	-0.58	0.57	0.55	-0.46	-0.54	-0.52	-0.27	0.73	0.82	0.13	0.01	-0.66	-0.36	0.64	0.96	0.46	0.95	0.47	0.15	-0.23	1.00								
Th	-0.31	-0.15	0.19	0.26	-0.04	-0.19	-0.11	-0.10	0.20	0.30	0.20	0.01	-0.24	0.01	0.30	0.41	0.11	0.44	0.22	0.13	0.21	0.41	1.00							
U	-0.15	-0.39	0.29	0.22	-0.22	-0.22	-0.17	-0.13	0.37	0.31	-0.03	0.04	-0.21	-0.35	0.10	0.32	0.32	0.34	0.26	0.05	-0.27	0.28	-0.15	1.00						
As	-0.28	-0.65	0.80	0.79	-0.42	-0.62	-0.48	-0.49	0.89	0.85	-0.20	0.30	-0.32	-0.39	0.46	0.65	0.60	0.68	0.69	0.40	-0.11	0.59	0.08	0.45	1.00					
W	-0.24	-0.72	0.76	0.73	-0.50	-0.65	-0.63	-0.45	0.88	0.97	-0.20	0.36	-0.54	-0.43	0.62	0.85	0.62	0.86	0.75	0.30	-0.19	0.79	0.33	0.32	0.78	1.00				
Bi	-0.21	-0.58	0.54	0.54	-0.42	-0.52	-0.38	-0.27	0.75	0.74	0.14	-0.01	-0.48	-0.35	0.51	0.86	0.45	0.87	0.43	0.21	-0.24	0.87	0.21	0.37	0.72	0.71	1.00			
Y	-0.31	-0.51	0.48	0.56	-0.38	-0.44	-0.46	-0.21	0.57	0.63	0.19	-0.07	-0.56	-0.30	0.51	0.78	0.37	0.78	0.42	0.19	-0.20	0.82	0.46	0.14	0.41	0.61	0.70	1.00		
Cd	-0.20	-0.68	0.59	0.55	-0.48	-0.60	-0.50	-0.32	0.74	0.85	0.04	-0.01	-0.55	-0.41	0.53	0.92	0.44	0.95	0.46	0.18	-0.26	0.89	0.35	0.33	0.74	0.84	0.90	0.72	1.00	
Hg	-0.31	-0.31	0.44	0.43	-0.41	-0.42	-0.24	-0.40	0.52	0.51	-0.23	0.14	0.04	-0.21	0.24	0.44	0.41	0.41	0.39	0.20	0.08	0.34	0.15	-0.10	0.49	0.51	0.43	0.29	0.46	1.00
	Ca	Ti	Mn	Fe	V	Cr	Co	Ni	Cu	Zn	Rb	Sr	Zr	Nb	Мо	Ag	Sn	Sb	Ва	La	Ce	Pb	Th	U	As	W	Bi	Y	Cd	Hg

smelting and agricultural/gardening activities. Nevertheless, element groupings are very interesting as will be shown below.

1.3.1. DENDROGRAPH OF GARDEN SOIL XRF/AAS ANALYTICAL DATA

The dendrograph (Fig. 1.1) brings out five principal associations of the elements determined by XRF/AAS on the 50 Lavrion garden soil samples subset, *i.e.*,

- (i) Zn-W,
- (ii) Mn-Fe,
- (iii) Pb-Ag,
- (iv) Ni-Cr, and
- (v) Ti-V.

The first three associations are related to soil developed or mixed with smelted ore wastes, and the latter two to lithology (gangue rocks and residual soil). Figure 1.2 shows diagrammatically the relationships of the principal clusters or groups with the other elements, and should be studied in conjunction with its corresponding dendrograph (Fig. 1.1).

The first two clusters of elements (A and B) are related to soil developed on wastes of smelted polymetallic ore. Clusters A1 and A2 appear to be associated with soil



Fig. 1.1. Dendrograph of Spearman rank correlation coefficients of elements determined by XRF and AAS on garden soil samples (n=50), Lavrion.

Σχ. 1.1. Δενδρογράφημα των συντελεστών συσχέτισης τάξεων του Spearman των στοιχείων που προσδιορίστηκαν με φασματομετρία ακτίνων-Χ και ατομική απορρόφηση στα δείγματα εδάφους από κήπους σπιτιών (n=50) του Λαυρίου.



Fig. 1.2. Schematic grouping of elements determined by XRF and AAS (refer to Fig. 1.1 and Table 1.6).

Σχ. 1.2. Σχηματική ομαδοποίηση των στοιχείων που προσδιορίστηκαν με φασματομετρία ακτίνων-Χ και ατομική απορρόφηση (βλέπε Σχ. 1.1). developed on wastes of skarn type smelted ore. Even tungsten minerals occur in the Lavrion mineralisation, such as scheelite (CaWO₄), cuproscheelite [(Cu,Ca)WO₄] and sanmartinite [(Zn,Fe,Ca,Mn)WO₄] (Marinos and Petrascheck, 1956).

Cluster B1 is, of course, related to the Mn-Fe mineralisation of the area, which is associated with cluster "A" elements, and in this case soil developed on or mixed with such wastes. Cluster AB1 elements in garden soil are related to the smelted hydrothermal ore wastes of the area, and are correlated to clusters A and B. Tin is also a common trace constituent of galena, sphalerite, pyrite and chalcopyrite (Table 1.7).

Clusters C1 and C2 show an association peculiar to soil developed or mixed with wastes of smelted hydrothermal sulphide ore. The dendrograph brings out fairly well the argentiferous galena relationship (cluster C1).

The complex polymetallic Lavrion mineralogy is hosted by marble, hence the relationship of clusters A, B and C with Ca (cluster ABC1). Calcium is also a common constituent of soil developed over marble. Hence, this element relationship in soil is explained by the mixing of metallurgical processing wastes rich in calcium with residual soil developed over calcium-rich rocks.

Cluster D elements of the dendrograph bring out the lithophile, gangue mineral wastes, association of Ti-V, as well as that of Ti-Nb, and their relationship with Ce (rare earths). The Ti-V association (cluster D1) is characteristic of soil developed on mafic rocks or their wastes produced during flotation/beneficiation of ore, whereas Nb-Ce is a rare-earths relationship peculiar to granitic pegmatites or their wastes.

The cluster E element relationship points to a lithophile association of these elements, *i.e.*, metamorphosed mafic rocks, *etc.*, and the granodioritic batholith and its porphyry apophyses or their wastes. The Ni-Cr-Co relationship, peculiar to soil developed on mafic rocks, is distally related to soil developed on acid intrusives, Rb-Zr association, through differentiation of mafic magma, a feature shown fairly well by the dendrograph; in this case, the interpretation is soil developed on schist or mafic rocks (prasinite) or on wastes of gangue material produced during flotation/beneficiation of ore.

The lithophile cluster D and E elements are related as shown by the tie line at a lower correlation level.

Finally, at a still lower correlation level the elements associated with soil developed or mixed with the wastes of the smelter ore and floated gangue/host rocks, *i.e.*, mineralisation and host lithology, are joined.

The dendrograph brings out fairly well the strong element relationships of soil, which has been developed, or strongly influenced, by the wastes of different types of beneficiated and smelted ore that has been processed in the Lavrion metallurgical plants (Marinos and Petrascheck, 1956; IGME Working Group, 1987; Demetriades *et al.*, 1994, 1996).

Table 1.7. Summary of selected trace and minor element contents of galena, sphalerite, chalcopyrite, pyrite, pyrrhotite and arsenopyrite, arranged in decreasing order of relative frequency of occurrence within each mineral (from Levinson, 1974, Table 2.5, p.67). All values in ppm, except where indicated.

Πίνακας 1.7. Συνοπτικός πίνακας επιλεγμένων ίχνο- και ολιγο-στοιχείων, που περιέχονται στο γαληνίτη, σφαλερίτη, χαλκοπυρίτη, πυρίτη, μαγνητοπυρίτη και αρσενοπυρίτη, τα οποία είναι ταξινομημένα σε φθίνουσα σειρά ανάλογα με τη σχετική συχνότητά τους σε κάθε ορυκτό. Όλες οι συγκεντρώσεις είναι σε ppm, εκτός όπου υποδεικνύεται διαφορετικά.

Mineral /	Maximum	Most com	mon range	Total No	Relative	Mineral /	Maximum	Most com	mon range	Total No	Relative
Element	content	rar	nge	of samples	frequency	Element	content	ra	nge	of samples	frequency
		(when p	oresent)	, considered	of occurrence			(when	present)	, considered	of occurrence
		Minimum	Maximum		(%)			Minimum	Maximum		(%)
Galena (P	bS)					Pyrrhotite	(Fe _{1-X} S)				
Ag	3%	500	5000	233	94	Ag	100		<10	20	70
As	1%	200	5000	229	22	Co	8500	200	500	252	65
Bi	5%	200	5000	327	62	Cu	7000	100	200	26	100
Cu	3000	10	200	51	96	Mn	3000	200	500	155	88
Fe	5000	10	50	89	43	Ni	7.47%	50	500	244	96
Mn	2000	10	50	90	41	Se	63	10	50	20	100
Ni	100	10	50	40	38						
Sb	3%	200	5000	224	84						
Sn	1300	< 10	50	338	24						
ТΙ	1000	< 10	50	148	36						
Sphalerite	e (ZnS)					Pyrite (Fe	S ₂)				
Ag	1%	10	100	448	84	Ag	200		<10	73	47
As	1%	200	500	235	25	As	~5%	500	1000	99	67
Bi	1000	10	50	186	22	Bi	100	10	50	17	35
Cd	4.40%	1000	5000	921	100	Co	>2.5%	200	5000	1094	86
Co	3000	10	100	413	49	Cu	~6%	10	1%	785	87
Cu	5%	1000	5000	297	80	Mn	1%	10	50	927	54
Ga	3000	10	200	962	66	Ni	~2.5%	10	500	1055	89
Ge	5000	50	200	959	48	Pb	5000	200	500	24	79
Hg	1%	10	50	225	37	Sb	700	100	200	35	23
In	1%	10	50	938	52	Se	300	10	50	115	97
Mn	5.40%	1000	5000	652	87	Sn	400	10	50	18	39
Ni	300	10	50	211	33	Ti	600	200	500	21	67
Sb	3%	10	50	197	24	ТΙ	100	50	100	17	35
Se	900		< 10	41	100	V	~1000	10	50	17	83
Sn	1%	100	200	585	40	Zn	~4.5%	1000	5000	722	36
ТІ	5000	10	50	310	25						
0											
Chaicopy	rite (CureS ₂)				Arsenopy	ite (FeAsS)			
Ag	2300	10	1000	8	100	Со	3.36%	1000	5000	54	87
Co	2000	10	50	88	38	Mn	3000	10	50	40	98
lin 	1000	<10	100	33	60	Ni	3000	200	500	54	85
Mn	2%	10	50	36	17						
Ni	2000	10	50	85	54						
Se	2100	10	50	43	100						
Sn	770	10	200	10	90						

1.3.2. DENDROGRAPH OF GARDEN SOIL ICP-AES ANALYTICAL DATA

The dendrograph (Fig. 1.3) brings out seven principal associations of the elements determined by ICP-AES on a ten garden soil sample subset, *i.e.*,

- (i) Zn-Cu,
- (ii) Pb-Ag,
- (iii) Mo-Fe,

Table 1.8. Spearman rank correlation coefficients of aqua regia extractable elements determined by ICP-AES on garden soil samples (n=50), Lavrion. Πίνακας 1.8. Συντελεστές συσχέτισης τάξεων του Spearman των στοιχείων που εκχυλίστηκαν με

βασιλικό νερό και προσδιορίστηκαν με συσκευή πλάσματος σε δείγματα εδάφους από κήπους σπιτιών (n=10) του Λαυρίου.

	Sr	Cd	Ва	SI	Mn	⊦e	Р	S	В	Mg	V	Na	MO	AI	Ве	Ca	Zn	Cu	Pb	LI	Zr	Co	NI	Sc	Ŷ	La	ĸ	Cr	As	Ag	11
Sr	1.00																														
Cd	0.35	1.00																													
Ва	-0.15	-0.36	1.00																												
Si	-0.33	-0.08	0.23	1.00																											
Mn	0.06	0.73	-0.68	-0.15	1.00																										
Fe	0.43	0.78	-0.59	-0.22	0.81	1.00																									
Ρ	-0.01	-0.54	0.52	-0.43	-0.68	-0.66	1.00																								
S	0.45	0.89	-0.48	-0.09	0.70	0.82	-0.67	1.00																							
В	0.25	0.47	-0.06	0.24	0.32	0.69	-0.57	0.49	1.00																						
Mg	0.05	-0.48	0.84	0.05	-0.70	-0.43	0.48	-0.39	0.12	1.00																					
V	0.50	-0.04	-0.11	-0.26	0.04	0.35	-0.19	0.05	0.36	0.08	1.00																				
Na	0.62	0.22	0.24	0.09	-0.15	0.18	-0.19	0.30	0.44	0.31	0.62	1.00																			
Мо	0.49	0.77	-0.40	-0.25	0.73	0.94	-0.55	0.73	0.74	-0.28	0.47	0.38	1.00																		
Al	0.47	-0.09	0.41	-0.13	-0.36	0.12	0.15	-0.05	0.30	0.49	0.60	0.43	0.16	1.00																	
Be	0.67	0.32	-0.35	-0.30	0.25	0.58	-0.27	0.35	0.32	-0.28	0.79	0.44	0.58	0.62	1.00																
Са	-0.35	-0.43	0.38	0.28	-0.36	-0.77	0.27	-0.41	-0.69	0.19	-0.42	-0.08	-0.71	-0.43	-0.64	1.00															
Zn	0.38	0.92	-0.51	-0.12	0.85	0.90	-0.62	0.89	0.58	-0.45	0.02	0.13	0.87	-0.15	0.30	-0.52	1.00														
Cu	0.33	0.90	-0.54	-0.03	0.88	0.85	-0.67	0.88	0.52	-0.52	-0.03	0.12	0.82	-0.26	0.24	-0.41	0.99	1.00													
Pb	0.21	0.85	-0.15	0.14	0.70	0.78	-0.70	0.83	0.73	-0.16	0.05	0.32	0.81	-0.01	0.18	-0.39	0.88	0.87	1.00												
Li	0.67	0.05	-0.02	-0.50	-0.67	0.36	0.03	0.16	0.27	0.18	0.88	0.58	0.43	0.78	0.84	-0.52	0.04	-0.05	0.03	1.00											
Zr	0.54	0.69	-0.43	0.03	0.68	0.85	-0.77	0.78	0.71	-0.29	0.52	0.56	0.89	0.12	0.58	-0.47	0.80	0.80	0.80	0.39	1.00										
Co	0.57	0.52	-0.36	-0.12	0.44	0.77	-0.58	0.62	0.78	-0.12	0.70	0.68	0.85	0.25	0.62	-0.61	0.61	0.58	0.62	0.59	0.90	1.00									
Ni	-0.04	-0.20	0.18	-0.27	-0.10	0.01	0.32	-0.08	0.15	0.53	-0.28	-0.28	-0.01	-0.07	-0.47	-0.10	0.05	-0.01	0.02	-0.16	-0.19	-0.09	1.00								
Sc	0.32	-0.09	-0.09	0.20	0.02	0.08	-0.35	-0.03	0.21	-0.07	0.78	0.68	0.24	0.21	0.52	0.04	-0.08	-0.03	0.02	0.47	0.50	0.55	-0.56	1.00							
Y	0.40	0.41	-0.24	-0.02	0.42	0.68	-0.58	0.41	0.71	-0.16	0.83	0.60	0.78	0.44	0.77	-0.61	0.44	0.41	0.53	0.66	0.81	0.87	-0.37	0.68	1.00						
La	0.54	0.65	-0.36	0.05	0.54	0.71	-0.62	0.67	0.69	-0.25	0.49	0.68	0.83	-0.01	0.47	-0.40	0.71	0.72	0.71	0.32	0.92	0.92	-0.20	0.56	0.76	1.00					
K	0.36	-0.21	0.65	-0.02	-0.54	-0.04	0.28	-0.18	0.40	0.78	0.44	0.47	0.07	0.90	0.31	-0.32	-0.24	-0.35	-0.01	0.60	0.01	0.20	0.22	0.10	0.28	-0.03	1.00				
Cr	-0.11	-0.62	0.73	-0.16	-0.71	-0.54	0.64	-0.52	-0.12	0.93	-0.02	0.08	-0.43	0.31	-0.42	0.26	-0.58	-0.64	-0.37	0.10	-0.50	-0.27	0.64	-0.21	-0.36	-0.44	0.60	1.00			
As	0.22	0.80	-0.73	-0.35	0.87	0.90	-0.58	0.81	0.45	-0.63	0.11	-0.02	0.81	-0.24	0.35	-0.61	0.88	0.85	0.68	0.13	0.68	0.61	0.00	-0.09	0.45	0.60	-0.39	-0.60	1.00		
Ag	0.21	0.85	-0.25	0.19	0.74	0.84	-0.74	0.80	0.72	-0.30	0.06	0.16	0.80	0.09	0.32	-0.52	-0.80	0.86	0.94	0.05	0.77	0.55	-0.07	-0.02	0.55	0.61	0.00	-0.52	0.69	1.00	
Ti	0.27	-0.39	0.25	-0.04	-0.31	-0.02	0.08	-0.35	0.15	0.33	0.77	0.31	0.04	0.83	0.62	-0.27	-0.36	-0.42	-0.25	0.72	0.08	0.20	-0.21	0.53	0.52	-0.04	0.68	0.21	-0.36	-0.12	1.00
	Sr	Cd	Ba	Si	Mn	Fe	Р	S	В	Ma	V	Na	Mo	AI	Be	Ca	Zn	Cu	Pb	Li	Zr	Co	Ni	Sc	Y	La	K	Cr	As	Aa	Ti

- (iv) La-Zr,
- (v) Al-K,
- (vi) Li-V, and
- (vii) Cr-Mg.

The first four associations are related to soil developed on or mixed with the wastes of the smelted polymetallic ore, and the latter three to lithology (gangue material and local residual soil). Figure 1.4 shows diagrammatically the relationship of the principal clusters with other elements, and should be studied in conjunction with the dendrograph (Fig. 1.3). Although the relationships shown by the dendrograph are interpretable, they are not going to be discussed further, for they are based on only ten samples.



Fig. 1.3. Dendrograph of Spearman rank correlation coefficients of aqua regia extractable elements determined by ICP-AES on garden soil samples (n=10), Lavrion. Σχ. 1.3. Δενδρογράφημα των συντελεστών συσχέτισης τάξεων του Spearman των στοιχείων που εκχυλίστηκαν με βασιλικό νερό και προσδιορίστηκαν με συσκευή πλάσματος σε δείγματα από κήπους σπιτιών (n=10) του Λαυρίου.



Fig. 1.4. Schematic grouping of elements, extracted by aqua regia and determined by ICP-AES (refer to Fig. 1.3 and Table 1.8).

Σχ. 1.4. Σχηματική ομαδοποίηση των στοιχείων, που εκχυλίστηκαν με βασιλικό νερό και προσδιορίστηκαν με φασματόμετρο πλάσματος (βλέπε Σχ. 1.3 και Πίνακα 1.8).

1.4. FACTOR ANALYSIS ON GARDEN SOIL GEOCHEMICAL DATA

R-mode factor analysis (Goddard and Kirby, 1976; Jöreskog *et al.*, 1976; Miesch, 1990) was used to obtain inter-element relationships and factors controlling soil contamination by smelting activities. Since, geochemical data are generally positively skewed, the analytical results were log-transformed (natural logarithms) and a constant introduced for the correction of skewness. In Table 1.9 the eigenvalues of the log-transformed data are tabulated. The first six factors, which have eigenvalues >1.0, account for 85.4% of total variability. Cattel's scree plot shows a sharp change at factor 4. Hence, a four-factor model was initially chosen, but there were no strong factor loadings on any of the elements of factor 4. So, a three-factor Varimax model was finally selected, accounting for 72.9% of total data variability.

Table 1.9. Eigenvalues of the first ten factors of the principal component model on the fifty garden soil sample subset, percentage variance explained by each factor and cumulative percentage variance, Lavrion.

Πίνακας 1.9. Τιμές «eigen» των δέκα πρώτων παραγόντων του μοντέλου κύριων συνιστώσων για την υπο-ομάδα των πενήντα δειγμάτων κηπευτικού εδάφους, ποσοστιαία μεταβλητότητα ερμηνευομένη από κάθε παράγοντα και ποσοστιαία αθροιστική μεταβλητότητα, Λαύριο.

Factor	Eigenvalue	Variance explained by factor	Cumulative variance	
		(%)	(%)	
1	13.86	47.81	47.81	
2	4.42	15.23	63.04	
3	2.85	9.83	72.87	
4	1.43	4.94	77.81	
5	1.19	4.10	81.91	
6	1.01	3.48	85.39	
7	0.74	2.56	87.95	
8	0.60	2.09	90.04	
9	0.53	1.81	91.85	
10	0.44	1.51	93.36	

Element associations of the 3-factor model, with weak (0.3-0.45), moderate (0.45-0.6) and strong (>0.6) Varimax factor loadings, are given below (refer to Table 1.10):

Factor 1:- (>0		Sb, Pb, Ag, Cd, Bi, Y, W, Zn;
	(0.45-0.6):	As, Cu, Mn, Fe;
	(0.3-0.45):	Th, Mo, Rb, U, Sn, Ba.
Factor 2:-	(>0.6):	Rb, Ce, La, V, Nb, Ti, Co;
	(0.45-0.6):	Ni, Cr.
Factor 3:-	(>0.6):	Ba, Fe, Cu, Mn, Sr, Zn, As, W, Sn;
	(0.45-0.6):	Mo, La;
	(0.3-0.45):	Cd, Pb, Ag, Bi.

Table 1.10. Varimax loadings for the three strongest factors of the fifty garden soil geochemical data subset. Correlation between varimax scores and transformed data.

[Strong positive loadings (>0.6) are shown by bold numbers, and the strong negative loading of Ca (<-0.6) in Varimax 2 is italicised].

Πίνακας 1.10. Φορτία «Varimax» για τους τρεις ισχυρότερους παράγοντες της υπο-ομάδας των 50 δειγμάτων κηπευτικού εδάφους. Συσχέτιση μεταξύ των φορτίων varimax και των μετασχηματισθέντων δεδομένων.

[Με έντονη γραφή: ισχυρά θετικά φορτία (>0.6). Με πλάγια γραφή: ισχυρό αρνητικό φορτίο (<-0.6) του Ca στο δεύτερο φορτίο «varimax»].

Element	Varlmax loadings			
	Factor 1	Factor 2	Factor 3	
Ag	0.897	-0.211	0.280	
As	0.521	-0.166	0.665	
Ва	0.266	0.048	0.879	
Bi	0.859	-0.066	0.263	
Са	-0.268	-0.752	-0.378	
Cd	0.874	-0.146	0.312	
Ce	-0.257	0.799	0.162	
Со	-0.348	0.667	-0.506	
Cr	-0.397	0.537	-0.514	
Cu	0.508	-0.058	0.820	
Fe	0.468	0.094	0.821	
La	0.124	0.725	0.487	
Mn	0.503	0.038	0.759	
Мо	0.413	-0.121	0.514	
Nb	-0.280	0.685	-0.302	
Ni	-0.034	0.543	-0.576	
Pb	0.916	-0.121	0.306	
Rb	0.341	0.800	-0.377	
Sb	0.932	-0.140	0.254	
Sn	0.275	-0.161	0.598	
Sr	-0.303	-0.124	0.748	
Th	0.430	0.216	0.089	
Ti	-0.483	0.680	-0.456	
U	0.294	-0.217	0.170	
V	-0.376	0.702	-0.251	
W	0.688	-0.180	0.632	
Y	0.815	-0.009	0.116	
Zn	0.662	-0.151	0.691	
Zr	-0.464	0.243	-0.037	
Eigenvalue	13.86	4.42	2.85	
Variance explained	47 81%	15 23%	9 83%	
by factor	47.0170	10.2070	0.0070	
Cumulative variance	47.81%	63.04%	72.87%	

Factors 1 and 3 account for 47.8% and 9.8% of total variance, and as indicated by their different element associations, describe different types of soil contamination by the smelter activities (Table 1.10). Whereas factor 2 accounts for 15.2% of total variability, and since the associated elements are classified as lithophile, it is related to garden soil with a strong lithological component. A distinction between felsic (Rb, Ce, La, Nb) and mafic (V, Ti, Co) affiliated elements cannot, however, be made for factor loadings >0.6. Elements such as Ni and Cr with moderate (0.45-6) factor loadings are associated with garden soil developed either over schist and mafic rocks occurring in the area, or over metallurgical processing wastes rich in these two elements.

It is interesting to note the strong negative loading of Ca on factor 2 (Table 1.10), which indicate that this particular element association is related to garden soil developed on the non-carbonate lithology of Lavrion, *i.e.*, the felsic and mafic rocks (schist and prasinite – a metamorphosed mafic rock), or on metallurgical processing wastes depleted in calcium.

1.5. DISCUSSION AND CONCLUSIONS

Lavrion garden soil samples, as has been described above, are highly contaminated, and most toxic elements are well above normal global soil median or mean values, as indicated by the estimated enrichment or contamination index (elements arranged in decreasing order), *i.e.*,

Cd> Pb> Zn> As> Ag> Sb> W> S> Cu> Bi> Ca> Mn> Ni> B> P> Ce> Mo> U> Hg> Cr> Mg> Sn> Fe> Sr> Ba> Rb> Co

Lavrion garden soil is extremely contaminated with respect to Cd (Contamination Index, CI: 1425.7), followed by Pb (CI: 550.6), Zn (CI: 277.8), As (CI: 221.3), Ag (CI: 218.8), Sb (CI: 95.7), W (CI: 33.1), Cu (CI: 16.6) and Bi (CI: 16.1). The remaining elements (Ca, Mn, Ni, B, P, Ce, Mo, U, Hg, Cr, Mg, Sn, Fe, Sr, Ba, Rb and Co) have contamination indices <10. Most of these elements are associated with the polymetallic sulphide ore, which was processed at the Lavrion metallurgical processing plants. It is concluded, therefore, that the smelting of polymetallic sulphide ore, and the wastes generated, are responsible for the multi-element contamination of the studied garden soil samples.

Garden soil is apparently depleted with respect to the following elements, which are arranged in order of the most to the less depleted element, *i.e.*,

K< Si< Zr< Na< Be< Ti< Al< Y< Nb< La< Li< Th< Sc< V

Cluster and factor analyses, performed on the multi-element data set of garden soil samples, were able to distinguish elements related to the smelting activities and to lithology or waste rocks.

This preliminary multi-element geochemical desk assessment of garden soil contamination in Lavrion has shown that the individual particle characterisation study should include the following elements: As, Ba, Ca, Cd, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Si, Ti and Zn (refer to Appendix Report 2 in this Volume). Aluminium and Cl were also included in the suite of twenty-five elements that can be determined simultaneously by the individual particle characterisation technique. The former, together with other lithophile elements, will be able to characterise particles derived from the weathering of rocks and residual uncontaminated soil, whereas the latter is significant for in Lavrion there occur minerals containing Cl, such as atacamite [Cu²⁺₂Cl(OH)₃], chlorargyrite [AgCl], georgiadesite [Pb₁₆(AsO₄)₄Cl₁₄O₂(OH)₂, halite [NaCl], lavendulan [(Na,Ca)₂Cu²⁺₅(AsO₄)Cl.5H₂O], matlokite [Pb₂OCl₂], mimetite [Pb₄(AsO₄)₃Cl], phosgenite [Pb₂CO₃Cl₂], *etc.* (Marinos and Petrascheck, 1956; Vourlakos, 1992; Katerinopoulos and Zissimopoulou, 1994).

This study, apart from selecting the elements to be determined by the individual particle characterisation study, has shown that garden soil is not only contaminated by As, Cd, Cu, Fe, Hg, Pb and Zn, which were analysed during the first urban geochemical study carried out in Lavrion by Hadjigeorgiou-Stavrakis and Vergou-Vichou (1992), but also by Ag, Sb, W, Bi, Ca, Mn, Ni, B, P, Ce, Mo, U, Cr, Mg, Sn, Sr, Ba, Rb and Co. Hence, soil contamination is more complex than was first anticipated by the 1992 study.

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Appendix Report 2

INDIVIDUAL PARTICLE ANALYSIS OF METALLURGICAL WASTES, OVERBURDEN AND HOUSEHOLD DUST FROM THE TOWN OF LAVRION, GREECE

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2.1. INTRODUCTION

Detailed mapping and geochemical surveys in the Lavrion urban area have provided invaluable data on the extent and severity of contamination. Metallurgical processing wastes have been widely distributed around the town by wind and water, as well as by human activity. The wastes have been extensively used for building roads and harbour structures. Dumps have frequently been built on. Altogether, there is an extremely intimate relationship between the smelter waste and the human population.

A number studies in other mining and smelting areas have demonstrated that lead and arsenic bioavailability may be reduced compared to soluble arsenic or urban lead sources (Cotter-Howells and Thornton, 1991, Davis *et al.*, 1993; Ruby *et al.*, 1994). A more recent study (Gasser *et al.*, 1996) found, in contrast, that mine waste impacted solids often readily release lead under simulated gastric conditions. It is, therefore, important to begin to study the chemical, mineralogical and physical forms of the metallic contaminants. To this end, a large number of sequential leaching analyses have been undertaken. The sequential extraction work has given insights into the solubility and availability on 22 chemical elements (refer to Chapters 7 and 8 in Volume 1 of this report). Bulk analysis, however, gives average results for all particles in a sample. Conventional analyses of the bulk sample, therefore, represent average values for many particles measured together and, thus, cannot provide information on the relative contribution of different emissions.

Microscopy based analysis, on the other hand, is very detailed at particle level and allows a high resolution description of the chemical variability across the sample, which may add greatly to the bulk analysis data. Although many microscopy based analytical methods can be considered to be Individual Particle Analysis (IPA) techniques, the term is in this case limited to particle characterisation by Computer Controlled Scanning Electron Microscopy (CCSEM). Specimen mounts are undertaken in such a way that features are separated from each other and may be analysed in isolation [chemical analysis is undertaken by Energy Dispersive X-ray Spectroscopy (EDS)]. The particle-by-particle measurement is computer controlled by linking SEM and EDS through automated image analysis software. By identifying individual particle "types" in a sample, the technique is able to resolve sources with dissimilar emission products at the individual particle level. A trace element may occur in a number of different ways in the specimen, all with different implications. An element, for example, occurring as a trace constituent in every particle in an assemblage, it is different from a trace appearing as a relatively few highly enriched particles, and yet both will give the same results in a bulk analysis.

This study therefore was undertaken to assess the potential of the technique of individual particle analysis (IPA) in the scanning electron microscope (SEM), and in particular to consider the opportunities offered by automated systems using computer control of data acquisition. In general, the analyst uses a series of measurements to build up a "picture" of each particle - in terms of its shape, its composition and its size. Judgements can be made about its origin or about processes that have operated upon it, and it can be given a name (*i.e.*, classified). By repeating this process, a comparison may be made between a population of features.

A detailed description of the techniques is provided in Appendix Report 3 (in this Volume, p.3.1-3.15). Attention is also drawn to Hunt *et al.* (1988a, 1988b, 1991, 1992, 1993), Johnson *et al.* (1985) and Watt (1990).

2.2. OBJECTIVES

The study is a pilot evaluation of the potential of automated electron microscopy to contribute to the understanding of the movement of metalliferous particulate matter and, in particular, to study routes of exposure of the local population. It was, therefore, decided to:

- 1. Undertake a field-sampling programme to gather samples to represent different sources of metals, perhaps associated with different industrial processes.
- 2. To examine the analyses of these materials and establish a classification scheme, which would reflect the different types of metalliferous particles within the samples.
- 3. If successful, to examine a number of overburden/soil and house dust samples to investigate the potential of this scheme for source apportionment.
- 4. To make recommendations for application of this technique, and hopefully of the classification scheme, in studies of human exposure routes.

2.3. SAMPLING

A two-day field-sampling programme was undertaken in the Lavrion area in December 1995. A preliminary evaluation showed that the area is extremely complex to sample with widespread distribution of heterogeneous smelter waste material and large tracts of derelict industrial land including the former smelter and its loading bays. Different parts of the waste dumps did appear to have a number of physical differences between them, and so it was decided that samples would be taken to reflect this heterogeneity. An attempt was made to obtain a sample from every observed textural type (often associated with colour differences), and to cover the important spatial distribution with respect to the smelter and to the local population. Map 2.13 in Volume 2 shows sample locations, and Photos 6-23 the extreme heterogeneity of some of the locations.
Table	2.1.	Concise	description	of sample	sites ar	id samples	from t	the L	avrion	urban	area	(refer
to Map	o 2.13	3 in Volum	າe 2).									

Πίνακας 2.1.	Συνοπτική	περιγραφή	ί των θέσεω	ν δειγματοληψί	ας και τω	ν δειγμάτων	από την	αστική
περιοχή του /	\αυρίου (βλ	Χάρτη 2.	13 στο Τόμα	2).				

Sample Number	Location	Material
LAV 1	Smelter site at Kiprianos	Fine-grained wash-out materials in black
		piles with coarse boulders (<i>pelletised</i> &
		lumpy slag)
LAV 2	Smelter site as for 1	Yellow clayey material
LAV 3	Smelter site as for 1	Brown stained clay
LAV 4	Smelter site as for 1	Brown sand in the face of a slope
LAV 5	Smelter site as for 1	White crust in a sheltered area
LAV 6	Smelter site as for 1	Yellow crust precipitated on a carbonate rock fragment
LAV 7	At the vicinity of smelting buildings at loading bays	Reddish-coloured fine grained material
LAV 8	Location as for 7	Lighter-black coloured materials from loading bays
LAV 9	Location as for 7	Purer reddish coloured material
LAV 10	Location as for 7	Green mineral visible
LAV 11	Smelter installations	Very fine 'ashy' material of light density
LAV 12	Location as for 11	Grey clayey material with green mineral
LAV 13	Area of dumped	Fine sandy material from the
	metalliferous sands	flotation/beneficiation residues
LAV 14	Another nearby dump	Fine sandy material from the
		flotation/beneficiation residues
LAV 15	Deposited slag waste	Distinctive fly ash layer (spheres visible
	close to harbour	under hand lens) within a slag heap
LAV 16	Beach	Pyritiferous sand
LAV 17	Beach	Fine-grained yellow clay material from the pyritiferous tailings
LAV 18	Main dump area of sand-	Very black fine-grained sand-blast
	blast material	material, not spherical under hand lens
LAV 19	Main dump area	Reddish clayey material from the oxidised pyritiferous tailings
LAV 20	Main dump area of	Dark pile with yellow crystal growth on
	pyritiferous wastes	surface from the oxidised pyritiferous
	NA - in allowers of the	tallings
LAV 21	Iviain dump area of	Purple-red pile with grey-white crystal
	pyritiferous wastes	growin from the oxidised pyritiferous
		laiings

2.4. INDIVIDUAL PARTICLE ANALYSIS

Dusts and soils were disaggregated, sieved to <20 μ m, suspended in absolute alcohol and filtered onto a surface filter, which was then mounted onto a glass slide with conducting carbon paint. All samples were coated with carbon.

Analyses were performed at an accelerating voltage of 25 kV, a beam current of 2nA and a 5s-acquisition time per particle. A relatively high backscattered electron image was used to specifically target the high atomic number metalliferous particles, in order to rapidly gain sufficient data for development of a source signature database.

This was accomplished by obtaining to begin with a backscattered electron image from particles of lead metal, iron oxide (Fe_3O_4) and rutile (TiO_2) respectively. Then the threshold was adjusted so that the rutile particles were disregarded, but the lead and iron oxide (and, therefore, anything with a mean atomic number in between) remained visible.

Data correction was accomplished using a specially created window file (see below).

2.4.1. WINDOW FILE DEVELOPMENT

Preliminary manual analysis, experience from the reconnaissance survey, and consideration of human health implications, were used to define the list of elements for analysis. This is given in Table 2.2, together with the correction factors obtained. A description of how these were developed is given in Annex A1 at the end of this chapter. Such information is useful in understanding complex overlaps, in the case a researcher is interested in studying the individual sample data with the MIDAS software (Watt, 1990).

Element	Window	Background	Background Window	Overlap Eactor	Overlap Window	Efficiency Eactor
Na	1	0.48	8	0 4600	20	1
Mg	2	1.00	8	10.0000	23	1
AI	3	1.44	8	0.2988	25	1
Si	4	2.00	8	0.1285	22	1
Р	5	0.84	8	0.4576	22	1
S	6	1.17	8	5.9650	22	1
CI	7	1.15	8	0.2808	22	1
Cd	9	1.00	8	0.0664	12	1
К	10	1.02	8	0.5542	9	1
Ca	11	1.01	8	0.0535	10	1
Sb	12	0.87	8	0	0	1
Ti	13	0.78	8	0	0	1
Ва	14	0.64	8	0	0	1
Mn	15	3.20	21	0	0	1
Fe	16	2.26	21	0.0884	15	1
Ni	18	1.58	21	0.0061	19	1
Cu	19	1.47	21	0.0185	18	1
Zn	20	1.60	21	0.0048	19	1
Pb	22	0.94	21	6.6878	23	1
As	23	0.79	21	0	0	1
Мо	25	0.86	24	0	0	1

Table 2.2. Lavrion window file for the correction of Individual Particle Analysis data. Πίνακας 2.2. Παραθυρικό αρχείο Λαυρίου για τη διόρθωση των δεδομένων της ανάλυσης χαρακτηρισμού σωματιδίων.

2.4.2. CLASSIFICATION

A customised classification scheme was developed for the Lavrion source samples. The method is described in Appendix Report 3 (in this Volume, p.3.0-3.14), and the scheme presented in Annex 3.1 of this report (p.3.13-3.14). Table 2.3 shows a summary of the families in the scheme.

Γιίνακας Ζ.δ. Ζχημα ταςινομησης των σωματιοίων	από τις διαφορές πηγές ρυττανότις στο Λαυρίο.		
Family Name	Number of Groups		
Fe and S	4		
Fe/Ca/Si/Zn	1		
Fe +	2		
Pb +	4		
Zn +	4		
As Bearing	1		
HiSb	1		
Contain V	1		
Ca +	5		
Al/Si +	1		

 Table 2.3. Classification scheme for Lavrion source particles.

 Πίνανας 2.3. Σχήμα ταξιγόμησης των συματιδίων από τις διάφορες πργές ούπαγαρς στο Δαύριο

2.5. INDIVIDUAL PARTICLE ANALYSIS RESULTS

The classification results for each sample individually is described and discussed in this section. Results are presented for a total of 35,517 particles (23,399 source particles and 12,118 from the slag, overburden and house dust samples).

Figures 2.1 to 2.21 show the percentage distribution of 24 groups, as well as the proportion of unclassified particles from the metallurgical processing wastes, the so called contamination source samples (refer to Map 2.13 in Volume 2 for sample location). Below each figure there is a table with Group name, Family name, Group number (shown in figure), Count (number of particles), and the Percentage proportion out of the total number of particles measured in each sample. The dominant families of particles are highlighted and mentioned in the figure caption.

Figures 2.22 to 2.31 show the particle characterisation of overburden/garden soil and house dust samples, and figures 2.32 to 2.35 compare the results of garden soil with their corresponding house dust or slag samples. For sample locations of overburden/garden soil and house dust refer to Maps 2.9 and 2.10 in Volume 2 of this report.



Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	223	5.58
Pyr 1	Fe and S	1	963	24.08
Pyr 2	Fe and S	2	1	0.03
Pyr 3	Fe and S	3	16	0.4
Pyr 4	Fe and S	4	46	1.15
FeCaSiZn	Fe/Ca/Si/Zn	5	151	3.78
Fe rich	Fe+	6	220	5.5
Fe 20-80	Fe+	7	678	16.95
PbCl	Pb+	8	0	0
PbS	Pb+	9	66	1.65
Pb>60%	Pb+	10	46	1.15
Intermed Pb	Pb+	11	63	1.58
ZnSiFe	Zn+	12	339	8.48
Mn/Zn	Zn+	13	55	1.38
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	372	9.3
As bearing	As bearing	16	144	3.6
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	51	1.28
CaS + Fe	Ca+	20	23	0.58
CaP	Ca +	21	1	0.03
Ca only	Ca+	22	62	1.55
Intermed Ca	Ca+	23	80	2
Al/Si+	Al/Si+	24	400	10
Total number of	particles examined:		4000	

Fig. 2.1. Sample LAV-1: Fine-grained washout material in black piles with boulders (*pelletised* & *lumpy slag*) from smelter area at Kiprianos. The sample is apparently rich in Fe, S, AI, Si, Zn, Ca and As, with minor Pb.

Σχ. 2.1. Δείγμα LAV-1: Λεπτόκοκκο ξεπλυμμένο υλικό σε μαύρους σωρούς με ογκόλιθους (συσφαιρώματα & πλινθώματα σκουριάς) από την περιοχή του εργοστασίου εμπλουτισμού στον Κυπριανό. Το δείγμα είναι εμφανώς πλούσιο σε Fe, S, Si, Al, Zn, Ca και As με μικρό ποσοστό Pb.



Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	0	0
Pyr 1	Fe and S	1	118	18.64
Pyr 2	Fe and S	2	0	0
Pyr 3	Fe and S	3	0	0
Pyr 4	Fe and S	4	4	0.63
FeCaSiZn	Fe/Ca/Si/Zn	5	0	0
Fe rich	Fe+	6	10	1.58
Fe 20-80	Fe+	7	13	2.05
PbCl	Pb+	8	0	0
PbS	Pb+	9	0	0
Pb>60%	Pb+	10	0	0
Intermed Pb	Pb+	11	0	0
ZnSiFe	Zn+	12	0	0
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	0	0
As bearing	As bearing	16	0	0
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	371	58.61
CaS + Fe	Ca+	20	113	17.85
CaP	Ca +	21	0	0
Ca only	Ca+	22	0	0
Intermed Ca	Ca+	23	0	0
Al/Si+	Al/Si+	24	4	0.63
Total number of	particles examined:		300	

Fig. 2.2. Sample LAV-2: Yellow clayey material from the smelter area at Kiprianos. The sample is rich in Ca, Fe and S.

Σχ. 2.2. Δείγμα LAV-2: Κίτρινο αργιλούχο υλικό από την περιοχή του εργοστασίου εμπλουτισμού στον Κυπριανό. Το δείγμα είναι πλούσιο σε Ca, Fe και S.



Name	Family	Group	Count	Percent		
Unclassified	Unclassified	0	2	0.49		
Pyr 1	Fe and S	1	203	49.88		
Pyr 2	Fe and S	2	0	0		
Pyr 3	Fe and S	3	0	0		
Pyr 4	Fe and S	4	8	1.97		
FeCaSiZn	Fe/Ca/Si/Zn	5	0	0		
Fe rich	Fe+	6	70	17.2		
Fe 20-80	Fe+	7	108	26.54		
PbCl	Pb+	8	0	0		
PbS	Pb+	9	0	0		
Pb>60%	Pb+	10	0	0		
Intermed Pb	Pb+	11	1	0.25		
ZnSiFe	Zn+	12	0	0		
Mn/Zn	Zn+	13	0	0		
Mn/Zn/S	Zn+	14	0	0		
Fe/Zn+	Zn+	15	0	0		
As bearing	As bearing	16	2	0.49		
Sb rich	High Sb	17	0	0		
V/Na+	Contain V	18	0	0		
CaS	Ca+	19	6	1.47		
CaS + Fe	Ca+	20	0	0		
CaP	Ca +	21	0	0		
Ca only	Ca+	22	0	0		
Intermed Ca	Ca+	23	0	0		
Al/Si+	Al/Si+	24	7	1.72		
Total number of pa	Total number of particles examined: 407					

Fig. 2.3. Sample LAV-3: Brown-stained clayey material from the smelter area at Kiprianos. The sample is rich in Fe and S.

Σχ. 2.3. Δείγμα LAV-3: Αργιλούχο υλικό με ορφνή αποχρωση από την περιοχή του εργοστασίου εμπλουτισμού στον Κυπριανο. Το δείγμα είναι πλούσιο σε Fe και S.



Name	Family	Group	Count	Percent		
Unclassified	Unclassified	0	1	0.21		
Pyr 1	Fe and S	1	363	76.42		
Pyr 2	Fe and S	2	0	0		
Pyr 3	Fe and S	3	2	0.42		
Pyr 4	Fe and S	4	54	11.37		
FeCaSiZn	Fe/Ca/Si/Zn	5	0	0		
Fe rich	Fe+	6	35	7.37		
Fe 20-80	Fe+	7	12	2.53		
PbCl	Pb+	8	0	0		
PbS	Pb+	9	0	0		
Pb>60%	Pb+	10	0	0		
Intermed Pb	Pb+	11	0	0		
ZnSiFe	Zn+	12	0	0		
Mn/Zn	Zn+	13	0	0		
Mn/Zn/S	Zn+	14	0	0		
Fe/Zn+	Zn+	15	0	0		
As bearing	As bearing	16	3	0.63		
Sb rich	High Sb	17	0	0		
V/Na+	Contain V	18	0	0		
CaS	Ca+	19	5	1.05		
CaS + Fe	Ca+	20	0	0		
CaP	Ca +	21	0	0		
Ca only	Ca+	22	0	0		
Intermed Ca	Ca+	23	0	0		
Al/Si+	Al/Si+	24	0	0		
Total number of p	Total number of particles examined: 475					

Fig. 2.4. Sample LAV-4: Brown sand from the face of a slope within the premises of the smelter at Kiprianos. The sample is rich in Fe and S.

Σχ. 2.4. Δείγμα LAV-4: Ορφνή άμμος από το μέτωπο κλιτύος στην περιοχή του εργοστασίου εμπλουτισμού στον Κυπριανό. Το δείγμα είναι πλούσιο σε Fe και S.



Fig. 2.5. Sample LAV-5: White crust in a sheltered area within the premises of the smelter at Kiprianos. The sample is rich in Fe and S, and contains a minor amount of Zn. Σχ. 2.5. Δείγμα LAV-5: Λευκό επάνθημα από καλυμμένη θέση στο χώρο του εργοστασίου εμπλουτισμού στον Κυπριανό. Το δείγμα είναι πλούσιο σε Fe και S. Περιέχει επίσης μικρές ποσότητες Zn.



Name	Family	Group	Count	Percent	
Unclassified	Unclassified	0	5	0.67	
Pyr 1	Fe and S	1	259	34.58	
Pyr 2	Fe and S	2	0	0	
Pyr 3	Fe and S	3	1	0.13	
Pyr 4	Fe and S	4	8	1.07	
FeCaSiZn	Fe/Ca/Si/Zn	5	3	0.4	
Fe rich	Fe+	6	23	3.07	
Fe 20-80	Fe+	7	53	7.08	
PbCl	Pb+	8	0	0	
PbS	Pb+	9	1	0.13	
Pb>60%	Pb+	10	0	0	
Intermed Pb	Pb+	11	0	0	
ZnSiFe	Zn+	12	0	0	
Mn/Zn	Zn+	13	0	0	
Mn/Zn/S	Zn+	14	0	0	
Fe/Zn+	Zn+	15	2	0.27	
As bearing	As bearing	16	1	0.13	
Sb rich	High Sb	17	0	0	
V/Na+	Contain V	18	0	0	
CaS	Ca+	19	244	32.58	
CaS + Fe	Ca+	20	110	14.69	
CaP	Ca +	21	0	0	
Ca only	Ca+	22	25	3.34	
Intermed Ca	Ca+	23	7	0.93	
Al/Si+	Al/Si+	24	7	0.93	
Total number of particles examined: 749					

Fig. 2.6. Sample LAV-6: Yellow crust precipitated on a carbonate rock fragment from the smelter area at Kiprianos. The sample is rich in Fe, S and Ca. Σχ. 2.6. Δείγμα LAV-6: Κίτρινη επιφλοίωση εναποτεθείσα πάνω σε τεμάχιο ανθρακικού πετρώματος από

το χώρο του εργοστασίου εμπλουτισμού στον Κυπριανό. Το δείγμα είναι πλούσιο σε Fe, S και Ca.



Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	39	1.89
Pyr 1	Fe and S	1	55	2.67
Pyr 2	Fe and S	2	0	0
Pyr 3	Fe and S	3	0	0
Pyr 4	Fe and S	4	0	0
FeCaSiZn	Fe/Ca/Si/Zn	5	0	0
Fe rich	Fe+	6	1850	89.68
Fe 20-80	Fe+	7	43	2.08
PbCl	Pb+	8	0	0
PbS	Pb+	9	0	0
Pb>60%	Pb+	10	0	0
Intermed Pb	Pb+	11	0	0
ZnSiFe	Zn+	12	0	0
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	3	0.15
As bearing	As bearing	16	0	0
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	1	0.05
CaS + Fe	Ca+	20	0	0
CaP	Ca +	21	0	0
Ca only	Ca+	22	0	0
Intermed Ca	Ca+	23	1	0.05
Al/Si+	Al/Si+	24	71	3.44
Total number of	particles examined:		2063	

Fig. 2.7. Sample LAV-7: Reddish-coloured fine-grained material from the loading bays of the

smelter at Kiprianos. The sample is rich in Fe. Σχ. 2.7. Δείγμα LAV-7: Κοκκινωπό λεπτόκοκκο υλικό από τα σιλό φόρτωσης του εργοστασίου εμπλουτισμού στον Κυπριανό. Το δείγμα είναι πλούσιο σε Fe.



Group

Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	26	3.08
Pyr 1	Fe and S	1	394	46.63
Pyr 2	Fe and S	2	0	0
Pyr 3	Fe and S	3	1	0.12
Pyr 4	Fe and S	4	24	2.84
FeCaSiZn	Fe/Ca/Si/Zn	5	1	0.12
Fe rich	Fe+	6	83	9.82
Fe 20-80	Fe+	7	152	17.99
PbCl	Pb+	8	0	0
PbS	Pb+	9	8	0.95
Pb>60%	Pb+	10	0	0
Intermed Pb	Pb+	11	3	0.36
ZnSiFe	Zn+	12	0	0
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	3	0.36
As bearing	As bearing	16	3	0.36
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	0	0
CaS + Fe	Ca+	20	6	0.71
CaP	Ca +	21	1	0.12
Ca only	Ca+	22	0	0
Intermed Ca	Ca+	23	0	0
Al/Si+	Al/Si+	24	140	16.57
Total number of	particles examined:		845	

Fig. 2.8. Sample LAV-8: Lighter-black coloured material from the loading bays of the smelter at Kiprianos. The sample is rich in Fe, S, Al and Si.

Σχ. 2.8. Δείγμα LAV-8: Ανοικτόχρωμο μαύρο υλικό από τα σιλό φόρτωσης του εργοστασίου εμπλουτισμού στον Κυπριανό. Το δείγμα είναι πλούσιο σε Fe, S, Al και Si.



Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	40	2.92
Pyr 1	Fe and S	1	16	1.17
Pyr 2	Fe and S	2	0	0
Pyr 3	Fe and S	3	0	0
Pyr 4	Fe and S	4	0	0
FeCaSiZn	Fe/Ca/Si/Zn	5	0	0
Fe rich	Fe+	6	1153	84.1
Fe 20-80	Fe+	7	105	7.66
PbCl	Pb+	8	0	0
PbS	Pb+	9	19	1.39
Pb>60%	Pb+	10	1	0.07
Intermed Pb	Pb+	11	3	0.22
ZnSiFe	Zn+	12	0	0
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	1	0.07
As bearing	As bearing	16	3	0.22
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	0	0
CaS + Fe	Ca+	20	0	0
CaP	Ca +	21	0	0
Ca only	Ca+	22	0	0
Intermed Ca	Ca+	23	2	0.15
Al/Si+	Al/Si+	24	28	2.04
Total number of particles examined: 1371				

Fig. 2.9. Sample LAV-9: Purer reddish coloured material from the loading bays of the smelter at Kiprianos. The sample is rich in Fe, with minor amount of AI, Si and Pb. Σχ. 2.9. Δείγμα LAV-9: Ερυθρό υλικό απο τα σιλό φόρτωσης του εργοστασίου εμπλουτισμού στον Καβοδόκανο. Το δείγμα είναι πλούσιο σε Fe με μικρή ποσότητα AI, Si και Pb.



Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	3	14.29
Pyr 1	Fe and S	1	0	0
Pyr 2	Fe and S	2	0	0
Pyr 3	Fe and S	3	0	0
Pyr 4	Fe and S	4	1	4.76
FeCaSiZn	Fe/Ca/Si/Zn	5	0	0
Fe rich	Fe+	6	6	28.57
Fe 20-80	Fe+	7	2	9.52
PbCl	Pb+	8	0	0
PbS	Pb+	9	0	0
Pb>60%	Pb+	10	2	9.52
Intermed Pb	Pb+	11	0	0
ZnSiFe	Zn+	12	2	9.52
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	2	9.52
As bearing	As bearing	16	0	0
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	0	0
CaS + Fe	Ca+	20	0	0
CaP	Ca +	21	0	0
Ca only	Ca+	22	0	0
Intermed Ca	Ca+	23	2	9.52
Al/Si+	Al/Si+	24	1	4.76
Total number of p	particles examined:		21	

Fig. 2.10. Sample LAV-10: Green mineral from the loading bays of the smelter at Kiprianos. The sample is rich in Fe with a minor amount of Zn, Pb, Ca, Al and Si.

Σχ. 2.10. Δείγμα LAV-10: Πράσινο ορυκτό από τα σιλό φόρτωσης του εργοστασίου εμπλουτισμού στον Κυπριανό. Το δείγμα είναι πλούσιο σε Fe με μικρή ποσότητα Zn, Pb, Ca, Al και Si.



Fig. 2.11. Sample LAV-11: Very fine-grained "ashy" material of light density from the smelter installations at Kiprianos. The sample is very rich in Sb with a minor amount of As. Σχ. 2.11. Δείγμα LAV-11: Πολύ λεπτόκοκκο «τεφρό» ελαφρύ υλικό από τις εγκαταστάσεις του εργοστασίου εμπλουτισμού στον Κυπριανό. Το δείγμα είναι πολύ πλούσιο σε Sb με μικρή ποσότητα As.



Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	15	0.9
Pyr 1	Fe and S	1	0	0
Pyr 2	Fe and S	2	22	1.32
Pyr 3	Fe and S	3	0	0
Pyr 4	Fe and S	4	0	0
FeCaSiZn	Fe/Ca/Si/Zn	5	0	0
Fe rich	Fe+	6	15	0.9
Fe 20-80	Fe+	7	19	1.14
PbCl	Pb+	8	250	14.96
PbS	Pb+	9	338	20.23
Pb>60%	Pb+	10	22	1.32
Intermed Pb	Pb+	11	136	8.14
ZnSiFe	Zn+	12	0	0
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	5	0.3
As bearing	As bearing	16	839	50.21
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	1	0.06
CaS + Fe	Ca+	20	0	0
CaP	Ca +	21	0	0
Ca only	Ca+	22	1	0.06
Intermed Ca	Ca+	23	6	0.36
Al/Si+	Al/Si+	24	2	0.12
Total number of	particles examined:		1671	

Fig. 2.12. Sample LAV-12: Grey clayey material with green mineral from the smelter installations at Kiprianos. The sample is very rich in As and Pb. Σχ. 2.12. Δείγμα LAV-12: Γκρίζο αργιλούχο υλικό με πράσινο ορυκτό από τις εγκαταστάσεις του εργοστασίου εμπλουτισμού στον Κυπριανό. Το δείγμα είναι πολύ πλούσιο σε As και Pb.



Name	Family	Group	Count	Percent	
Unclassified	Unclassified	0	37	3.27	
Pyr 1	Fe and S	1	57	5.04	
Pyr 2	Fe and S	2	1	0.09	
Pyr 3	Fe and S	3	0	0	
Pyr 4	Fe and S	4	0	0	
FeCaSiZn	Fe/Ca/Si/Zn	5	3	0.27	
Fe rich	Fe+	6	168	14.85	
Fe 20-80	Fe+	7	243	21.49	
PbCl	Pb+	8	2	0.18	
PbS	Pb+	9	14	1.24	
Pb>60%	Pb+	10	20	1.77	
Intermed Pb	Pb+	11	26	2.3	
ZnSiFe	Zn+	12	230	20.34	
Mn/Zn	Zn+	13	0	0	
Mn/Zn/S	Zn+	14	0	0	
Fe/Zn+	Zn+	15	9	0.8	
As bearing	As bearing	16	72	6.37	
Sb rich	High Sb	17	0	0	
V/Na+	Contain V	18	0	0	
CaS	Ca+	19	0	0	
CaS + Fe	Ca+	20	0	0	
CaP	Ca +	21	3	0.27	
Ca only	Ca+	22	28	2.48	
Intermed Ca	Ca+	23	35	3.09	
Al/Si+	Al/Si+	24	183	16.18	
Total number of	Total number of particles examined: 1131				

Fig. 2.13. Sample LAV-13: Fine sandy material from the flotation residues at Santorineika. The sample is rich in Fe, Zn, Al and Si with a minor amount of As, Ca and Pb. $\Sigma\chi$. 2.13. $\Delta\epsilon$ ίγμα LAV-13: Λεπτόκοκκο αμμώδες υλικό από τα απορρίμματα εμπλουτισμού στα Σαντορινέϊκα. Το δείγμα είναι πλούσιο σε Fe, Zn, Al και Si με μικρή ποσότητα As, Ca και Pb.



Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	15	2.06
Pyr 1	Fe and S	1	31	4.26
Pyr 2	Fe and S	2	0	0
Pyr 3	Fe and S	3	0	0
Pyr 4	Fe and S	4	0	0
FeCaSiZn	Fe/Ca/Si/Zn	5	3	0.41
Fe rich	Fe+	6	97	13.34
Fe 20-80	Fe+	7	164	22.56
PbCl	Pb+	8	2	0.28
PbS	Pb+	9	10	1.38
Pb>60%	Pb+	10	29	3.99
Intermed Pb	Pb+	11	65	8.94
ZnSiFe	Zn+	12	68	9.35
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	7	0.96
As bearing	As bearing	16	64	8.8
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	0	0
CaS + Fe	Ca+	20	0	0
CaP	Ca +	21	1	0.14
Ca only	Ca+	22	4	0.55
Intermed Ca	Ca+	23	25	3.44
Al/Si+	Al/Si+	24	142	19.53
Total number of	particles examined:		727	

Fig. 2.14. Sample LAV-14: Fine sandy material from the flotation residues at Prasini Alepou. The sample is rich in Fe, Al and Si with a minor amount of Zn, Pb, As and Ca. Σχ. 2.14. Δείγμα LAV-14: Λεπτόκοκκο αμμώδες υλικό από τα απορρίμματα εμπλουτισμού της Πράσινης Αλεπούς. Το δείγμα είναι πλούσιο σε Fe, Al και Si με μικρή ποσότητα Zn, Pb, As και Ca.



Unclassified	Unclassified	0	42	4.47
Pyr 1	Fe and S	1	4	0.43
Pyr 2	Fe and S	2	48	5.11
Pyr 3	Fe and S	3	0	0
Pyr 4	Fe and S	4	2	0.21
FeCaSiZn	Fe/Ca/Si/Zn	5	0	0
Fe rich	Fe+	6	311	33.09
Fe 20-80	Fe+	7	249	26.49
PbCl	Pb+	8	0	0
PbS	Pb+	9	40	4.26
Pb>60%	Pb+	10	0	0
Intermed Pb	Pb+	11	10	1.06
ZnSiFe	Zn+	12	1	0.11
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	0	0
As bearing	As bearing	16	0	0
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	7	0.74
CaS + Fe	Ca+	20	1	0.11
CaP	Ca +	21	17	1.81
Ca only	Ca+	22	0	0
Intermed Ca	Ca+	23	9	0.96
Al/Si+	Al/Si+	24	199	21.17
Total number of particles examined:940				

Fig. 2.15. Sample LAV-15: Distinctive fly ash layer (spheres visible under hand lens) within slag heap close to the Lavrion harbour. The sample is rich in Fe, AI and Si with a minor amount of S and Pb.

Σχ. 2.15. Δείγμα LAV-15: Εμφανές στρώμα ιπτάμενης τέφρας (οι σφαίρες είναι εμφανείς με λούπα) μέσα σε σωρό σκουριών πλησίον του λιμανιού του Λαυρίου. Το δείγμα είναι πλούσιο σε Fe, Al και Si με μικρή ποσότητα S και Pb.



Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	51	1.92
Pyr 1	Fe and S	1	38	1.43
Pyr 2	Fe and S	2	1191	44.94
Pyr 3	Fe and S	3	0	0
Pyr 4	Fe and S	4	42	1.58
FeCaSiZn	Fe/Ca/Si/Zn	5	0	0
Fe rich	Fe+	6	6	0.23
Fe 20-80	Fe+	7	395	14.91
PbCl	Pb+	8	0	0
PbS	Pb+	9	578	21.81
Pb>60%	Pb+	10	0	0
Intermed Pb	Pb+	11	136	5.13
ZnSiFe	Zn+	12	0	0
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	0	0
As bearing	As bearing	16	10	0.38
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	51	1.92
CaS + Fe	Ca+	20	46	1.74
CaP	Ca +	21	0	0
Ca only	Ca+	22	0	0
Intermed Ca	Ca+	23	9	0.34
Al/Si+	AI/Si+	24	97	3.66
Total number of	particles examined:		2650	

Fig. 2.16. Sample LAV-16: Pyritiferous sand from the tailings on the beach at Komobil. The sample is rich in Fe, S and Pb with a minor amount of Al, Si and Ca. $\Sigma \chi$. 2.16. $\Delta \epsilon i \gamma \mu \alpha$ LAV-16: Πυριτούχος άμμος από τα απορρίμματα στην παραλία της Κομομπίλ. Το δείγμα είναι πλούσιο σε Fe, S και Pb με μικρή ποσότητα Al, Si και Ca.



Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	11	0.77
Pyr 1	Fe and S	1	12	0.84
Pyr 2	Fe and S	2	812	56.51
Pyr 3	Fe and S	3	1	0.07
Pyr 4	Fe and S	4	70	4.87
FeCaSiZn	Fe/Ca/Si/Zn	5	231	16.08
Fe rich	Fe+	6	11	0.77
Fe 20-80	Fe+	7	197	13.71
PbCl	Pb+	8	0	0
PbS	Pb+	9	4	0.28
Pb>60%	Pb+	10	2	0.14
Intermed Pb	Pb+	11	2	0.14
ZnSiFe	Zn+	12	2	0.14
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	5	0.35
As bearing	As bearing	16	14	0.97
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	1	0.07
CaS + Fe	Ca+	20	40	2.78
CaP	Ca +	21	0	0
Ca only	Ca+	22	4	0.28
Intermed Ca	Ca+	23	14	0.97
Al/Si+	Al/Si+	24	4	0.28
Total number of particles examined: 1437				



Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	20	2.5
Pyr 1	Fe and S	1	27	3.38
Pyr 2	Fe and S	2	4	0.5
Pyr 3	Fe and S	3	1	0.13
Pyr 4	Fe and S	4	2	0.25
FeCaSiZn	Fe/Ca/Si/Zn	5	542	67.75
Fe rich	Fe+	6	30	3.75
Fe 20-80	Fe+	7	114	14.25
PbCl	Pb+	8	0	0
PbS	Pb+	9	2	0.25
Pb>60%	Pb+	10	4	0.5
Intermed Pb	Pb+	11	2	0.25
ZnSiFe	Zn+	12	6	0.75
Mn/Zn	Zn+	13	2	0.25
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	14	1.75
As bearing	As bearing	16	12	1.5
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	0	0
CaS + Fe	Ca+	20	0	0
CaP	Ca +	21	0	0
Ca only	Ca+	22	3	0.38
Intermed Ca	Ca+	23	4	0.5
Al/Si+	Al/Si+	24	11	1.38
Total number of	particles examined:		800	

Fig. 2.18. Sample LAV-18: Very black fine-grained sand-blast material (not spherical under hand lens) from Kavodokanos. The sample is rich in Fe, Ca, Si and Zn. Σχ. 2.18. Δείγμα LAV-18: Κατάμαυρο λεπτόκοκκο υλικό αμμοβολής (όχι σφαιρικό όπως προκύπτει από παρατήρηση με τη λούπα) από τον Καβοδόκανο. Το δείγμα είναι πλούσιο σε Fe, Ca, Si και Zn.



Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	0	0
Pyr 1	Fe and S	1	65	14.16
Pyr 2	Fe and S	2	0	0
Pyr 3	Fe and S	3	2	0.44
Pyr 4	Fe and S	4	370	80.61
FeCaSiZn	Fe/Ca/Si/Zn	5	0	0
Fe rich	Fe+	6	5	1.09
Fe 20-80	Fe+	7	15	3.27
PbCl	Pb+	8	0	0
PbS	Pb+	9	0	0
Pb>60%	Pb+	10	0	0
Intermed Pb	Pb+	11	0	0
ZnSiFe	Zn+	12	0	0
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	0	0
As bearing	As bearing	16	0	0
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	0	0
CaS + Fe	Ca+	20	2	0.44
CaP	Ca +	21	0	0
Ca only	Ca+	22	0	0
Intermed Ca	Ca+	23	0	0
Al/Si+	Al/Si+	24	0	0
Total number of particles examined: 459				

Fig. 2.19. Sample LAV-19: Reddish clayey material from the oxidised heaps of pyritiferous wastes at Kavodokanos. The sample is rich in Fe and S.

Σχ. 2.19. Δείγμα LAV-19: Ερυθρωπό αργιλούχο υλικό από τους οξειδωμένους σωρούς των πυριτούχων απορριμμάτων στον Καβοδόκανο. Το δείγμα είναι πλούσιο σε Fe και S.

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			Group		
Name	e	Family	Group	Count	Percent
Unclassified		Unclassified	0	13	7.51
Pyr 1		Fe and S	1	1	0.58
Pyr 2		Fe and S	2	0	0
Pyr 3		Fe and S	3	0	0
Pyr 4		Fe and S	4	0	0
FeCaSiZn		Fe/Ca/Si/Zn	5	0	0
Fe rich		Fe+	6	3	1.73
Fe 20-80		Fe+	7	13	7.51
PbCl		Pb+	8	0	0
PbS		Pb+	9	1	0.58
Pb>60%		Pb+	10	0	0
Intermed Pb		Pb+	11	0	0
ZnSiFe		Zn+	12	0	0
Mn/Zn		Zn+	13	0	0
Mn/Zn/S		Zn+	14	0	0
Fe/Zn+		Zn+	15	0	0
As bearing		As bearing	16	0	0
Sb rich		High Sb	17	0	0
V/Na+		Contain V	18	126	72.83
CaS		Ca+	19	10	5.78
CaS + Fe		Ca+	20	3	1.73
CaP		Ca +	21	0	0
Ca only		Ca+	22	0	0
Intermed Ca		Ca+	23	2	1.16
Al/Si+		Al/Si+	24	1	0.58
Total numbe	r of p	articles examined:		173	

Fig. 2.20. Sample LAV-20: Dark waste pile with yellow crystal growth on surface from the oxidised pyritiferous heap at Kavodokanos. The sample is rich in V with a minor amount of Fe. Σχ. 2.20. Δείγμα LAV-20. Σκοτεινόχρους σωρός απορριμμάτων με ανάπτυξη κιτρινωπών κρυστάλλων στην επιφάνειά του, από τους οξειδωμένους πυριτούχους σωρούς απορριμμάτων στον Καβοδόκανο. Το δείγμα είναι πλούσιο σε V με μικρή ποσότητα Fe.



Name	Family	Group	Count	Percent		
Unclassified	Unclassified	0	47	7.53		
Pyr 1	Fe and S	1	239	38.3		
Pyr 2	Fe and S	2	0	0		
Pyr 3	Fe and S	3	33	5.29		
Pyr 4	Fe and S	4	12	1.92		
FeCaSiZn	Fe/Ca/Si/Zn	5	0	0		
Fe rich	Fe+	6	138	22.12		
Fe 20-80	Fe+	7	25	4.01		
PbCl	Pb+	8	98	15.71		
PbS	Pb+	9	8	1.28		
Pb>60%	Pb+	10	0	0		
Intermed Pb	Pb+	11	6	0.96		
ZnSiFe	Zn+	12	0	0		
Mn/Zn	Zn+	13	0	0		
Mn/Zn/S	Zn+	14	1	0.16		
Fe/Zn+	Zn+	15	5	0.8		
As bearing	As bearing	16	10	1.6		
Sb rich	High Sb	17	0	0		
V/Na+	Contain V	18	0	0		
CaS	Ca+	19	0	0		
CaS + Fe	Ca+	20	0	0		
CaP	Ca +	21	0	0		
Ca only	Ca+	22	0	0		
Intermed Ca	Ca+	23	0	0		
Al/Si+	Al/Si+	24	2	0.32		
Total number of pa	Total number of particles examined: 624					

Fig. 2.21. Sample LAV-21: Purple-red pile with grey-white crystal growth from the oxidised pyritiferous tailings at Kavodokanos. The sample is rich in Fe, S and Pb. Σχ. 2.21. Δείγμα LAV-21: Πορφυρο-κόκκινος σωρός με γκριζόλευκους αναπτυσσόμενους κρυστάλλους

από τα οξειδωμένα πυριτούχα απορρίμματα στον Καβοδόκανο. Το δείγμα είναι πλούσιο σε Fe, S και Pb.



Group

Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	28	5.87
Pyr 1	Fe and S	1	4	0.84
Pyr 2	Fe and S	2	1	0.21
Pyr 3	Fe and S	3	0	0
Pyr 4	Fe and S	4	0	0
FeCaSiZn	Fe/Ca/Si/Zn	5	157	32.91
Fe rich	Fe+	6	65	13.63
Fe 20-80	Fe+	7	43	9.01
PbCl	Pb+	8	0	0
PbS	Pb+	9	0	0
Pb>60%	Pb+	10	4	0.84
Intermed Pb	Pb+	11	3	0.63
ZnSiFe	Zn+	12	12	2.52
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	7	1.47
As bearing	As bearing	16	28	5.87
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	0	0
CaS + Fe	Ca+	20	0	0
CaP	Ca +	21	2	0.42
Ca only	Ca+	22	54	11.32
Intermed Ca	Ca+	23	9	1.89
Al/Si+	Al/Si+	24	60	12.58
Total number of	particles examined:		477	

Fig. 2.22. Sample L-6A: Garden soil sample from Kavodokanos. The sample is rich in Fe, Ca, Si and Zn with a minor amount of Al, Ca and As (compare with corresponding house dust sample, Fig. 2.23 and Fig. 2.32).

Σχ. 2.22. Δείγμα L-6A: Δείγμα κηπευτικού εδάφους από τον Καβοδόκανο. Το δείγμα είναι πλούσιο σε Fe, Ca, Si και Zn με μικρές ποσότητες Al, Ca και As (σύγκρινε με το αντίστοιχο δείγμα σκόνης σπιτιών, Σχ. 2.23 και 2.32).



Group

Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	15	4.08
Pyr 1	r 1 Fe and S		7	1.9
Pyr 2	yr 2 Fe and S		1	0.27
Pyr 3	Fe and S	3	0	0
Pyr 4	Fe and S	4	0	0
FeCaSiZn	Fe/Ca/Si/Zn	5	24	6.52
Fe rich	Fe+	6	25	6.79
Fe 20-80	Fe+	7	34	9.24
PbCl	Pb+	8	0	0
PbS	Pb+	9	1	0.27
Pb>60% Pb+		10	0	0
Intermed Pb	Pb+	11	3 2	0.82 0.54
ZnSiFe	Zn+	12		
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	2	0.54
As bearing	As bearing	16	11	2.99
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	4	1.09
CaS + Fe	Ca+	20	1	0.27
CaP	Ca +	21	4	1.09
Ca only	Ca+	22	178	48.37
Intermed Ca	Ca+	23	19	5.16
Al/Si+	Al/Si+	24	37	10.05
Total number of	particles examined:		368	

Fig. 2.23. Sample L-6C: House dust sample from Kavodokanos. The sample is rich in Ca a minor amount of Al, Si, Fe, Zn and As (compare with corresponding garden soil sample, Fig. 2.22 and Fig. 2.32).

Σχ. 2.23. Δείγμα L-6C: Δείγμα σκόνης σπιτιών από τον Καβοδόκανο. Το δείγμα είναι πλούσιο σε Ca με μικρές ποσότητες Al, Si, Fe, Zn και As (σύγκρινε με το αντίστοιχο δείγμα κηπευτικού εδάφους, Σχ. 2.22 και 2.32).



Name	Family	Group	Count	Percent		
Unclassified	Unclassified	0	124	4.05		
Pyr 1	Fe and S	1	111	3.63		
Pyr 2	Fe and S	2	2	0.07		
Pyr 3	Fe and S	3	1	0.03		
Pyr 4	Fe and S	4	0	0		
FeCaSiZn	Fe/Ca/Si/Zn	5	1087	35.52		
Fe rich	Fe+	6	297	9.71		
Fe 20-80	Fe+	7	286	9.35		
PbCl	Pb+	8	0	0		
PbS	Pb+	9	21	0.69		
Pb>60%	Pb+	10	57	1.86		
Intermed Pb	Pb+	11	37	1.21		
ZnSiFe	Zn+	12	105	3.43		
Mn/Zn	Zn+	13	1	0.03		
Mn/Zn/S	Zn+	14	0	0		
Fe/Zn+	Zn+	15	19	0.62		
As bearing	As bearing	16	162	5.29		
Sb rich	High Sb	17	0	0		
V/Na+	Contain V	18	0	0		
CaS	Ca+	19	2	0.07		
CaS + Fe	Ca+	20	1	0.03		
CaP	Ca +	21	5	0.16		
Ca only	Ca+	22	384	12.55		
Intermed Ca	Ca+	23	101	3.3		
Al/Si+	Al/Si+	24	257	8.4		
Total number of p	Total number of particles examined: 3060					

Fig. 2.24. Sample L-11A: Garden soil sample from Kavodokanos. The sample is rich in Fe, Ca, Si and Zn with a minor amount of Al, Si and As (compare with corresponding house dust sample, Fig. 2.25 and Fig. 2.33).

Σχ. 2.24. Δείγμα L-11Α: Δείγμα κηπευτικού εδάφους από τον Καβοδόκανο. Το δείγμα είναι πλούσιο σε Fe, Ca, Si και Zn με μικρές ποσότητες Al, Si και As (σύγκρινε με το αντίστοιχο δείγμα σκόνης σπιτιών, Σχ. 2.25 και 2.33)



Name	Family	Group	Count	Percent	
Unclassified	Unclassified	0	40	6.51	
Pyr 1	Fe and S	1	20	3.26	
Pyr 2	Fe and S	2	1	0.16	
Pyr 3	Fe and S	3	1	0.16	
Pyr 4	Fe and S	4	0	0	
FeCaSiZn	Fe/Ca/Si/Zn	5	11	1.79	
Fe rich	Fe+	6	68	11.07	
Fe 20-80	Fe+	7	123	20.03	
PbCl	Pb+	8	0	0	
PbS	Pb+	9	0	0	
Pb>60%	Pb+	10	3	0.49	
Intermed Pb	Pb+	11	7	1.14	
ZnSiFe	Zn+	12	13	2.12	
Mn/Zn	Zn+	13	0	0	
Mn/Zn/S	Zn+	14	0	0	
Fe/Zn+	Zn+	15	9	1.47	
As bearing	As bearing	16	23	3.75	
Sb rich	High Sb	17	0	0	
V/Na+	Contain V	18	0	0	
CaS	Ca+	19	20	3.26	
CaS + Fe	Ca+	20	4	0.65	
CaP	Ca +	21	6	0.98	
Ca only	Ca+	22	88	14.33	
Intermed Ca	Ca+	23	90	14.66	
Al/Si+	AI/Si+	24	87	14.17	
Total number of	Total number of particles: 614				

Fig. 2.25. Sample L-11C: House dust sample from Kavodokanos. The sample is rich in Fe, Ca, AI and Si with a minor amount of As (compare with corresponding garden soil sample, Fig. 2.24 and Fig. 2.33).

Σχ. 2.25. Δείγμα L-11C: Δείγμα σκόνης σπιτιών από τον Καβοδόκανο. Το δείγμα είναι πλούσιο σε Fe, Ca, Al και Si με μικρή ποσότητα As (σύγκρινε με το αντίστοιχο δείγμα κηπευτικού εδάφους, Σχ. 2.24 και 2.33)



Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	14	2.89
Pyr 1	Fe and S	1	27	5.58
Pyr 2	Fe and S	2	0	0
Pyr 3	Fe and S	3	0	0
Pyr 4	Fe and S	4	0	0
FeCaSiZn	Fe/Ca/Si/Zn	5	4	0.83
Fe rich	Fe+	6	77	15.91
Fe 20-80	Fe+	7	39	8.06
PbCl	Pb+	8	0	0
PbS	Pb+	9	14	2.89
Pb>60%	Pb+	10	7	1.45
Intermed Pb	Pb+	11	10	2.07
ZnSiFe	Zn+	12	28	5.79
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	4	0.83
As bearing	As bearing	16	22	4.55
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	0	0
CaS + Fe	Ca+	20	1	0.21
CaP	Ca +	21	2	0.41
Ca only	Ca+	22	124	25.62
Intermed Ca	Ca+	23	23	4.75
Al/Si+	Al/Si+	24	88	18.18
Total number of	narticles examined:		484	

Fig. 2.26. Sample L-111A: Garden soil sample from Ayios Andreas. The sample is rich in Ca, AI, Si and Fe with a minor amount of Zn and As (compare with corresponding house dust sample, Fig. 2.27 and Fig. 2.34).

Σχ. 2.26. Δείγμα L-111Α: Δείγμα κηπευτικού εδάφους από τον Άγιο Ανδρέα. Το δείγμα είναι πλούσιο σε Ca, Al, Si και Fe με μικρή ποσότητα Zn και As (σύγκρινε με το αντίστοιχο δείγμα σκόνης σπιτιών, Σχ. 2.27 και 2.34).



Fig. 2.27. Sample L-111C: House dust sample from Ayios Andreas. The sample is rich in Fe, Zn, Si and Al with a minor amount of As and Ca (compare with corresponding garden soil sample, Fig. 2.26 and Fig. 2.34).

Σχ. 2.27. Δείγμα L-111C: Δείγμα σκόνης σπιτιών από τον 'Αγιο Ανδρέα. Το δείγμα είναι πλούσιο σε Fe, Zn, Si και Al με μικρή ποσότητα As και Ca (σύγκρινε με το αντίστοιχο δείγμα κηπευτικού εδάφους, Σχ. 2.26 και 2.34).



Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	116	12.96
Pyr 1	Fe and S	1	51	5.7
Pyr 2	Fe and S	2	2	0.22
Pyr 3	Fe and S	3	1	0.11
Pyr 4	Fe and S	4	7	0.78
FeCaSiZn	Fe/Ca/Si/Zn	5	4	0.45
Fe rich	Fe+	6	300	33.52
Fe 20-80	Fe+	7	203	22.68
PbCl	Pb+	8	0	0
PbS	Pb+	9	0	0
Pb>60%	Pb+	10	2	0.22
Intermed Pb	Pb+	11	0	0
ZnSiFe	Zn+	12	24	2.68
Mn/Zn	Zn+	13	5	0.56
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	40	4.47
As bearing	As bearing	16	39	4.36
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	18	2.01
CaS + Fe	Ca+	20	7	0.78
CaP	Ca +	21	5	0.56
Ca only	Ca+	22	1	0.11
Intermed Ca	Ca+	23	2	0.22
Al/Si+	Al/Si+	24	68	7.6
Total number of	narticles examined [.]		895	

Fig. 2.28. Sample L-122SL: Slag sample from Ayia Paraskevi. The sample is rich in Fe with a minor amount of Al, Si, Zn and As (compare with corresponding house dust sample, Fig. 2.29 and Fig. 2.35). Σχ. 2.28. Δείγμα L-122SL: Δείγμα σκουριάς από την Αγία Παρασκευή. Το δείγμα είναι πλούσιο σε Fe με μικρή ποσότητα Al, Si, Zn και As (σύγκρινε με το αντίστοιχο δείγμα σκόνης σπιτιών, Σχ. 2.29 και 2.35).



Group

Name	Family	Group	Count	Percent
Unclassified	Unclassified	0	190	6.87
Pyr 1	Fe and S	1	60	2.17
Pyr 2	Fe and S	2	2	0.07
Pyr 3	Fe and S	3	1	0.04
Pyr 4	Fe and S	4	0	0
FeCaSiZn	Fe/Ca/Si/Zn	5	39	1.41
Fe rich	Fe+	6	476	17.22
Fe 20-80	Fe+	7	536	19.39
PbCl	Pb+	8	0	0
PbS	Pb+	9	0	0
Pb>60%	Pb+	10	2	0.07
Intermed Pb	Pb+	11	3	0.11
ZnSiFe	Zn+	12	102	3.69
Mn/Zn	Zn+	13	0	0
Mn/Zn/S	Zn+	14	0	0
Fe/Zn+	Zn+	15	103	3.73
As bearing	As bearing	16	20	0.72
Sb rich	High Sb	17	0	0
V/Na+	Contain V	18	0	0
CaS	Ca+	19	156	5.64
CaS + Fe	Ca+	20	45	1.63
CaP	Ca +	21	20	0.72
Ca only	Ca+	22	470	17.00
Intermed Ca	Ca+	23	159	5.75
Al/Si+	Al/Si+	24	381	13.78
Total number of	particles examined:		2765	

Fig. 2.29. Sample L-122C: House dust sample from Ayia Paraskevi. The sample is rich in Fe, Ca, Al and Si with a minor amount of Zn (compare with corresponding slag sample, Fig. 2.28 and 2.35). $\Sigma \chi$. 2.29. $\Delta \epsilon i \gamma \mu \alpha L$ -122C: $\Delta \epsilon i \gamma \mu \alpha \sigma \kappa \delta v \eta \varsigma \sigma \pi i \tau i \omega v \alpha \pi \delta \tau \eta v A \gamma i \alpha \Pi \alpha \rho \alpha \sigma \kappa \epsilon u \eta$. To $\delta \epsilon i \gamma \mu \alpha \epsilon i v \alpha i \pi \lambda \delta u \sigma \sigma \epsilon$ Fe, Ca, Al και Si $\mu \epsilon \mu i \kappa \rho \eta \pi \sigma \delta \tau \eta \tau \alpha T$ (σύγκρινε $\mu \epsilon \tau \sigma \alpha v \tau i \sigma \tau \sigma \sigma \delta \epsilon i \gamma \mu \alpha \sigma \kappa \delta \tau \chi$. 2.35).



Group

Family	Group	Count	Percent
Unclassified	0	20	3.15
Pyr 1 Fe and S		11	1.73
Fe and S	2	1	0.16
Fe and S	3	0	0
Fe and S	4	0	0
Fe/Ca/Si/Zn	5	0	0
Fe+	6	25	3.94
Fe+	7	48	7.56
Pb+	8	0	0
Pb+	9	1	0.16
Pb+	10	0	0
Pb+	11	2	0.31
Zn+	12	1	0.16
Zn+	13	0	0
Zn+	14	0	0
Zn+	15	2	0.31
As bearing	16	1	0.16
High Sb	17	0	0
Contain V	18	0	0
Ca+	19	11	1.73
Ca+	20	6	0.94
Ca +	21	2	0.31
Ca+	22	253	39.84
Ca+	23	48	7.56
Al/Si+	24	203	31.97
	FamilyUnclassifiedFe and SFe and SFe and SFe and SFe and SFe/Ca/Si/ZnFe+Pb+Pb+Pb+Pb+Zn+Zn+Zn+Zn+Zn+Ca+<	Family Group Unclassified 0 Fe and S 1 Fe and S 2 Fe and S 3 Fe and S 4 Fe/Ca/Si/Zn 5 Fe+ 6 Fe+ 7 Pb+ 8 Pb+ 9 Pb+ 10 Pb+ 12 Zn+ 13 Zn+ 13 Zn+ 15 As bearing 16 High Sb 17 Contain V 18 Ca+ 20 Ca+ 21 Ca+ 23 Al/Si+ 24	FamilyGroupCountUnclassified020Fe and S111Fe and S21Fe and S30Fe and S40Fe/Ca/Si/Zn50Fe+625Fe+748Pb+91Pb+91Pb+100Pb+112Zn+121Zn+130Zn+152As bearing161High Sb170Contain V180Ca+212Ca+22253Ca+2348Al/Si+24203

Fig. 2.30. Sample L-126C: House dust sample from Ayia Paraskevi. The sample is rich in Ca, AI and Si with a minor amount of Fe.

Σχ. 2.30. Δείγμα L-126C: Δείγμα σκόνης σπιτιών από την Αγία Παρασκευή. Το δείγμα είναι πλούσιο σε Ca, Al και Si με μικρή ποσότητα Fe.



Name	Family	Family Group		Percent	
Unclassified	Unclassified	0	10	2.76	
Pyr 1	Fe and S	1	27	7.46	
Pyr 2	Fe and S	2	2	0.55	
Pyr 3	Fe and S	3	0	0	
Pyr 4	Fe and S	4	1	0.28	
FeCaSiZn	Fe/Ca/Si/Zn	5	0	0	
Fe rich	Fe+	6	102	28.18	
Fe 20-80	Fe+	7	55	15.19	
PbCl	Pb+	8	0	0	
PbS	Pb+	9	0	0	
Pb>60%	Pb+	10	0	0	
Intermed Pb	Pb+	11	0	0	
ZnSiFe	Zn+	12	0	0	
Mn/Zn	Zn+	13	0	0	
Mn/Zn/S	Zn+	14	0	0	
Fe/Zn+	Zn+	15	2	0.55	
As bearing	As bearing	16	4	1.10	
Sb rich	High Sb	17	0	0	
V/Na+	Contain V	18	0	0	
CaS	Ca+	19	33	9.12	
CaS + Fe	Ca+	20	3	0.83	
CaP	Ca +	21	0	0	
Ca only	Ca+	22	31	8.56	
Intermed Ca	Ca+	23	11	3.04	
Al/Si+	Al/Si+	24	81	22.38	
Total number of	particles examined:		362		

Fig. 2.31. Sample L-288A: Overburden sample from Kiprianos. The sample is rich in Fe, Al and Si with a minor amount of Ca and S.

Σχ. 2.31. Δείγμα L-288Α: Δείγμα εδαφικού καλύμματος από τον Κυπριανό. Το δείγμα είναι πλούσιο σε Fe, Al και Si με μικρή ποσότητα Ca και S.



Marras	F amily	0	Sample L-6A	(Garden soil)	Sample L-6C	(House dust)
Name	Family	Group	Count	Percent	Count	Percent
Unclassified	Unclassified	0	28	5.87	15	4.08
Pyr 1	Fe and S	1	4	0.84	7	1.9
Pyr 2	Fe and S	2	1	0.21	1	0.27
Pyr 3	Fe and S	3	0	0	0	0
Pyr 4	Fe and S	4	0	0	0	0
FeCaSiZn	Fe/Ca/Si/Zn	5	157	32.91	24	6.52
Fe rich	Fe+	6	65	13.63	25	6.79
Fe 20-80	Fe+	7	43	9.01	34	9.24
PbCl	Pb+	8	0	0	0	0
PbS	Pb+	9	0	0	1	0.27
Pb>60%	Pb+	10	4	0.84	0	0
Intermed Pb	Pb+	11	3	0.63	3	0.82
ZnSiFe	Zn+	12	12	2.52	2	0.54
Mn/Zn	Zn+	13	0	0	0	0
Mn/Zn/S	Zn+	14	0	0	0	0
Fe/Zn+	Zn+	15	7	1.47	2	0.54
As bearing	As bearing	16	28	5.87	11	2.99
Sb rich	High Sb	17	0	0	0	0
V/Na+	Contain V	18	0	0	0	0
CaS	Ca+	19	0	0	4	1.09
CaS + Fe	Ca+	20	0	0	1	0.27
CaP	Ca +	21	2	0.42	4	1.09
Ca only	Ca+	22	54	11.32	178	48.37
Intermed Ca	Ca+	23	9	1.89	19	5.16
Al/Si+	Al/Si+	24	60	12.58	37	10.05
Total number	of particles exa	mined:	477		368	

Fig. 2.32. Comparative plot and table of garden soil and house dust results from site L-6A/C at Kavodokanos. It is quite apparent that there is no correlation between the two samples. Σχ. 2.32. Συγκριτικό διάγραμμα και πίνακας των αποτελεσμάτων των δειγμάτων κηπευτικού εδάφους και σκόνης σπιτιών από τη θέση L-6A/C στον Καβοδόκανο. Είναι προφανές ότι δεν υπάρχει συσχέτιση μεταξύ των δύο δειγμάτων.



Name	Family	Group	L-11A (Garden soil)		L-11C (House dust)	
			Count	Percent	Count	Percent
Unclassified	Unclassified	0	124	4.05	40	6.51
Pyr 1	Fe and S	1	111	3.63	20	3.26
Pyr 2	Fe and S	2	2	0.07	1	0.16
Pyr 3	Fe and S	3	1	0.03	1	0.16
Pyr 4	Fe and S	4	0	0	0	0
FeCaSiZn	Fe/Ca/Si/Zn	5	1087	35.52	11	1.79
Fe rich	Fe+	6	297	9.71	68	11.07
Fe 20-80	Fe+	7	286	9.35	123	20.03
PbCl	Pb+	8	0	0	0	0
PbS	Pb+	9	21	0.69	0	0
Pb>60%	Pb+	10	57	1.86	3	0.49
Intermed Pb	Pb+	11	37	1.21	7	1.14
ZnSiFe	Zn+	12	105	3.43	13	2.12
Mn/Zn	Zn+	13	1	0.03	0	0
Mn/Zn/S	Zn+	14	0	0	0	0
Fe/Zn+	Zn+	15	19	0.62	9	1.47
As bearing	As bearing	16	162	5.29	23	3.75
Sb rich	High Sb	17	0	0	0	0
V/Na+	Contain V	18	0	0	0	0
CaS	Ca+	19	2	0.07	20	3.26
CaS + Fe	Ca+	20	1	0.03	4	0.65
CaP	Ca +	21	5	0.16	6	0.98
Ca only	Ca+	22	384	12.55	88	14.33
Intermed Ca	Ca+	23	101	3.3	90	14.66
Al/Si+	Al/Si+	24	257	8.4	87	14.17
Total number of particles examined:			3060		614	

Fig. 2.33. Comparative plot and table of garden soil and house dust results from site L-11A/C at Kavodokanos. It is quite apparent that there is no correlation between the two samples. Σχ. 2.33. Συγκριτικό διάγραμμα και πίνακας των αποτελεσμάτων των δειγμάτων κηπευτικού εδάφους και σκόνης σπιτιών από τη θέση L-11A/C στον Καβοδόκανο. Είναι προφανές ότι δεν υπάρχει συσχέτιση μεταξύ των δύο δειγμάτων.


Group

Name	Family	Group	L-111A (Garden soil)		L-111C (H	ouse dust)
			Count	Percent	Count	Percent
Unclassified	Unclassified	0	14	2.89	177	10.23
Pyr 1	Fe and S	1	27	5.58	78	4.51
Pyr 2	Fe and S	2	0	0	11	0.64
Pyr 3	Fe and S	3	0	0	0	0
Pyr 4	Fe and S	4	0	0	1	0.06
FeCaSiZn	Fe/Ca/Si/Zn	5	4	0.83	12	0.69
Fe rich	Fe+	6	77	15.91	454	26.23
Fe 20-80	Fe+	7	39	8.06	420	24.26
PbCl	Pb+	8	0	0	0	0
PbS	Pb+	9	14	2.89	7	0.4
Pb>60%	Pb+	10	7	1.45	9	0.52
Intermed Pb	Pb+	11	10	2.07	28	1.62
ZnSiFe	Zn+	12	28	5.79	120	6.93
Mn/Zn	Zn+	13	0	0	3	0.17
Mn/Zn/S	Zn+	14	0	0	0	0
Fe/Zn+	Zn+	15	4	0.83	55	3.18
As bearing	As bearing	16	22	4.55	90	5.2
Sb rich	High Sb	17	0	0	0	0
V/Na+	Contain V	18	0	0	0	0
CaS	Ca+	19	0	0	2	0.12
CaS + Fe	Ca+	20	1	0.21	5	0.29
CaP	Ca +	21	2	0.41	9	0.52
Ca only	Ca+	22	124	25.62	49	2.83
Intermed Ca	Ca+	23	23	4.75	89	5.14
Al/Si+	Al/Si+	24	88	18.18	112	6.47
Total number	of particles exa	mined:	484		1731	

Fig. 2.34. Comparative plot and table of garden soil and house dust results from site L-111A/C at Ayios Andreas. It is quite apparent that there is no correlation between the two samples. Σχ. 2.34. Συγκριτικό διάγραμμα και πίνακας των αποτελεσμάτων των δειγμάτων κηπευτικού εδάφους και σκόνης σπιτιών από τη θέση L-111A/C στον 'Αγιο Ανδρέα. Είναι προφανές ότι δεν υπάρχει συσχέτιση μεταξύ των δύο δειγμάτων.



Marra		0	L-122SL (G	Garden soil)	L-126C (House dust)			
Name	Family	Group	Count	Percent	Count	Percent		
Unclassified	Unclassified	0	116	12.96	20	3.15		
Pyr 1	Fe and S	1	51	5.7	11	1.73		
Pyr 2	Fe and S	2	2	0.22	1	0.16		
Pyr 3	Fe and S	3	1	0.11	0	0		
Pyr 4	Fe and S	4	7	0.78	0	0		
FeCaSiZn	Fe/Ca/Si/Zn	5	4	0.45	0	0		
Fe rich	Fe+	6	300	33.52	25	3.94		
Fe 20-80	Fe+	7	203	22.68	48	7.56		
PbCl	Pb+	8	0	0	0	0		
PbS	Pb+	9	0	0	1	0.16		
Pb>60%	Pb+	10	2	0.22	0	0		
Intermed Pb	Pb+	11	0	0	2	0.31		
ZnSiFe	Zn+	12	24	2.68	1	0.16		
Mn/Zn	Zn+	13	5	0.56	0	0		
Mn/Zn/S	Zn+	14	0	0	0	0		
Fe/Zn+	Zn+	15	40	4.47	2	0.31		
As bearing	As bearing	16	39	4.36	1	0.16		
Sb rich	High Sb	17	0	0	0	0		
V/Na+	Contain V	18	0	0	0	0		
CaS	Ca+	19	18	2.01	11	1.73		
CaS + Fe	Ca+	20	7	0.78	6	0.94		
CaP	Ca +	21	5	0.56	2	0.31		
Ca only	Ca+	22	1	0.11	253	39.84		
Intermed Ca	Ca+	23	2	0.22	48	7.56		
Al/Si+	Al/Si+	24	68	7.6	203	31.97		
Total number	of particles exar	nined:	895		635			

Fig. 2.35. Comparative plot and table of garden soil and house dust results from site L-122SL/C at Ayia Paraskevi. It is quite apparent that there is no correlation between the two samples. Σχ. 2.35. Συγκριτικό διάγραμμα και πίνακας των αποτελεσμάτων των δειγμάτων κηπευτικού εδάφους και σκόνης σπιτιών από τη θέση L-122SL/C στην Αγία Παρασκευή. Είναι προφανές ότι δεν υπάρχει συσχέτιση μεταξύ των δύο δειγμάτων.

2.6. DISCUSSION

This is a fascinating data set. As was hoped at the outset there are a number of distinctive particle types, which can be clearly seen and classified. For ease of interpretation of the supplied data, the classification scheme (Annex 3.1 of Appendix Report 3 in this Volume p.3.13-3.14) contains a comment line in each group, which shows one or more samples within which the particular particle type may be found.

It should be noted that the technique does not give a mineralogical analysis. Group names should be treated, therefore, with caution as they are based solely on presence of elements interpreted with an estimate of the mineral most likely to occur. In some cases, group names are simply presented as a combination of elements, which strictly speaking is the more correct approach. An examination of various combinations of source samples, with the aid of the MIDAS software package, will quickly reveal the extent to which they can be differentiated.

A number of clearly recognisable particle types associated with specific source samples are immediately apparent. Iron and sulphur groups (almost certainly pyrite) dominate LAV-3, 4, 5, 6, 8, 16, 17 and 19 (Figs. 2.3, .4, .5, .6, .8, .16, .17 & .19). These are not all identical and the "pyrite" family actually distinguishes four different particle types. Some of these samples also contain particles from the Fe+ family, where iron dominates in the absence of sulphur. Other samples have these groups without much (or any) pyrite, *i.e.*, LAV-7, 9, 10, 13 and 14 (Figs. 2.7, .9, .10, .13 & .14). These are likely to be iron oxides in this locality. An examination of the colour suggests that haematite may dominate (compare LAV-7 and 9 in Table 2.1). Other obvious colour differences can also be explained by the chemistry, *i.e.*, sample LAV- 2 (Fig. 2.2), described as a yellow clayey material in the field notes, is gypsum, and is present in LAV-6 too (Fig. 2.6). The grey ashy material sampled within the premises of the smelter (LAV-11 and 12) is particularly interesting. This light, fine dust is high in arsenic and antimony (Figs. 2.11 & .12). The very black, fine-grained sand-blast material of sample LAV-18 is also distinctive, and contains iron, calcium, silicon and zinc (Fig. 2.18).

One feature that was also apparent in the field-sampling programme was the occurrence of what looked like crusts formed on some of the waste piles. This is indicative of great mobility of some of the metal species in these samples. Sample LAV- 21 shows that the analysis did not isolate a particular particle type, perhaps because the crust particles were rather mixed with other particles (Fig. 2.21). In the case, however, of LAV-20 a very distinctive, vanadium rich class was apparent (Fig. 2.20). It is not certain what the implications of these mobile crusts are, but certainly further investigation could be very interesting and important.

The second objective of the study, to examine the analyses of the source materials and to establish a classification scheme, which would reflect the different types of metalliferous particles within the samples, seems, therefore, to have been satisfactorily achieved. As might be expected some of the "source" samples, *i.e.*, LAV-1, are rather more mixed, reflecting the heterogeneity of the sample location (Fig. 2.1.).

The next objective was to examine a number of overburden/garden soil and house dust samples to investigate the potential of this scheme for source apportionment. The results of this part too are very promising. Garden soil samples L-6A and L-11A from Kavodokanos are the only ones to show significant amounts of the iron, calcium, silicon and zinc particles resembling the LAV-18 source sample (sand-blast material) [Figs. 2.22, 2.24 & 2.18]. This sand-blast source sample was taken from close by. The L-111A/C and

L-122SL/C garden soil, house dust and slag samples show large amounts of the high Fe groups (Figs. 2.26, .27, .28 & .29). They have an encouraging level of resemblance to each other, suggesting that the mix of particles is representative of all the overburden/garden soil and dust samples round these dwellings. The nearby source samples (LAV-13, 14 and 15, Figs. 2.13, .14 & .15) show similar classification patterns.

It is very interesting, and disturbing, to notice that there are arsenic containing particles in all of the receptor samples analysed to date. The L-11 suite all have also lead and zinc containing particles (Fig. 2.11), with zinc particles featuring in the L-122 set of samples too (Figs. 2.28-.29). Not all the household dusts are very contaminated, *i.e.*, L-126C has mainly calcareous and alumino-silicate particles. These data demonstrate the presence of distinctive types in the external and internal household environment.

Direct comparison between (a) garden soil and indoor dust samples (*i.e.*, samples L-6A/C, 11A/C, 111A/C – Figs. 2.32, .33 & .34), and (b) slag and indoor dust (L-122SL/C – Fig. 2.35) from the same house, shows that the two samples (outdoor and indoor) are not correlated. This feature has already been pointed out in Chapter 8 of Volume 1.

Hand-to-mouth activity is known to be an important route of exposure of young children to lead (Davies *et al.*, 1990; Davies and Watt, 1986). Previous work at Imperial College (Watt and Thornton, 1990; Watt *et al.*, 1993) has demonstrated the presence of other mineral lead particles on children's hands and in indoor dusts, such as pyromorphite [Pb₅Cl(PO₄)₃] particles that can be considered to have their origin in the external environment, at least in the Winster situation (Derbyshire, U.K.) in which they were first described (Cotter-Howells and Thornton, 1991; Watt *et al.*, 1993; Thornton et al., 1994). It is, therefore, likely that pyromorphite "type" particles generally indicate an external source of Pb, whether found in floor dust or on the child's hands. Thus, they were used as a tracer in studies seeking to evaluate the importance of soil Pb in terms of human exposure.

In general, for a tracer to be effective, it must be easy to distinguish in the matrix within which it is to be sampled, and it should behave in the same way as the material that it represents. What was especially advantageous about pyromorphite material was that there was no need to provide a surrogate for the contaminant of interest, since it was itself so distinctive. This avoided all the usual problems of ensuring the distribution of the tracer in the source area was comparable to that of the substance it was desired to mimic.

It seems very likely that one or more of the particle types described in this pilot study could be used for similar applications. Davies et al (1990) describes a large exposure route assessment for lead rich particles in urban United Kingdom, which measured inputs from food, water, air, dust, and soil. In an area with such demonstrable levels of health problems (Nakos, 1985; Maravelias, 1989; Eikmann *et al.*, 1991; Makropoulos *et al.*, 1991, 1992; Hadjigeorgiou-Stavrakis and Vergou-Vichou, 1992; Stavrakis *et al.*, 1994; Demetriades *et al.*, 1996; Kafourou *et al.*, 1997), it seems prudent to study the exposure routes of both children and adults in some detail (refer to Chapter 11 in Volume 1 of this report, p.311-349). Further, the presence of so many distinctive particle types offers great potential for physical tracing of exposure routes with the important objective of quantifying, which parts of the area offer an immediate hazard. This type of data would be of great value in setting up an agenda for cost-effective remediation.

Overburden/soil contaminated by metalliferous wastes represents complex mixtures of many different compounds both inorganic and organic in nature. It is generally accepted that the bioavailability of a metal in the soil environment can be strongly influenced by its mineral and chemical form. In a contaminated soil, a metal can be present in a number of different phases, *i.e.*, soluble, exchangeable, specifically adsorbed, occluded to oxides of iron and manganese, organically bound, precipitated as a secondary mineral or held in the lattice of a primary mineral or anthropogenic waste particle (refer to Chapter 7 in Volume 1 of this report, p.191-234). Considerable research has been aimed at assessing the fraction of the total metal that is present in each of these phases in overburden/soil/house dust of the Lavrion area. Such data are of value for two reasons:

- firstly, they provide far more information on the potential risks to plant, animal and human health from metal contamination in soil than does a single measure of total metal concentration; and
- secondly, they allow an assessment, albeit limited, of the ongoing processes in contaminated soil, such as the weathering of waste materials, leading to the release of metals and the control of adsorption and retention by soil.

The studies undertaken in Winster, mentioned above, have shown that the mineral form in which lead occurs is an important control on human exposure. Highly elevated lead concentrations in soil in the historical lead-mining district of Derbyshire were not reflected in the blood lead concentrations in young children, which were within the normal range for the United Kingdom (Cotter-Howells and Thornton, 1991; Thornton *et al.*, 1994). Analysis of contaminated soil by scanning electron microscopy (SEM) showed the presence of appreciable amounts of the mineral pyromorphite (Pb₅(PO₄)₃Cl) formed by the weathering of galena (PbS) and cerussite (PbCO₃). In this case, the extremely low solubility of pyromorphite was considered to contribute to the low human bioavailability of lead. Experimental and theoretical evidence in support of this hypothesis have subsequently been reported from the U.S.A. (Davis *et al*, 1993; Ruby *et al*, 1994).

For soils contaminated by metalliferous wastes, a popular analytical approach has been sequential extraction schemes using operationally defined fractions, the scheme adapted from Tessier *et al.* (1979) by Li (1993) in the current case.

Relatively few studies, using sequential extraction, have attempted to relate the extractability of a metal to its bioavailability. The use of sequential extractions to investigate the kinetics of the soil/plant or soil/animal system has two limitations;

- firstly, the fraction of metal extracted is operationally defined and may not correspond directly to the amount of metal present in a particular phase in soil; and
- secondly, sequential extraction techniques provide only a static measure of the amount of a metal likely to be present in each phase.

Further insight might well be gained by the combination of soil extraction procedures with scanning electron microscopy techniques.

Scanning electron microscopy has generally been used to identify the presence of specific phases in metal-rich particles. The techniques described above, and in Appendix Report 3 (this Volume p.3.0-3.14), have increased the capacity of the method to detect, isolate and classify metal-rich particulate material. Studies have demonstrated

the usefulness of the technique in providing a representative analysis of the metal-rich phases of heterogeneous materials, such as contaminated soil and dust (Hunt *et al.*, 1991, 1992, 1993; Watt and Thornton, 1990; Watt *et al.*, 1993). Until recently, less attention has been paid to the relationship between the mineral and chemical form of a metal and its extractability at the particulate scale. Within the few years, the work undertaken at Imperial College has involved the development of a new technique designed to study the solubility of contaminant particles, whilst maintaining much of the matrix associated with the original soil. Using this approach, termed Differential Individual Particle Analysis (DIPA), metal-rich particles previously identified in the conventional manner, are precisely re-located and re-analysed for chemical and morphological changes, following the in-situ application of an extractant. Preliminary DIPA studies have established the feasibility of *'in-situ*' procedures, and have identified variations in solubility between different lead minerals using a dilute acid attack.

Complementary to the high resolution, but rather labour intensive technique of *"in situ"* DIPA, is a technique using one of the principal advantages of automated particle analysis, and the ability to identify and measure large numbers of particles in a short period of time. For *"ex situ"* DIPA there is no attempt to re-locate individual features, but instead populations of particles are characterised after each step of an extraction procedure. This has been applied to a preliminary examination of the Tessier *et al.* (1979) extraction sequence (Hunt *et al.,* 1994).

Taken together, the two methods of DIPA provide an unrivalled ability to examine the effect of each reagent on the individual components of the heterogeneous mixture that is a contaminated soil. They provide the possibility of focusing on likely process controls the consequences of which are much more difficult to isolate with bulk techniques. Examination at the particle level thus permits the study of the influence of particle size, mineral form, matrix interactions as well as synergistic and antagonistic effects between metals.

It is suggested that further research in the Lavrion area using these new techniques could provide great insights into the controls on intake and uptake of pollutant material in the area. This would be achieved using a co-ordinated analytical approach combining chemical extraction and scanning electron microscopy. The results will be related to the bioavailability of these metals, which would be assessed under field and laboratory conditions. The use of *in vitro* bioavailability chambers (*i.e.*, Ruby *et al.*, 1995), which simulate human stomach and intestines also offers great potential.

2.7. CONCLUSIONS

The study was designed to be an initial evaluation of the potential of automated electron microscopy to contribute to the understanding of movement of metalliferous particulate matter and, in particular, to study routes of exposure of the local population.

A successful field-sampling programme was undertaken, which obtained 21 samples representing different sources of metals. These were analysed and used to design a classification scheme, which reflected the different types of metalliferous particles within the samples.

Subsequently, a number of overburden/soil and house dust samples were analysed and classified. Comparisons were made with the distribution of the source samples and, in a number of cases, it was shown that receptor samples reflected particle types from nearby sources. This is only a pilot survey, however, and sample numbers are therefore low.

Undoubtedly, this area has a number of acute problems with respect to the exposure of its population to toxic heavy metals. There is, therefore, considerable scope for expansion of this work. Computer controlled scanning electron microscopy has been shown to be capable of identifying different particle types, which are sufficiently distinctive to offer great potential for studying exposure routes. Information on particle size and elemental composition will be invaluable in setting priorities for exposure reduction and, ultimately, cost-effective remediation.

Further, possibilities of extending the SEM techniques to complement speciation studies concerned with human bioavailability have been discussed. Quite apart from the urgent need to set priorities for reducing risk in such conditions of extreme contamination, it should be recognised that situations, such as the one described in Lavrion, represent important locations for the study of intake and uptake of metals, and a great deal of important work can be accomplished here.

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Appendix Report 3

AN INTRODUCTION TO THE TECHNIQUE OF INDIVIDUAL PARTICLE ANALYSIS (IPA) USING COMPUTER CONTROLLED SCANNING ELECTRON MICROSCOPY (CCSEM)

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3.1. INTRODUCTION

Although many microscopy based analytical methods can be considered to be individual particle analysis techniques, the term is in this case is limited to particle characterisation by **C**omputer **C**ontrolled **S**canning **E**lectron **M**icroscopy (CCSEM). Specimen mounts are undertaken in such a way that features are separated from each other, and may be analysed in isolation [chemical analysis is undertaken by **E**nergy **D**ispersive **X**-ray analysis (EDX)]. The particle-by-particle measurement is computer controlled by linking SEM and EDX through automated image analysis software.

By identifying individual particle "types" in a sample, the technique is able to resolve sources, the emission products of which are dissimilar at the individual particle level. Conventional analyses of the bulk sample represent average values for many such particles measured together and, thus, cannot provide information on the relative contribution of different emissions.

Most of the techniques described in this section have been specially developed at Imperial College. The analyses were all undertaken on the JEOL® 733 Superprobe SEM in the Department of Geology. Particle selection and X-ray data collection were controlled by the Link Analytical® (now Oxford Instruments) programme "DIGISCAN". Data interpretation was mainly undertaken using the custom built programme MIDAS.

3.2. THE REASONS FOR AUTOMATION

Although digital image analysers cannot match the unrivalled versatility of the human eye/brain, they extend the capabilities of the human analyst in a number of important ways. In the context of the analysis of particulate material, these may be summarised as:

Increased Speed. Computer control of the electron beam enables particle location, analysis and data recording to be a great deal quicker than is possible for a human operator.

Increased Efficiency. Allied to greater speed is the fact that machines are far less subject to distraction than people. Barring malfunctions, they will proceed continuously through an operation until completion, without interruption. The increase in usage of

equipment is substantial, especially where applications are suited to long "runs" where analysis can be performed through the night.

Increased Objectivity. Machines do not get bored; or seduced by interesting shapes in the image - "pretty" particles, which distract the operator for periods far in excess of their worth in solving the problem at hand.

Increased Throughput. This is the consequence of the above factors, and substantial enhancement of throughput means that statistically significant numbers of analyses can be performed efficiently within relatively short periods.

Large data sets. The full range of multivariate statistical techniques is available to assess the quality of the data and to examine associations within it. Characteristics of populations can be examined and subdivision undertaken, at the same time as attention is paid to individual features of interest.

Naturally, there are costs associated with these advantages:

Lack of Intuition. What computers are good at is following a series of simple instructions quickly and reliably. What they cannot do is to think for themselves. Therefore, while they may take some of the drudgery out of repetitive analyses, they do not replace the expert microscopist.

Lack of Flexibility. Machines follow a series of instructions and if something unexpected happens they cannot react. Odd results (including complete failures) have to be interpreted by the operator, who then issues fresh instructions.

Information Loss. There are many sources of this and an understanding of it is vital to an evaluation of the data. Every computer programme, including those based on expert systems, are a coding of what a person wants to achieve and how he perceives the best way to achieve it. For reasons already discussed, these involve a simplification.

Opacity. The fundamental weakness of automated "black boxes" is that they do not explain the processes by which a result was achieved, and can thus conceal pitfalls. If a set of "rules" - a programme - is established by one operator, and applied by another, there may be misunderstandings of the functions the system is actually carrying out. Programmes developed by Imperial College within this research have been constructed, so that "raw" data can be examined and checks undertaken.

3.3. PRINCIPAL STAGES IN AUTOMATED ANALYSIS OF PARTICLES

These may be considered to be:

- 1. Sampling and Sample Preparation.
- 2. Calibration of SEM.
- 3. Primary image acquisition.
- 4. Definition of features of interest.
- 5. Measurement.
- 6. Assessment of data quality.
- 7. Statistical and graphical interpretation.
- 8. Classification.
- 9. Presentation of results.

3.4. SAMPLING AND SAMPLE PREPARATION

IPA is useful for the examination of solid particulate material from a number of sources and each has different sampling methods. Dust and soil obtained as solid samples are commonly disaggregated, suspended in liquid and filtered onto a surface filter, which is then mounted on a stub or slide and coated. Alternatively dry samples may be aerosolised (dispersed in a chamber by compressed air) and deposited onto doublesided tape. This is especially useful if solubility in a liquid medium is likely to be a problem. However, there will be some sorting of the sample due to variations in aerodynamic characteristics, unless it is a uniform powder.

Atmospheric aerosol can be sampled actively (filtered) or passively (on natural or surrogate surfaces). Passive samplers such as leaves, or double-sided tape, are especially easy to use, since they can often be examined directly with minimal further treatment other than coating (see below). Loading (see below) can be controlled by time of exposure.

Lint free cotton swabs soaked in particle free absolute alcohol have been successfully used to sample particulate material on the hands of young children.

Filter (or tape) loading should be controlled, so that an even distribution is obtained, which minimises overlap or aggregation of features in the image. This optimum is only achieved by experiment.

Coating of specimens usually uses carbon as the conducting layer to avoid addition of elemental peaks into the analysis, as happens with metallic coats.

Where appropriate, pre-concentration techniques can be very useful. These may include density and magnetic separations or chemical methods.

3.5. CALIBRATION OF SEM

3.5.1. SPECIMEN/BEAM INTERACTIONS IN THE ELECTRON MICROSCOPE

Any scanning electron microscope is an individual member of a family of different types of instrument, comprising several different potential micro-analytical systems. In each case, a beam of electrons is focused onto a specimen and a number of signals result. These are measured by suitable detectors which, in the case of the research reported here using a JEOL® 733 Superprobe, made use of three detected signals - secondary electrons, backscattered electrons and X-rays. Each may be used to gather images of a whole field of view in the instrument or used to gather data from individual particles if the scan of the beam is restricted to within its boundaries. It should be noted that specimen beam interactions occur within a volume of the specimen rather than at a point as is suggested by Figure 3.1. A representation of this "volume of excitation" is given in Figure 3.2.

3.5.1.1. Secondary Electrons

These are electrons that have been ejected from the specimen by the passage of a high-energy electron from the beam of the instrument. They contain a great deal of information on morphology and texture, and are commonly used to produce photomicrographs.



Fig. 3.1. Specimen/beam interactions in the electron microscope. Σχ. 3.1. Αλληλοεπιδράσεις δείγματος/ακτίνων στο ηλεκτρονικό μικροσκόπιο.



Fig. 3.2. Volume of excitation. Σχ. 3.2. Χώρος διέγερσης.

3.5.1.2. Backscattered electrons

Backscattered electrons (BSE) are high-energy electrons from the incident beam of the SEM, which have been diverted by a series of collision events in the target (sample). Because the output signal strength is proportional to the mean atomic number (the Z number), images derived from this signal may be readily subdivided based on useful threshold values (see definition of features of interest and thresholding below).

3.5.1.3. X-rays

X-rays are generated as a result of the release of energy, which accompanies the movement of an electron from an outer shell to replace a dislodged secondary electron. The amount of each element in the target is given by the output of characteristic X-rays, measured by their wavelength or energy (a technique often known as electron microprobe analysis, EPMA). For the examples described here, data were gathered using Energy Dispersive X-ray Spectroscopy (EDS). <u>The detector used in these studies can measure any element heavier than sodium</u>. The resulting spectra can be used to determine which elements are present in the particle as a whole, or at different points on its surface. The height of the peak is proportional to the number of X-ray photons detected and, thus, the relative proportion of each element present in a feature may be estimated.

Classic microprobe analysis uses optically flat specimens and standards. A number of correction factors may applied to the detected X-ray signal from the specimen. Quantitative analysis may be undertaken by calibrating the instrument with respect to standard materials. Particulate material, usually unpolished, provides a number of extra problems because factors such as secondary fluorescence or absorption become much more important (Fig. 3.3). The analysis described should, therefore, be regarded as being semi-quantitative, and different authors have adopted different approaches to estimating relative abundance of elements. It is an assumption of the method, however, that the data obtained are sufficient to differentiate between different particle types, provided that the uncertainties can be understood.



Fig. 3.3. Causes of uncertainty in analysis of rough specimens. Σχ. 3.3. Αιτίες αβεβαιότητας στην ανάλυση δειγμάτων με ανώμαλη (τραχεία) επιφάνεια.

3.5.2. OPTIMISATION OF THE SEM

Analysis is a compromise. To achieve one target (*i.e.*, speed) the operator may have to make sacrifices in other directions (*i.e.*, resolution), and he will not wish to waste resources by acquiring unnecessary information. Experiments are being carried out to establish the best calibration to undertake a given analysis.

Once an optimal system has been developed and tested, it is recorded and complied with for all other analyses in the experimental set, to ensure that real differences between samples are recorded, rather than changes in analytical conditions.

3.6. IMAGE ACQUISITION

Digital imaging is the process by which an essentially continuous range of values is changed into a series of discrete numeric values suitable for storage and manipulation. These numbers represent expressions of space and intensity (tone). In the JEOL_®/LINK_® system, the spatial division is into a square grid of picture points (pixels), the size of which may be set to 128, 256, 512, 1024, 2048 or 4096. The actual distance between grid points in relation to the field of view on the specimen depends on the magnification in the SEM.

The intensity is displayed as 256 grey levels. What this intensity actually represents obviously corresponds to the input signal being monitored - secondary or backscattered electrons or X-rays. In practice the BSE image is the signal most frequently used as the primary image for feature selection on our system. The image is then processed to select features for analysis, which results in a binary image.

3.7. DEFINITION OF FEATURES OF INTEREST

The intensity of the input signal is expressed as a number (0-255) for each image pixel. The principle of particle selection is, therefore, very straightforward - a decision making function is generated, which sets criteria for acceptance or rejection based on the measured parameter. In other words **threshold** values may be established which define the acceptability, or otherwise, of each pixel. This produces a binary image (*i.e.*, those pixels that fall within the thresholds are given the value 1, and those that do not are set to zero). These can be plotted as black and white to illustrate the effect of the current thresholding decision. It is relatively straightforward to then agglomerate sets of touching "acceptable" pixels into features for analysis (*i.e.*, the beam is driven to touching 1 value (white) pixels and skips over zero value (black areas).

Backscatter contrast may, therefore, be used to perform the equivalent of an on-line density separation - by the technique of BSE thresholding. By the selection of suitable upper and lower thresholds, features of any given band of mean atomic number can be isolated. Suitable intensity values from X-ray maps may also be used. The controlling image analysis program (DIGISCAN_®) uses this information to locate and size any features in the resulting binary image. All touching pixels in a feature are summed to give its two dimensional area. The beam is then driven back under computer control to each feature in turn for the collection of shape and X-ray information.

3.7.1. IMAGING STANDARDS

To ensure comparability between different analyses on different occasions it is necessary to establish some standard conditions, which will apply to all measurements in a data set. In chemical analysis, this is confirmed by the analysis of check standards of known composition, before analysing any samples. In just the same way, SEM conditions are set according to the particular protocol for the analysis in hand, but must then be checked by examination of the waveform for a standard material. A reliable method of achieving this is to provide an image standard, since precisely the same features can be used to set the waveforms for every analysis. A number of particles of each of the following minerals/metals was, therefore, mounted into a suitable standard holder: Quartz (SiO₂), rutile (TiO₂), iron oxide (Fe₃O₄), barium sulphate (BaSO₄), cadmium metal (Cd), lead sulphate (PbSO₄), and lead metal (Pb). These represent an ascending series of mean atomic number and can, thus, be used to calibrate the BSE signal with high reproducibility.

3.8. MEASUREMENT

Once the features have been identified in the image, the beam is driven back to each in turn for collection of shape and X-ray data.

3.8.1. SHAPE DATA

DIGISCAN[®] does not record anything but very simple shape data. The total number of pixels occupied by a particle in the binary location image is recorded as its 'true area'. This is the area scanned by the beam, but its value is very dependent on threshold selection, as discussed previously. Any holes in the image of the particle are not included and the beam is stepped over them.

Diameters (maximum, minimum and mean) are calculated on the basis of feret projections. As Figure 3.4 shows, these comprise pairs of parallel tangents, which enclose the particle. Up to sixty pairs may be selected in the DIGISCAN® initialisation and, in practice, this number was always chosen. The approach is somewhat limited, because different shapes may have similar projected diameters. The ratio between maximum and minimum diameter is used to calculate aspect ratio. A final parameter, convex area, is calculated by joining the touch points of the feret pairs and recording the enclosed area. It is suggested, in the DIGISCAN® program manual, that a ratio between true area and convex area might give an indication of indentation, but experience has proved otherwise.

3.8.2. CHEMICAL ANALYSIS

The energy dispersive X-ray spectrum is represented as a histogram of the total X-ray photons counted by each channel of the multi-channel analyser in the detection system (Fig. 3.5). Each element, detectable by the system, has one or more characteristic energy levels at which X-rays will be detected, provided it is present in the sample. A background (Bremstrahlung) radiation distribution is generated by random noise, and the elements present show as peaks superimposed on this. These peaks span several channels in the multi-channel analyser and a convenient way to summarise the data is to delimit a *"region of interest"* (often termed *"to paint a window"*) over the channels

concerned and to record the total counts in the whole region. This leads to a significant reduction in required storage space, since the counts for each element are now represented by a single number, and it is not necessary to record a value for each channel. The windows are represented by the darker regions in Figure 3.5.



Fig. 3.4. Measurement of particle shape in automated SEM by use of Feret projections. Σχ. 3.4. Μέτρηση του σχήματος των σωματιδίων με το αυτοματοποιημένο ηλεκτρονικό μικροσκόπιο (SEM) χρησιμοποιώντας τις προβολές *«Feret»*.



Fig. 3.5. An example of an energy dispersive X-Ray spectrum showing defined regions of interest for the estimation of selected elements.

Σχ. 3.5. Παράδειγμα ενός φάσματος διασκορπιζόμενης ενέργειας ακτίνων-Χ όπου οριοθετούνται περιοχές ενδιαφέροντος για τον προσδιορισμό επιλεγμένων στοιχείων.

3.8.3. X-RAY CORRECTION FACTORS

For the automated particle analysis using the DIGISCAN® program, up to 25 regions of interest are defined on the spectrum, and the numbers of X-ray counts falling in each region (or "window") are stored. Several regions are defined on parts of the spectra where no elemental peaks are expected to occur. These are used to subtract the background counts from under each of the other regions of interest, which are defined at the energy levels characteristic of the elements desired to measure. This is known as "background correction".

In certain cases, a peak for one element will overlap a peak for another. The "M" line for lead for example, falls in the same region as the "K" line for sulphur. Lead, however, has other lines (the "L series") visible in the 25 kV spectrum and, therefore, lead is estimated from one of these regions and the number of counts that should occur in the "M" region is predicted and subtracted from the joint peak. The remainder can be designated as sulphur. The proportion of one peak subtracted from another in this manner is termed the "overlap correction".

A final correction factor (*"efficiency factor"*) allows a linear scaling of the elemental analysis to account for differences in detector efficiency between elements. The set of definitions of X-ray regions of interest, and the correction factors to be applied to them, is stored in a separate computer file, termed a "*window file*", since it will be used repeatedly to correct the results for all measured features.

3.8.4. NORMALISATION

Different sized particles of the same material will yield different absolute totals of X-ray counts in each of the specified regions of interest. The results are, therefore, normalised by expressing them as a percentage of the total sum of the counts in all the regions of interest (after correction). This normalisation procedure means that apparent values for an element may appear very similar between two features, where in fact the true percentage is very different. Thus, carbon is not detectable, but forms a large percentage of the chemical composition of, for example, coal particles. The remaining elements may occur as traces, but appear to be major constituents once the normalisation has occurred. Thus, a full quantitative analysis by an appropriate method might give two analyses:

- 1. Carbon = 97%, Si = 1%, Al = 2%
- 2. Si = 33%, Al = 25%, K = 20%, Ca = 22%.

but a normalised analysis of the elements detectable in the current equipment would give an identical Si percentage (33%). In this type of analysis, it is usually possible to find other elements on which to perform a split, or to use other characteristics of the particles.

3.9. DATA QUALITY - EXAMINATION OF NEGATIVE VALUES, 'FIT' AND 'T-COUNT'.

In this type of semi-quantitative analysis, average factors are derived which work reasonably well for the majority of situations. They, therefore, do not work optimally for every feature and over-correction may occur. If the spread around the "true" value of a known standard material is examined, insight can be gained into the variability introduced by the analysis.

A special case occurs where an element is known to be absent and apparent negative concentrations are recorded. A plot of the estimates for a number of such features can be termed the "zero population" (Fig. 3.6). *Negative values clearly have no literal chemical meaning and can be <u>set to zero</u>, but they are commonly retained to allow assessment of the overall data quality, since several elements in a window file will be absent in any given feature. The total negative values will thus give a rapid indication of the way the correction factors are behaving. A parameter known as <i>'fit'* has



Fig. 3.6. An example of a "Zero Population" (population "A"), which demonstrates the distribution of estimated values around the "true" analysis (zero in this case). Σχ. 3.6. Παράδειγμα ενός «Μηδενικού Πληθυσμού» (πληθυσμός "A"), ο οποίος δείχνει την κατανομή των εκτιμηθεισών τιμών γύρω από την «πραγματική» ανάλυση (σ' αυτή την περίπτωση μηδέν).

been derived to assess this for an individual feature. *'Fit'* is a scaled ratio between positive and negative values, and the larger it is, the less efficiently the correction factors are operating.

Large values of fit may indicate that an analysis is unsuitable and should be rejected. In other cases, however, the apparent negative values contain useful information. This information relates to the detection of elements, which are not specifically included in a window file, *i.e.*, where an element is detected, and has a peak occurring in a portion of the spectrum, which had been delimited for the assessment of background radiation.

3.10. WINDOW FILES - GENERAL

Data from DIGISCAN_® are not always easy to interpret at first glance. Since, they are normalised, missing elements are not apparent. Further, due to limitations in the correction routines (allowing only a single overlap correction for example), there may be perfectly valid analyses, which give a positive value to an element that actually does not occur in the sample. It is worth stressing, therefore, that in many of the cases reported the object of the analysis is to <u>distinguish</u> different types of particles from each other, in order to classify and count them. It is not important to have an 'accurate' analysis for each particle defined, as one that gives the 'true' percentage of each element, as long as the analysis is 'precise' in the sense that a material always gives the <u>same</u> result, and that other materials give a different (though also constant) result.

The ability to define 25 regions of interest, means that in complex situations choices have to be made about which elements to include in the window file. Results from a number of analyses must have been obtained using the same window file if they are to be fully comparable.

3.11. CLASSIFICATION - GENERAL

A classification scheme, in this case, is simply a set of particle descriptions (limits are set on sufficient parameters to separate out a particular particle type). When a feature is analysed, the computer searches through the list until a description is found that fulfils the conditions. In the present case the feature is then ascribed to that class without further search (other systems use some form of "best fit" criterion).

The classes can be developed in several ways. Analysis of a complex unknown sample may be undertaken and the whole data set examined for any obvious groups or associations within it. This is undertaken as follows. Preliminary subdivisions are made by examination of the distribution of single elements using *quantile* plots and pairs of elements using *scatter* plots. Figures 3.7 and 3.8 are examples of such plots. In each case, the value obtained for the amount of the element in every individual particle in a data set, or combination of data sets, is plotted.

Use is made of any obvious discontinuities to split the data into the various populations revealed. The mechanism for subdivision in the scatter plots is to draw boundaries around any obvious clusters, and to use these ranges to select a subset of the data. The quantile plots show breaks in slope if subgroups exist in the data set, which can then be split at the point of change. These derived subsets are then examined for all the other stored parameters to produce a description of the particle type.

Subsets of the data can be examined separately to assess the homogeneity of particle types described from plots of the entire data set. If no further potential for subdivision is apparent, the particle type description is added to the classification scheme. This temporary selection feature is particularly useful for examining unclassified particles in isolation, as further work may be necessary on them.

Other methods of producing classes, they either start with known standard materials or samples from known emission sources, and seek to build-up a library of chemical classes, each containing the *"fingerprint"* or *"signature"* of a different material, which has been examined in isolation, *i.e.*, clay mineral standards. This also forms a classification scheme, and if "unknown" particle types remain, then new source type materials have to



Fig. 3.7. Example of a "quantile plot" for Si. Such plots show normal distributions as a straight line; inflected curves represent mixed populations.

Fig. 3.7. Παράδειγμα ενός «τεταρτημοριο-γραφήματος» για το πυρίτιο (Si). Τέτοια διάγραμματα απεικονίζουν τις κανονικές κατανομές ως ευθείες γραμμές, ενώ οι μικτοί πληθυσμοί αντιπροσωπεύονται από τις κυρτές καμπύλες.





Σχ. 3.8. «Διασπορόγραμμα» του αργιλίου (AI) και πυριτίου (Si), το οποίο είναι χρήσιμο στην αναγνώριση ομάδων που αντιπροσωπεύουν διαφορετικούς τύπους υπο-πληθυσμών των σωματιδίων.

be identified and examined. Empirical trials of likely element combinations derived from the operator's experience or relevant scientific literature can also be useful.

The plots may show that there is a large number of unclassified features, and perhaps highlight the intermediate position of many of these features between clusters of groups, which have been classified. Further work would have to be undertaken to assess whether this was due to aggregation of particles of two or more of the described types, or to the presence of as yet undescribed particle types. Quite clearly, however, this capability of examining distributions, and placing unclassified features in a variety of contexts on plots of different element combinations, has great power in the assessment of the sample in relation to a classification. Nevertheless, even in a fully developed scheme, the unclassified features can often provide extra information.

3.12. PRACTICAL PROBLEMS – AGGREGATION

One of the most troublesome problems in this type of analysis concerns aggregation of features/particles. Sample preparation is designed to achieve an optimal spread of particles such that as many as possible can be analysed in a single field but as few as possible overlap. If fields are selected visually, rather than on a regular grid then areas with large numbers of aggregates can be avoided.

In systems that store an image of each field analysed, operator examination of particle morphology may be undertaken without the need for re-examination in the SEM. This will often be sufficient to address the problems raised above. Automated analysis of shape and morphology would clearly be a useful adjunct here, but development of such systems lags far behind chemical classification. Current developments of the Imperial College system are aimed at providing better textural and morphological information within the automated analysis data set.

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ANNEX 3.1

CLASSIFICATION SCHEME

Number of classes = 24

Column 1	Column 2	Column 3	Column 4
@ Fe and S 1 developed from LAV1 Pyr 1 S 11.00 45.00 Fe 40.00 75.00 * 2 developed from LAV16 Pyr 2 Fe 24.00 48.00 Pb -2.00 2.00 S 50.00 70.00 Si -5.00 2.00 S 50.00 70.00 Si -5.00 2.00 Sb -1.00 2.00 Zn -1.0 1.00 Mn -2.0 2.00 Mn -2.0 2.00 * 3 developed from LAV 5 Pyr 3 Fe 20.0 55.0 S 30.0 50.0 Zn 3.0 25.0 Mn 0.0 25.0 * 4 Developed from LAV 19 Pyr 4 Fe 10 60 S 35 60 Cu -1 1 Zn 0.5 4 Na -2 0 * @ Fe/Ca/Si/Zn 5 developed from LAV18 FeCaSiZn Fe 21.00 45.00 Ca 17.00 42.00 Si 8.00 30.00 Zn 2.00 10.00 *	Fe + 6 Various (LAV21) Fe rich Fe 75.00 100.00 * 7 from LAV1 Fe 20-80 Fe 20 80 * @ Pb + 8 From LAV 12 & 21 PbCl Pb 12.0 35.0 CI 60.0 85.0 * 9 From LAV 12 & 21 PbS Pb 15.0 65.0 S 10.0 80.0 * 10 from LAV1 Pb>60% Pb 60 100 * 11 from LAV 5, 14 & 20 Intermed Pb Pb 10 60 * @ Zn+ 12 from LAV 13 & 14 ZnSiFe Zn 25.00 70.00 Si 15.00 50.00	Fe 0.00 35.00 * 13 from LAV1 Mn/Zn Mn 20 50 Zn 25 60 * 14 from LAV 5, 14 & 20 Mn/Zn/S Mn 5 45 Mn 5 45 25 S 45 65 * 15 from LAV1 Fe/Zn + Fe Fe 15 75 Zn 15 from LAV1 Fe/Zn + Fe 15 70 S -2500 -30 * @ As Bearing 16 from LAV12 As bearing As bearing As 1 70 S -2500 -30 * @ HiSb 17 developed from LAV11 Sb rich Ca 30.00 55.00 Sb 23.00 45.00 Pb -10.00 20.00 Fe -3.00 1.00 As -250.00 -50.00 Si -18.00 -9.00 S -250.00 -50.00 <td>Contain V 18 from LAV 20 V/Na + Ba 5 90 Na 7.5 65 * @ Ca + 19 from LAV 6 CaS Ca 20.0 50.00 S 20.0 50.00 Fe -4.0 4.0 * 20 from LAV6 CaS + Fe Ca 20.00 50.00 S 20.0 50.00 Fe 4.0 40.00 * 21 Various CaP Ca 50 65 P 20 30 Pb -2 2.5 * 22 from LAV6 Ca only Ca 70.00 100.0 * 23 Various Intermed Ca Ca 20 70 * @ Al/Si + 24 from LAV1 Al/Si + Al 5 50 Si 24 80 *</td>	Contain V 18 from LAV 20 V/Na + Ba 5 90 Na 7.5 65 * @ Ca + 19 from LAV 6 CaS Ca 20.0 50.00 S 20.0 50.00 Fe -4.0 4.0 * 20 from LAV6 CaS + Fe Ca 20.00 50.00 S 20.0 50.00 Fe 4.0 40.00 * 21 Various CaP Ca 50 65 P 20 30 Pb -2 2.5 * 22 from LAV6 Ca only Ca 70.00 100.0 * 23 Various Intermed Ca Ca 20 70 * @ Al/Si + 24 from LAV1 Al/Si + Al 5 50 Si 24 80 *
			ļ

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Name	Family
Sb rich	High Sb
As bearing	As bearing
Pyr 4	Fe and S
Pyr 3	Fe and S
Pyr 1	Fe and S
Pyr 2	Fe and S
FeCaSiZn	Fe/Ca/Si/Zn
Fe rich	Fe+
PbCl	Pb+
PbS	Pb+
CaS	Ca+
CaS + Fe	Ca+
Ca only	Ca+
ZnSiFe	Zn+
Mn/Zn/S	Zn+
Mn/Zn	Zn+
Fe/Zn+	Zn+
Pb>60%	Pb+
Al/Si+	Al/Si+
Fe 20-80	Fe+
CaP	Ca +
Intermed Ca	Ca+
V/Na+	Contain V
Intermed Pb	Pb+
	Name Sb rich As bearing Pyr 4 Pyr 3 Pyr 1 Pyr 2 FeCaSiZn Fe rich PbCl PbS CaS CaS + Fe Ca only ZnSiFe Mn/Zn/S Mn/Zn Fe/Zn+ Pb>60% Al/Si+ Fe 20-80 CaP Intermed Ca V/Na+ Intermed Pb

Order of examination of classes (.cla file)

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Appendix Report 4

SUBSURFACE GEOCHEMISTRY OF THE LAVRION URBAN AREA: Drill-hole and vertical profile results

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4.1. INTRODUCTION

The objective of the subsurface geochemical study of the Lavrion urban area was to determine:

- 1. the level and depth of contamination in the loose overburden materials, including metallurgical processing wastes, residual and fluvial sediments, and
- 2. the vertical distribution and possible vertical movement of contaminants, which could endanger in the future ground-water resources.

For this purpose, twenty-two drill-holes and two vertical profiles were executed (Map 2.14 in Volume 2). Drill-hole drilling and vertical profile sites were selected on the basis of detailed mapping of the metallurgical processing wastes at a scale of 1:5000 (Map 2.3 in Volume 2). Out of the twenty-two drill-holes only twenty were sampled; two drill-holes were used for the determination of physical properties, *i.e.*, G1 and G8, and one due to technical problems (G20) was not carried out. Before sampling a detailed log of lithology was made, and samples were taken according to macroscopic stratigraphic differences of overburden materials.

Sampling, sample preparation and analysis are described in Chapter 2A (Section 2A.2.8, p. 30), Chapter 2A (Section 2A.3.8, p.32) and Chapter 2B (Section 2B.2.7.1, p.42) respectively in Volume 1 of this report. Only six of the forty-six elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Ga, Ge, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, U, V, W, Y, Zn, Zr) determined on the samples are presented, together with pH, in this report, *i.e.*, Cd, Pb, Zn, As, Hg and Sb, since these are considered to present the greatest potential hazard in the Lavrion area, and especially to ground water resources.

The descriptive and quantitative parts of the drill-hole logs were plotted with the program Drill-tools compiled by E. Vassiliades in 1994. Two plots have been drawn for each drill-hole, *i.e.*, showing (1) the distribution of Cd, Pb, Zn and pH, and (2) the distribution of As, Hg, Sb and Hg in bar form, and their minimum and maximum values. In both cases, there is a coloured pattern log of the stratigraphy and a short coded description. Abbreviations used can easily be deciphered in conjunction with the logs of each drill-hole, which are given in this chapter.

It is noted for ease of reading reference to Tables and Figures are made after the title of each drill-hole. References to other volumes of this report are made at the relevant point within the text.

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4.2. DRILL-HOLE DESCRIPTION

4.2.1. DRILL-HOLE G2 (Table 4.1, Figs. 4.1-.2)

Drill-hole G2 was sited on the pyrite tailings at the Komobil beach (Map 2.14 in Volume 2). The proportion of pyrite is very high up to a depth of 2.30 m. From 2.3 to 4.50 m pyrite is disseminated, and at a greater depth its proportion is minor. This distinct change at a depth of 2.30 m with the high clay content layer and the reduction in the proportion of pyrite is well shown by the geochemistry. It is worth mentioning that this area generates acid drainage and up to a depth of 2.30 m the pH of sludge is 2.42. At a depth of 2.30 m pH rises to 5.88, and from 2.80 m downwards it is in the alkaline range (>7.5). There is, therefore, a definite pH barrier at a depth of 2.30 m.

It is quite apparent from the above description that mobility of elements is governed by the generation of acid drainage and resulting low pH conditions. Elements with low to medium mobility under all pH conditions, such as As and Sb, have their greatest concentrations up to a depth of 2.30 m (36211 ppm As; 252 ppm Sb) (Table 6.2, p.132, Volume 1); mobile elements as Pb²⁺, Cd²⁺, Zn²⁺ and Hg²⁺ with pH of hydrolysis of 6.0, 6.7, 7.0 and 7.3 respectively, begin to precipitate when there is an increase in pH (Table 6.1, p.131, Volume 1). Hence, the greatest concentration of these elements is below a depth of 2.30 m.

Regarding subsurface contamination, it is quite obvious from the results that the whole length of the drill-hole is contaminated down to a depth of 5 m. Undoubtedly, contamination should go even deeper, since at a depth of 5 m the concentration of toxic elements are: Cd 95 ppm, Pb 14400 ppm, Zn 15300 ppm, As 1763 ppm, Hg 1 ppm and Sb 250 ppm.

Depth	Description
 (<i>m</i>)	
0-0.60:	Greyish material with pyrite, iron oxides and quartz.
0.60-1.30:	Greyish material with pyrite, iron oxides and quartz.
1.30-2.30:	Pale grey material with pyrite and quartz.
2.30-2.80:	Brownish-yellow material with high clay content, quartz and disseminated pyrite
	(similar to G4: 0-0.48 m).
2.80-3.40:	Greyish-yellow fine-grained material with quartz and disseminated pyrite.
3.40-4.50:	Greyish fine-grained material with quartz and disseminated pyrite.
4.50-5.00:	Greyish-yellow fine-grained material with quartz, minor pyrite and the odd
	sandstone pebble.

Table 4.1. Log of drill-hole G2: pyrite tailings at Komobil beach. Πίνακας 4.1. Περιγραφή γεώτρησης G2: πυριτούχα απορρίμματα στην παραλία της Κομομπίλ.

Blank back page Λευκή οπίσθια σελίδα ΕΡΓΟ: ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΥΣ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G2

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

BAOOD	ΔΙΘΟΛΟΓΙΚΗ					0		0		
m	томн	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΟΝ	0.5	94.9	7350.0	1030.0		27000.	2.0	7.6
60		Γκρίζο υλικό, py, FeOx, Qtz								
.00		Γκρίζο υλικό, py, FeOx, Qtz					•			
.30		Γκρίζο υλικό, py, Qtz								
30		ΚΚι, Qtz & αργιλικά ορυκτά								
3.40		ΓΚι υλικό, py, Qtz								
		Γκρίζο υλικό, py, Qtz								
1.50		ΓΚι, ολίγος py. Qtz. ψαμμίτης								
5.00	0 0 0		V///////	1/1	VA	 1///	11		VIL	111111

ΣΧΗΜΑ 4.1, σελίδα 4.2

ΕΡΓΟ: ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΥΣ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G2

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			As (ppm)	Hg (ppm)	Sb (ppm)	pH
ΒΑΘΟΣ	ΛΙΘΟΛΟΓΙΚΗ	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	63.0		0.0	
0.60		Γκρίζο υλικό, py, FeOx, Qtz	17	0.5	39	3.6
0.00 .		Γκρίζο υλικό, py, FeOx, Qtz				
1.30 .		Γκρίζο υλικό, py, Qtz				
2.30		ΚΚι, Qtz & αργιλικά ορυκτά				
3.40		ΓΚι υλικό, py, Qtz				
		Γκρίζο υλικό, py, Qtz				
4.50 .		ΓΚι, ολίγοs py. Qtz. ψαμμίτης				
5.00 .	0-0-0		1			///////////////////////////////////////

4.2.2. DRILL-HOLE G3 (Table 4.2, Figs. 4.3-.4)

The drill-hole was sited on the oxidised pyrite tailings within the premises of the smelter at Kiprianos (Map 2.14). Due to the intense oxidation and downward percolation of acid drainage over a period of years pH is presently in the alkaline range (>7.5). At a depth of 3.90-4.90 m there is a sudden rise in the concentration of all elements. Below this section there is an abrupt drop in the level of all elements, except Zn. There appears, therefore, to be a geochemical barrier at this depth, and only the most mobile elements, such as Cd and Zn, are present in comparatively high levels below this depth. The greatest concentrations of Zn occur, in fact, below this depth, and reach 55,200 ppm at the end of the drill-hole (depth: 6.00-6.50 m).

It is quite apparent, from the results, that the whole length of the drill-hole is contaminated down to a depth of 6.50 m, and contamination should go even deeper, since at this depth the concentration of toxic elements are: Cd 131 ppm, Pb 1610 ppm, Zn 55,200 ppm, As 292 ppm, Hg <1 ppm and Sb 21 ppm.

Table 4.2. Log of drill-hole G3: pyrite tailings within smelter premises at Kiprianos. Πίνακας 4.2. Περιγραφή γεώτρησης G3: πυριτούχα απορρίμματα στο χώρο του εργοστασίου εμπλουτισμού στον Κυπριανό.

Depth	Description
(<i>m</i>)	
0-2.50:	Brownish-yellow fine-grained material with disseminated quartz grains (similar to G4: 0-0.48 m).
2.50-3.90:	Greyish-yellow fine-grained material with quartz grains (similar to G5: 0-1.90 m).
3.90-4.90:	Brownish-yellow fine-grained material with quartz grains, and greyish concretions of fine-grained pyritiferous material.
4.90-6.00:	Conglomerate consisting from angular pebbles of marble and schist, which are cemented by calcareous argillaceous sandstone.
6.00-6.50:	Conglomerate consisting from angular pebbles of marble and schist, which are cemented by calcareous argillaceous sandstone.

Blank back page Λευκή οπίσθια σελίδα ΕΡΓΟ: ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΥΣ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G3

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

ΒΑΘΟΣ	ΛΙΘΟΛΟΓΙΚΗ	TEPIPPATH SYHWATISMON		0	0.	0.0	0.	0.0		
m	томн		15.0	260.	1610	3320	4050	5520	7.5	7.7
		ΚΚι λεπτόκοκκο υλικό. Qtz						•		
3.90 -		Γκρ λεπτόκοκκο υλικό, Qtz						7772		
4.90 _		ΚΚι λεπτόκοκκο υλικό, Qtz								
2.00	0 1 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	Κροκάλες από Mrb και Sch								
	0 0 0 0	Κροκάλες από Mrb και Sch			4					
5.50 _			VIII	IA I			VIII	//////	V////	11/1

ΣΧΗΜΑ 4.3, σελίδα 4.5

ΕΡΓΟ: ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΥΣ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G3

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

m	TOMH	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	292.2	25413	0.5 2.5	20.6	480.0	7.5
			-					
		ΚΚι λεπτόκοκκο υλικό, Qtz						
2.50		Γκρ λεπτόκοκκο υλικό. Qtz						
4.90 _		ΚΚι λεπτόκοκκο υλικό, Qtz						
6.00 _	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	Κροκάλες από Mrb και Sch						77777777777777777777
6 50	0 0 0	Κροκάλες από Mrb και Sch						

ΣΧΗΜΑ 4.4, σελίδα 4.6
4.2.3. DRILL-HOLE G4 (Table 4.3, Figs. 4.5-.6)

The drill-hole was sited, as G3, on the oxidised pyrite tailings within the premises of the smelter at Kiprianos (Map 2.14). The pH in this case is in the acid range (3.80-6.94) down to a depth of 1.90 m; the remaining profile has alkaline pH values. The most mobile elements, Cd and Zn, have apparently been leached down to a depth of 4.75 m; the greatest concentration of these two elements occurs in the conglomeratic layer. The different leaching characteristics of the less mobile elements, such as Pb, As and Sb, is depicted by their patterns, which show comparatively moderately high concentrations down to a depth of 4.30 m. For these three elements the bottom section (4.30-4.75 m) of the grey fine-grained clayey calcareous material appears to be a geochemical barrier, since the levels are comparatively higher from the previous sections. The highest concentrations of Pb (7380 ppm), As (4325 ppm) and Sb (73.3 ppm) occur in the underlying conglomerate, and specifically in the top section (4.75-5.00 m).

It is quite apparent from the results that the whole length of the drill-hole is contaminated down to a depth of 7.80 m, and contamination should go even deeper, since at this depth the concentrations of toxic elements are: Cd 180 ppm, Pb 363 ppm, Zn 73,000 ppm, As 84 ppm, Hg <1 ppm and Sb 7 ppm.

Depth	Description
 (<i>m</i>)	
 0-0.48:	Brownish-yellow fine-grained material with disseminated quartz grains (similar
	to G3: 0-2.50 m).
0.48-0.78:	Brownish-grey fine-grained material with disseminated quartz grains and iron
	oxides. At a depth of 0.48-0.58 cm there occur a compact layer with iron
	oxides.
0.78-1.90:	Brownish-yellow highly compact clayey material, slightly coarser than above
	section, with disseminated quartz grains and iron oxides.
1.90-2.70:	Grey very fine-grained calcareous material.
2.70-3.50:	Grey fine-grained material with concretions of yellow calcareous clayey
	material.
3.50-4.30:	Grey fine-grained clayey calcareous material with iron oxide staining from 3.50
4.30-4.75:	to 5.00. The three different sections were sampled on the basis of minor colour
4.75-5.00:	and textural differences.
5.00-5.80:	Tertiary deposits made from conglomerate with marble and angular schist
5.80-6.50:	pebbles, which are cemented by a calcareous sandstone matrix; locally there
6.50-7.50:	are calcite crystals and is porous. The four-sample division from 5.00 to 7.80
7.50-7.80:	m is based on minor visual differences.

Table 4.3. Log of drill-hole G4: pyrite tailings within smelter premises at Kiprianos. Πίνακας 4.3. Περιγραφή γεώτρησης G4: πυριτούχα απορρίμματα στο χώρο του εργοστασίου εμπλουτισμού στον Κυπριανό.

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G4

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			Cd (ppm)	Pb (ppm)	Zn	(ppm)	pH
ΒΑΘΟΣ	ЛІӨОЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	0.9	63.0	530.0	00000	8.
	<u> </u>	ΚΚι, αργιλικό με κόκκουs Qtz	- 0				
0.48		ΚΓκρ, αργιλικό, Qtz, FeOx					
1.00		ΚΚι, αργιλικό, Qtz, FeOx				•	
1.90		Γκρίζο πολύ λεπτόκοκκο υλικό					
2.70		Γκρ. λεπτομερές αργιλικό υλικό					
3.50		Γκρ, αργιλικό, ανθρακικά, FeOx					
4.50		Γκρ, αργιλικό, ανθρακικά, FeOx					
4.75 5.00	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Κροκ/γές, κορήματα Mrb & Sch				A	
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Κροκ/γές, κορήματα Mrb & Sch					
5.80	-~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Κροκ/γές, κορήματα Mrb & Sch					
6.50	-~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Κροκ/γές, κορήματα Mrb & Sch					
7.50	-~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Koor / ris roomugra Mrh & Sch				HA	
7.80	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	hpok/jes, kopijuura mi b a seli	VIIIA	11	1////	11/1/	

ΣΧΗΜΑ 4.5, σελίδα 4.8

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G4

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

		·	As (ppm)	Sb (ppm)	pH
ΒΑΘΟΣ	ΛΙΘΟΛΟΓΊΚΗ	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	5.0		
m	TOMH		83.7 432	6.6	3.8
	0 - 0 - 0	KK, and the restrong Ota			
0.48	0 0 0 0	Mat, appratio pe nonous giz			
	0 0 0 0	ΚΓκρ, αργιλικό, Qtz, FeOx	T I	a -	
0.78	0 0 0 0		8	4	
	0 0 0 0				
	0-0-0	ΚΚι. αργιλικό. Qtz. FeOx			1
	0-0-0				
1.00	0 - 0 - 0				
1.90	- 0 <u>- 0</u>			777	
	0 - 0 - 0	Fun /to moto to make and and			
	0 _ 0 _ 0	TEPILO HOND REHTORORRO ONTRO			
2.70	0-0-0				
	0 - 0 - 0				
	0 0 0 0	Γκρ, λεπτομερές αργιλικό υλικό			
0.50	0-0-0				
3.50	<u> </u>			11/m	
	°°°°°°°°	Γκρ, αργιλικο, ανυρακικα, ΓεΟχ			
4.30	000000000		A	1/1A	
		Γκρ. αργιλικό, ανθρακικά, FeOx			
4.75	00000000			1111111	
5.00	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Κροκ/γές, κορήματα Mrb & Sch			
	~~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Κροκ/γές, κορήματα Mrb & Sch			
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
5.80	-~~~~~		22	H	
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Kong / wis Konnung Mrb & Sch		E	
	~~~~~				
6.50	-~~~~~~	· · · · · · · · · · · · · · · · · · ·		A	
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Κροκ/γές, κορήματα Mrb & Sch			
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
7.50	_~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Κροκ/γές, κορήματα Mrb & Sch			

ΣΧΗΜΑ 4.6, σελίδα 4.9

4.2.4. DRILL-HOLE G5 (Table 4.4, Figs. 4.7-.8)

The drill-hole was sited on the pyritiferous sand at the Kiprianos beach (Map 2.14). The pH although in the alkaline range is higher in the top section (pH 8.1), and gradually becomes lower to a value of 7.5 at the bottom. The tendency of all elements concentrations to increase from top to bottom suggests that there were leached downwards.

It is quite apparent from the results that the whole length of the drill-hole is contaminated down to a depth of 6.50 m, and contamination should go even deeper, since at this depth the concentrations of toxic elements are: Cd 89 ppm, Pb 6860 ppm, Zn 29,000 ppm, As 8360 ppm, Hg <1 ppm and Sb 72 ppm.

Table 4.4. Log of drill-hole G5: pyritiferous sand at the Kiprianos beach.

Πίνακας 4.4. Περιγραφή γεώτρησης G5: πυριτούχοι άμμοι στην παραλία του Κυπριανού.						
Depth	Description					
(<i>m</i>)						
0-1.90:	Greyish yellow fine-grained material with disseminated quartz.					
1.90-2.50:	Grey fine-grained material with pyrite and quartz.					
2.50-3.70:	Grey fine-grained material with pyrite and quartz.					
3.70-4.30:	Grey fine-grained material with pyrite and quartz.					
4.30-5.20:	Pale grey fine-grained material with pyrite and quartz.					
5.20-6.50:	Grey fine-grained material with pyrite, and quartz; a few quartz grains are					
	coated with iron oxide.					

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G5

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

ΒΑΘΟΣ	ΛΙΘΟΛΟΓΙΚΗ	TEPIPPAGH SYHMATISMON			0.	0.0	
m	томн		1.4	281.(6860	0.078	7.5
		ΓΚι, λεπτόκοκκο υλικό με Qtz				•	
.90 .		Γκρ λεπτόκοκκο υλικό με Qtz.py					
2.50 _		Γκρ λεπτόκοκκο υλικό με py, Qtz					
1.30 -		Γκρ λεπτόκοκκο υλικό με py,Qtz					
.20 _		Γκρ λεπτόκοκκο υλικό με py.Qtz					
		Гкр. ру, Qtz, FeOx					
.50 _	• • • • •				A		

ΣΧΗΜΑ 4.7, σελίδα 4.11

APIOMOS EPFOY LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G5

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

DAGOT	ATRONOTIVIT				Section 2
m m	ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	172.7	6.1	7.5 8.1
		ΓΚι, λεπτόκοκκο υλικό με Qtz			
L.90 2.50		Γκρ λεπτόκοκκο υλικό με Qtz, py			
		Γκρ λεπτόκοκκο υλικό με py, Qtz			
3.70 4.30		Γκρ λεπτόκοκκο υλικό με py.Qtz			
		Γκρ λεπτόκοκκο υλικό με py.Qtz			
5.20		Г <i>кр.</i> ру. Qtz. FeOx			
3.50				VIIIIIIII	

ΣΧΗΜΑ 4.8, σελίδα 4.12

4.2.5. DRILL-HOLE G6 (Table 4.5, Figs. 4.9-.10)

The drill-hole was sited on the pyritiferous tailings at Kavodokanos (Map 2.14). This is one of the drill-holes that reached bedrock at a depth of 7.40 m. Hence, local background conditions can be estimated. The pH is in the alkaline range; it varies, in the pyritiferous tailings from 7.76 to 7.86, and in the marble from 8.12 to 8.34. The highest concentrations for all elements are in the top section of the pyritiferous tailings (0-1.0 m). There is a minor variation in the distribution of elements in the remaining section of the pyritiferous tailings, suggesting that the composition of the wastes is approximately similar.

As has already been noted, this is one of the drill-holes that have penetrated the local bedrock, in this case marble. The whole section of the pyritiferous tailings has high toxic element concentrations down to the bedrock, *e.g.*, Cd 22 ppm, Pb 4070 ppm, Zn 7000 ppm, As 4098 ppm, and Sb 22 ppm. Since, the marble is highly fractured it appears that its top section between 7.40-8.20 is slightly contaminated. Whereas, the lower marble section may represent local background conditions, *i.e.*, Cd 1 ppm, Pb 100 ppm, Zn 240 ppm, As 21 ppm, and Sb <5 ppm.

Πίνακας 4.5. Πε	εριγραφή γεωτρησης G6: πυριτούχα απορριμματα στον Καβοδόκανο.
Depth	Description
(<i>m</i>)	
0-1.00:	Brownish-yellow fine-grained material with quartz grains (similar to G3: 0-2.50 m,
	and G4: 0-0.48).
1.00-1.70:	Grey fine-grained material with quartz grains.
1.70-2.40:	Grey fine-grained material with quartz grains.
2.40-3.70:	Dark grey fine-grained material with quartz grains.
3.70-4.30:	Dark grey fine-grained material with quartz grains.
4.30-6.30:	Greyish-yellow fine-grained material with quartz, some pyrite and concretions
	of iron oxides.
6.30-7.00:	Greyish-yellow fine-grained material with quartz, some pyrite and concretions
	of iron oxides.
7.00-7.40:	Greyish-yellow fine-grained material with quartz and angular, sub-angular to
	rounded pebbles of marble. It appears to be local material.
7.40-8.20:	Grey marble with iron oxides along its joints and fractures.
8.20-9.50:	Grey marble with less iron oxides along its joints and fractures.

Table 4.5.	Log of o	drill-hole G6:	pyritiferous	tailings	at Kavodoka	nos		
<u> </u>	_		~ ~				~	

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G6

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

BAΘOΣ m	ЛІФОЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	.5 02.2	0.0	40.0 3400.0	a, e,
			1	8	N N	8
						A
		ΚΚι λεπτόκοκκο υλικό με Qtz				
	· · · · · · · · · · · · · · · · · · ·					A
.00				44444	4441111	A
	0 0 0			VIIIA	12 .	
	0 0 0 0	Γκρ λεπτόκοκκο υλικό με Qtz				0
.70	_ 0 0 0		A			A
	0 0 0 0			VIIIA		
	0 0 0	Γκρ λεπτόκοκκο υλικό με Qtz				A
2.40	0 0 0					
	° ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° °					0
	00000000					
	° ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° ° °	Γκρ λεπτόκοκκο υλικό με Qtz				A
	000000000					a
	00000000					0
3.70				//////		F
	000000000	Γκο λεπτόκοκκο υλικό με Qtz				8
30	00000000					8
	00000000					Γ
	· · · · · · · · · · · · · · · · · · ·					
	00 0 0 0 0 0 0 0					
	°°°°°°°°°					
	00000000	ΓΚι λεπτόκοκκο υλικό με Qtz, py				
	· · · · · · · · · · · · · · · · · · ·			VIIIA		
	000000000					
	00000000					
5.30	0,00000					
	000000000000000000000000000000000000000	TV. Ot Falle				
	0000000	IKI, QUZ, py, reox				
.00	000000					
2 10	0_0_0	ΓKι, Qtz, Mrb				
.40			~~~			7/////
		Μάρμαρο με σιδπροξείδια				
		with high of his of the second				
3.20						HHAM
		Μάρμαρο με σιδηροξείδια				
50						

ΣΧΗΜΑ 4.9, σελίδα 4.14

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G6

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			As (ppm)	Hg (ppm)	Sb (ppm)	pH
BAΘOΣ m	ліоологікн томн	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	20.6 3047.2	3.5 1.8	2.5 35.9	7.8 3.3
1.00		ΚΚι λεπτόκοκκο υλικό με Qtz				
		Γκρ λεπτόκοκκο υλικό με Qtz				
1.70 .		Γκρ λεπτόκοκκο υλικό με Qtz				
2.40 .	0 0 0 0 000000000000000000000000000000					
		Γκρ λεπτόκοκκο υλικό με Qtz				
3.70 .						
4.30 .		ικρ λεπτοκοκκο υλικο με QLZ				
		ΓΚι λεπτόκοκκο υλικό με Qtz, py				
6.30 _						
7 00		ΓKι, Qtz, py, FeOx				
7.40	0_7_0	ΓKι, Qtz, Mrb				
8.20 .		Μάρμαρο με σιδηροξείδια				
		Μάρμαρο με σιδηροξείδια				

ΣΧΗΜΑ 4.10, σελίδα 4.15

4.2.6. DRILL-HOLE G7 (Table 4.6, Figs. 4.11-.12)

This is the second drill-hole that was sited on the pyritiferous tailings at Kavodokanos (Map 2.14). The first was G6 (refer to section 4.2.5). This is another drill-hole that has reached bedrock at a depth of 3.50 m. Hence, local background conditions can be estimated. The pH is in the alkaline range for almost the whole section (7.12-8.3), except the top layer (0-0.40 m), which has a pH of 5.8. The highest concentrations for all elements, except Zn, are in the top section of the pyritiferous tailings (0-0.40 m). Cadmium and Zn (except the top section) show a gradual decrease in the tailings from top to bottom. The levels of Pb, As and Sb are variable downwards with a peak, however, at a depth of 1.60-2.50, which corresponds to the layer with iron oxides, suggesting possible scavenging effects; below this section, towards the top of the bedrock at 3.0 m, their concentrations become gradually lower.

In the marble section, from 4.60 to 8.20 m, As (50 ppm) and Sb (<5 ppm), following an interval of 2.30-m thickness with local background conditions, they reach anomalous levels. This sudden increase presumably indicates primary conditions. Since, there is not a concurrent increase in the levels of Cd, Pb and Zn, the primary mineralisation should be pyrite or arsenopyrite with minor amounts of copper; malachite was observed along the joints and fractures of marble.

Depth	Description
(<i>m</i>)	
0-0.40:	Brownish-yellow fine-grained material with quartz grains, angular pebbles of
	oxidised marble up to 3 cm and slag fragments.
0.40-1.00:	Brownish-yellow fine-grained material with quartz grains and angular pebbles of marble up to 1.5 cm.
1.00-1.20:	Brownish-red porous calcrete with iron oxidation.
1.20-1.60:	Brownish-red material with quartz and angular marble pebbles (0.1-10 cm).
1.60-2.50:	Greyish-yellow fine-grained material with quartz grains, and small concretions of iron oxides.
2.50-2.90:	Brownish-red fine-grained material with angular to sub-angular and sub- rounded pebbles of marble, and angular pebbles of schist (0.3-4 cm).
2.90-3.50:	Grey fine-grained calcareous material with angular to sub-rounded marble pebbles up to 4 cm.
3.50-3.90:	Rose coloured calcareous material with fractures, which are infilled with iron oxides and malachite.
3.90-4.00:	Grey coloured marble.
4.00-4.60:	Pale rose coloured calcareous fine-grained material.
4.60-5.00:	Grey coloured marble with iron oxides along its joints and fractures.
5.00-5.50:	Grey coloured marble.
5.50-6.00:	Rose coloured marble.
6.00-6.20:	Rose coloured marble.
6.20-6.40:	Rose coloured porous marble.
6.40-7.10:	Brownish-red marble.
7.10-8.00:	Brownish-red marble with malachite along its joints and fractures.
8.00-8.20:	Brownish-red marble.

Table 4.6. Log of drill-hole G7: pyritiferous tailings at Kavodokanos. Πίνακας 4.6. Περιγραφή γεώτρησης G7: πυριτούχα απορρίμματα στον Καβοδόκανο.

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G7

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			Cd (ppm)	Pb (ppm)	Zn (ppm)	pH
ΒΑΘΟΣ	ΛΙΘΟΛΟΓΙΚΗ	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	N	0.0	0	
m	томн		0.5	452	32.(5.8
0.40	0 - 0 - 0	ΚΚι, λεπτ. υλικό, Qtz, oxMrb, Slg				77777
	0 0 0 0	ΚΚι, λεπτόκοκκο υλικό, Qtz, Mrb				
1.00	-1-1-1-1-1-	Who malageres to to to the Fear			HHHH	HIMA
1.20		KRO, abopartro nerpapa pe reor				CHIIIIA
1.60		ΚΚο, λεπτόκοκκο υλικό, Qtz, Mr b				
		ΓΚι, λεπτ. υλικό, Qtz, FeOx				
2.50	0 0 0 0 0	ΚΚο, λεπτόκοκκο υλικό, Mrb, Sch				
2.90	019	Γκα λεπτόκοκκα υλικό Μτο		4	4	
0.50	0_9_0					
3.50		Ροζέ ανθρακικό υλικό, FeOx. Mal				
3:88		Γκρίζο μάρμαρο				
4.60		Ροζέ ανθρακικό υλικό				
5.00		Γριζωπό μάρμαρο με FeOx				
5.50		Γκρίζο μάρμαρο				
		Ροζέ μάρμαρο				
6.00		Ροζέ μάρμαρο				
6.20	0000	Ροζέ πορώδες ανθρακικό υλικό				
0.40		Καφεκόκκινο μάρμαρο				
7.10			-			
		Καφεκόκκινο μάρμαρο, + Μαλαχίτη				
8.00		Καμετόκτιμο μάρμαρο				
8.20		Καφεκοκκινο μαρμαρο	1	LI	Ш	VIIIII

ΣΧΗΜΑ 4.11, σελίδα 4.17

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G7

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			As (ppm)	Sb (ppm)	pH
ΒΑΘΟΣ	ΛΙΘΟΛΟΓΊΚΗ				
m	томн	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	7.0	32.5	aj ej
	000		0 0	1	8
	0_0_0	ΚΚι, λεπτ. υλικό, Qtz, oxMrb, Slg			
0.40	0_0_0				7777777
	P 0 4	ΚΚι λεπτόκοκκο υλικό Otz. Mrb			
1.00	0_9_0				
1.00		ΚΚο, ανθρακικό πέτρωμα με FeOx		1	
1.80		With Dependence and and Other Mark			
1.60		KKO, AETTOKOKKO UAIKO, QUZ, MID			
	0 - 0 - 0				
	<u> </u>	FK Jam al ing Ot a Folly			
	0 0 0 0	TRE, ACHT. DALKO, QLZ, FOOX			
2 50	0 _ 0 _ 0				
2.00	D 0 4	KKa) satisfactor a) ind Mah Sah		F	
2.90	0-0-0	ARO, ACATORORRO DATRO, MI D, SCH			
	10				
		Γκρ, λεπτόκοκκο υλικό, Mrb			
3.50					
		Ροζέ ανθρακικό υλικό, FeOx, Mal			
3:98		Γκρίζο μάρμαρο			
		Ροζε ανθρακικό υλικό			
4.60	0 0 0				CHHHHH
5.00		Γριζωπό μάρμαρο με FeOx			
5.00					
		Γκρίζο μάρμαρο			
5.50				8	
		Ροζέ μάρμαρο		1	
6.00					
6.20		Ροζέ μάρμαρο		777	
6.40		Ροζε πορωσες ανυρακικό υλικό	4	Ammin	
		W. 1 1			
	****	Καφεκοκκινο μαρμαρο			
7.10			A	HIIIA	
	TTTTTT				
		Καφεκόκκινο μάρμαρο, + Μαλαχίτη			
8.00		V			
8.20		Καφεκοκκινο μαρμαρο		VIIIA	

4.2.7. DRILL-HOLE G9 (Table 4.7, Figs. 4.13-.14)

This drill-hole is one of five that were sited on the beneficiation/flotation residues or tailings. The other drill-holes are: G10, G18, G19 and G20; it is noted that samples from drill-hole G8 were not analysed. The stratigraphy of the beneficiation/flotation tailings has minor variations, and this is reflected in the geochemistry too, which shows little variation down to a depth of 7.50 m. The clay material from 5.20 to 7.50 m, and the increase in the proportion of carbonates below a depth of 7.50, seemed to have created either a geochemical barrier, for below this depth there is a pronounce decrease in the levels of all elements, or local natural materials have been penetrated. The second interpretation appears, however, to be more plausible for section 8.75-9.10 m has the minimum values for all elements, *i.e.*, Cd 1 ppm, Pb 75 ppm, Zn 156 ppm, As 14.4 ppm, Hg <1 ppm and Sb <5 ppm.

Below this section there is a minor increase in the levels of almost all elements, except Hg, with a simultaneous decrease in pH, although still in the alkaline range. This minor, but significant, increase suggests that there is a slow leaching of toxic elements downwards. A process that may pose potential problems to ground-water resources. In fact the indications from the preliminary ground water geochemical survey is that contamination of the local aquifer has already started (refer to Chapter 10 in Volumes 1 & 2 and Appendix Report 4B in Volume 1B).

Depth	Description
(<i>m</i>)	
0-0.60:	Brown fine-grained calcareous material with organic remains (roots), quartz grains, and angular pebbles of marble up to 1.5 cm.
0.60-1.40:	Brownish-yellow fine-grained calcareous material with quartz grains, and angular pebbles of marble up to 2.5 cm.
1.40-5.20:	Brownish-yellow fine-grained calcareous material with quartz grains, angular pebbles of marble and schist up to 4 cm.
5.20-5.80:	Brown fine-grained calcareous material with quartz grains, angular pebbles of marble and schist up to 3 cm.
5.80-7.50:	Brown fine-grained calcareous material with quartz grains, and angular pebbles of marble up to 2 cm. In the fine-grained material there are clay minerals.
7.50-8.10:	Brown fine-grained calcareous material with quartz grains, and angular pebbles of marble up to 2.5 cm. The proportion of carbonates is comparatively higher from this layer down to the bottom of the drill-hole.
8.10-8.25:	Brown fine-grained calcareous material with quartz grains, and angular pebbles of marble and schist up to 2 cm.
8.25-8.75:	Brownish-yellow fine-grained porous calcareous material.
8.75-9.10:	Brownish-yellow fine-grained calcareous material.
9.10-9.30:	Grey fine-grained material with angular pebbles of grey marble up to 5 cm, which have iron oxides along their joints.
9.30-10.00:	Greyish-yellow fine-grained calcareous and clayey material.

Table 4.7. Log of drill-hole G9: beneficiation/flotation tailings at Prasini Alepou. Πίνακας 4.7. Περιγραφή γεώτρησης G9: απορρίμματα εμπλουτισμού/επίπλευσης (σαβούρα) στην Πράσινη Αλεπού.

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G9

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			Cd	(ppm)	P	b (ppm)		n (ppm)	pF	I
BAθOΣ m	ЛІӨОЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	1.0	140.8	75.0	28400.0	156.0	19700.0	8.2	8.8
0.60	0 0 0	Καφέ έδαφος με Org, Qtz, Mrb								
	010	ΚΚι έδαφος με Qtz, Mrb								
1.40	101010									
	0,0,0									
	0,									
	0101	ΚΚι έδαφος με Qtz, Mrb, Sch								
	0101 010 010									
•	0,0,0									
5.20	0,0,0									
5.80		Καφέ έδαφος, Mrb, Qtz, αργιλικά								
0.00	$- \vee - \vee - \vee - \vee - \vee - \vee$									
		Καφέ έδαφος, Mrb, Qtz, αργιλικά								
7 50	v - v - v - v - v -									
R 10	000000	Καφέ έδαφοs, Qtz, Sch, ανθρακικά								
8.25		Καφέ έδαφος, Qtz, Sch, ανθρακικά ΚΚι έδαφος με ανθρακικά								
8.75 9.10		ΚΚι έδαφος με ανθρακικά								
9.30		Γκρ εδαφος με Mrb, FeOx ΓΚι έδαφος με ανθρακικά			2					
10.00	<u> </u>								V/////	

ΣΧΗΜΑ 4.13, σελίδα 4.20

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G9

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			As (ppm)	Hg (ppm)	Sb (ppm)	pH
BAθOΣ m	ліоологікн томн	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	14.4 1782.7	0.5	2.5 462.0	8.2 8.2
0.60	0 0 0	Καφέ έδαφος με Org. Qtz. Mrb				
	010	ΚΚι έδαφος με Qtz, Mrb				
1.40 .	010010					
	010					
	0 0 0					
	10,010	KKι έδαφος με Qtz, Mrb, Sch				
	0 -0 -0					
5.00	0 0 0					
5.80		Καφέ έδαφος, Mrb, Qtz, αργιλικά				
0.00	$ \begin{array}{c} - \vee - \vee - \\ \vee - \vee - \vee \\ - \vee - \vee \\ - \vee - \vee \\ - \vee - \\ \end{array} $					
	$\begin{array}{c} - \mathbf{v} - \mathbf{v} - \mathbf{v} \\ - \mathbf{v} - \mathbf{v} - \mathbf{v} \\ - \mathbf{v} - \mathbf{v} - \mathbf{v} \end{array}$	Καφέ έδαφος, Mrb, Qtz, αργιλικά				
7.50	V - V - V - V - V -					
8.10 8.25		Καφέ έδαφος, Qtz, Sch, ανθρακικά Καφέ έδαφος, Qtz, Sch, ανθρακικά				
8.75		ΚΚι έδαφος με ανθρακικά				
9.10 9.30		ΚΚι έδαφος με ανθρακικά Γκρ έδαφος με Mrb, FeOx			2	
		ΓΚι έδαφος με ανθρακικά				

ΣΧΗΜΑ 4.14, σελίδα 4.21

4.2.8. DRILL-HOLE G10 (Table 4.8, Figs. 4.15-.16)

This drill-hole is sited on the beneficiation/flotation residues or tailings at Noria. The stratigraphy of the beneficiation/flotation tailings, as described for drill-hole G10, has minor variations, and this is reflected in the geochemistry too, which shows little variation down to a depth of 13.70 m. The section from 13.70 to 14.60 m is a mixture of residual soil, developed on marble and the beneficiation tailings, and this is indicated by the distinct lower concentrations of all elements.

This is another drill-hole that has penetrated bedrock. Element concentrations in the marble are, however, geochemically anomalous, *i.e.*, Cd 34.8 ppm, Pb 2230 ppm, Zn 330 ppm, As 142.3 ppm, Hg <1 ppm and Sb 35.7 ppm. In fact, the lithogeochemical maps show that there is a geochemically anomalous zone in this area (refer to Maps 3.1 and 4.30 in Volume 2).

Table 4.8. Log of drill-hole G10: beneficiation/flotation tailings at Noria. Πίνακας 4.8. Περιγραφή γεώτρησης G10: απορρίμματα εμπλουτισμού/επίπλευσης (σαβούρα) στην περιοχή Νόρια.

Depth	Description
(<i>m</i>)	
0-8.50:	Brownish-yellow fine-grained material with quartz grains, and angular pebbles
	of schist up to 4 cm.
8.50-9.00:	Brownish-yellow material with quartz grains, and angular pebbles of marble
	and schist up to 3 cm.
9.00-10.70:	Brownish-yellow material with quartz grains, and angular pebbles of marble
	and schist up to 2 cm.
10.70-12.30:	Dark brownish-yellow fine-grained material with quartz grains, and angular
	pebbles of schist and marble up to 3 cm.
12.30-13.70:	Brown fine-grained material with quartz grains, and sub-angular pebbles of
	marble up to 2 cm.
13.70-14.60:	Brownish-red fine-grained material with angular pebbles of marble up to 3 cm.
14.60-15.40:	Grevish marble.

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G10

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			Cd (ppm)	Pb (ppm)	Zn (ppm)	pH
BAθOΣ m	ЛІООЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	34.8 307.6	2230.0	330.0 31800.0	8.6
	10 10 10 10 10 10 10 10 10 10 10 10 10 1	KKι έδαφος με Qtz, Sch				
8.50 9.00		ΚΚι έδαφος με Qtz, Sch, Mrb				
10.70		ΚΚι έδαφος με Qtz, Sch, Mrb				
10.00		ΚΚι έδαφος με Qtz, Sch, Mrb				
12.30	0000	Καφέ έδαφος με Qtz, Mrb				
13.70		ΚΚο έδαφος με Mrb, ανθρακικά				
15.40		Γκριζωπό μάρμαρο				

ΣΧΗΜΑ 4.15, σελίδα 4.23

ΕΡΓΟ: ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΤΣ ΣΤΟ ΔΗΜΟ ΛΑΤΡΙΟΥ ΑΡΙΘΜΟΣ ΕΡΓΟΥ LIFE: 93/GR/A14/GR/4576 Γεώτρηση: G10 Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης $\frac{As (ppm)}{m} \frac{Hg (ppm)}{Sb (ppm)} \frac{Sb (ppm)}{pH}$

			11	3.	35 32	8 8
	101 011 011 012 012 012 012 012 012 012	ΚΚι έδαφος με Qtz, Sch				
8.50 9.00	· · · · · ·	KKι έδαφος με Qtz, Sch, Mrb				
10.70		KKι έδαφος με Qtz, Sch, Mrb				
12.30		KKι έδαφοs με Qtz, Sch, Mrb				
13.70	0 0 0 0 0 0	Καφέ έδαφος με Qtz, Mrb				
14.60		ΚΚο έδαφος με Mrb, ανθρακικά				
15.40		Γκριζωπό μάρμαρο				

ΣΧΗΜΑ 4.16, σελίδα 4.24

4.2.9. DRILL-HOLE G11 (Table 4.9, Figs. 4.17-.18)

The drill-hole was sited on the pyritiferous sand between Komobil and Kiprianos (Map 2.14). The pH although in the alkaline range, it is lower in the top section (pH 8.1) and gradually increases in value towards the bottom of the drill-hole (pH 8.6). There appears to be a gradual increase of Pb, As, Hg and Sb from the top layer (0-1.00 m) down to the reducing layer (1.60-3.20 m); Cd and Zn patterns are almost uniform. Below the reducing layer there is a sudden drop in the concentrations of all elements towards "normal" anomalous concentrations of fluvial sediments (3.80-6.75 m).

It is quite apparent from the results that the metallurgical processing wastes have a thickness of 3.20 m in this drill-hole. The underlying section, between 3.20-3.80 m, appears to have been contaminated by the overlying wastes. Whereas, the fluvial sediments from 3.80 to 6.75 m, although they have comparatively anomalous concentrations for most elements, *i.e.*, Cd 3.2 ppm, Pb 484 ppm, Zn 480 ppm, As 72.8 ppm, Hg <1 ppm and Sb <15.3 ppm, they do not seem to have been enriched (contaminated) by downward movement of elements from the overlying metallurgical wastes. A factor that does not favour the mobility of elements is the prevailing alkaline pH >8.0 of the fluvial sediments.

Table 4.9. Log of drill-hole G11: pyritiferous sand between Komobil and Kiprianos.

Πινακας 4.9. Π	εριγραφη γεωτρησης G11: πυριτουχοι αμμοι μεταξυ Κομομπιλ και Κυπριανου.
Depth	Description
(<i>m</i>)	
0-1.00:	Brown fine-grained clayey material with quartz grains.
1.00-1.60:	Brown fine-grained clayey material with quartz grains.
1.60-3.20:	Brown fine-grained clayey material with quartz grains; grey-black spots
	indicating reducing conditions.
3.20-3.80:	Grey clayey material with quartz grains; similar to G4: 1.90-2.70 m.
3.80-5.50:	Grey clayey material with quartz grains.
5.50-6.75:	Brownish-yellow clayey material with quartz grains.

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G11

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

DAGON	4100400000		GI	(Trial)	(FFill)	Pri
m	томн	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	3.2	484.0	480.0 23200.0	8.1 3.6
		Καφέ έδαφος με Qtz, αργιλικά				
1.60	• • • • • • • • • • • • • • • • • • •	Καφέ έδαφος με Qtz, αργιλικά				
		Καφέ έδαφοs με ΓκρΜα κηλίδες				
3.20 - 3.80 -	$\begin{array}{c} & & & & & & \\ & & & & & & \\ & & & & & $	Γκρίζο έδαφος με Qtz, αργιλικά				
5.0		Γκρίζο έδαφος με Qtz, αργιλικά				
o.50 _	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	ΚΚι έδαφος με Qtz, αργιλικά				
.75 _	0-0-0					

ΣΧΗΜΑ 4.17, σελίδα 4.26

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G11

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

		1	As (ppm)	Hg (ppm)	Sb (ppm)	pH
BAΘOΣ m	ЛІООЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	72.8	0.5	15.3 658.0	8.1 8.6
		Καφέ έδαφος με Qtz, αργιλικά				
1.00	· · · · · · · · · · · · · · · · · · ·	Καφέ έδαφος με Qtz, αργιλικά				
		Καφέ έδαφος με ΓκρΜα κηλίδες				
3.20 . 3.80 .	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	Γκρίζο έδαφος με Qtz, αργιλικά				
		Γκρίζο έδαφος με Qtz, αργιλικά				
5.50 _		ΚΚι έδαφος με Qtz, αργιλικά				
6.75 _	0-0-0					

ΣΧΗΜΑ 4.18, σελίδα 4.27

4.2.10. DRILL-HOLE G12 (Table 4.10, Figs. 4.19-.20)

The drill-hole was sited on pyritiferous sand at Kiprianos (Map 2.14). It is stressed that the surface at this site has a thin veneer of other wastes. Hence, the pyritiferous nature of the underlying wastes is not visible.

The pH in the two top sections (0-5.30 m) is in the acid range (6.02-6.58); section 5.30-7.10 m has a neutral pH value of 7.0, followed by a slight drop to 6.84 in section 7.10-8.00 m, and then a sudden rise to alkaline pH conditions of 8.16. Element patterns appear to be governed by the pH of hydrolysis (Table 6.1, p.131, Volume 1), *i.e.*, Cd²⁺ 6.7, Pb²⁺ 6.0, Zn²⁺ 7.0 and Hg²⁺ 7.3. Lead due to its low pH of hydrolysis (6.0) is comparatively immobile and remains in the top section (0-4.0 m), which has a pH value of 6.0. Whereas Cd, Zn, Hg, and probably Sb, with higher pH of hydrolyses are leached downwards and are precipitated in the underlying layers (4.00-7.10 m) with a higher pH. From 8.0 to 10.00 m there is a sudden drop to "normal" anomalous concentrations, *i.e.*, Cd 10.3 ppm, Pb 1330 ppm, Zn 2310 ppm, As 190.8 ppm, Hg <1 ppm and Sb 20.9 ppm.

It is quite apparent from the results that the top section of this drill-hole (0-8.00 m) is made up from metallurgical processing wastes, and mainly pyritiferous sand as indicated by the high Fe (9.79-20.00%), S (4.10-10.54%) and Mn (4859-13522 ppm). The underlying section, between 8.00-10.00 m, appears be made from fluvial sediments, for apart from the sudden drop in Cd, Pb, Zn, As, Hg and Sb, there is also a distinct decrease in the levels of Fe, S and Mn. Evidently, the high pH (>8.0) of the fluvial sediments.

Depth	Description
<i>(m)</i>	
0-4.00:	Brownish-red clayey material with quartz grains and carbonates.
4.00-5.30:	Brownish-yellow clayey material with quartz grains; similar to G4: 0-0.48 m.
5.30-7.10:	Brownish-red clayey material with quartz grains.
7.10-8.00:	Brownish-red clayey material with quartz grains.
8.00-10.00:	Brownish-red clayey material with quartz grains.

Table 4.10. Log of drill-hole G12: pyritiferous sand at Kiprianos.

Πίνακας 4.10. Περιγραφή γεώτρησης G12: πυριτούχοι άμμοι στον Κυπριανό.

ΕΡΓΟ: ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΥΣ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576 Γεώτρηση: G12 Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης | Cd (ppm) || Pb (ppm) || Zn (ppm) || pH 174000.0 ΒΑΘΟΣ ΛΙΘΟΛΟΓΙΚΗ 84000.0 858.9 2310.0 ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ 10.3 томн m 8.2 ΚΚο έδαφος με Qtz, Αργ., Ανθρ. 4.00 ΚΚι έδαφος με Qtz, αργιλικά 5.30 ΚΚο με Qtz, αργιλικά 0 7.10 ΚΚι έδαφος με Qtz, αργιλικά 8.00 ΚΚι έδαφος με Qtz. αργιλικά

10.00

ΣXHMA 4.19, σελίδα 4.29

ΕΡΓΟ: ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΥΣ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576 Γεώτρηση: G12 Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης | As (ppm) || Hg (ppm) || Sb (ppm) || pH 11944.0 ΒΑΘΟΣ ΛΙΘΟΛΟΓΙΚΗ ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ 190.8 523.0 6.0 23.1 томн m 8.2 ΚΚο έδαφος με Qtz, Αργ., Ανθρ. 4.00 ΚΚι έδαφος με Qtz, αργιλικά 5.30 0 0 ΚΚο με Qtz, αργιλικά 7.10 0 0 ΚΚι έδαφος με Qtz, αργιλικά 8.00 ΚΚι έδαφος με Qtz. αργιλικά 10.00

ΣΧΗΜΑ 4.20, σελίδα 4.30

4.2.11. DRILL-HOLE G13 (Table 4.11, Figs. 4.21-.22)

The drill-hole was sited close to the 3rd Primary School between Komobil and Santorineika, and on reported pyritiferous sand (Map 2.14). It is stressed that the surface at this site has a thin veneer of other wastes, *e.g.*, construction wastes. Hence, the nature of the underlying metallurgical processing wastes was not visible.

The pH is in the alkaline range, and has a tendency to increase from 8.6 at the top to 9.1 at the bottom. Element patterns do not appear to be governed by pH changes in this case. The greatest element concentrations occur in the top layers up to a depth of 3.20 m. There is a sudden drop in the level of contaminant elements in the underlying section from 3.20 to 5.30 m. Element concentrations in the remaining part of the drillhole from 5.30 to 15.20 m, although they have minor variations, they are distinctly lower.

This is another drill-hole that has intersected the parent rocks of the area. In this case schist at a depth of 15.30 m, which is highly weathered and resembles the soil C-horizon. The lowest concentrations for almost all elements, except Hg, are in the schist, *i.e.*, Cd 1.6 ppm, Pb 107 ppm, Zn 480 ppm, As 19.9 ppm, Hg 1 ppm, Sb <5 ppm.

It is apparent from the drill-hole log and the geochemical patterns that the metallurgical processing wastes have a thickness of 5.30 m, and have been mixed with fluvial sediments. Underlying this section from a depth of 5.30 to 15.30 m there are only fluvial sediments.

Table 4.11. Log of drill-hole G13: metallurgical wastes and fluvial deposits close to the 3rd Primary School in Lavrion.

Πίνακας 4.11.	Περιγραφή γεώτρηα	σης G13:	μεταλλουργικά	απορρίμματα	και ποτάμιες	αποθέσεις	δίπλα
στο Γ' Δημοτικ	ό Σχολείο του Λαυρί	ίου.					

Depth	Description
(<i>m</i>)	
0-0.40:	Brown clayey-sand with angular and subangular pebbles of marble, a quartz pebble and red bricks up to 2 cm.
0.40-1.00:	Brownish-red clayey-sand with a high proportion of clay; angular to subangular pebbles of marble up to 4 cm. and a few slag fragments.
1.00-3.20:	Brownish-red clayey-sand with a high proportion of clay; angular to subangular to subrounded pebbles of marble up to 4 cm, and a few slag fragments.
3.20-5.30:	Brownish-red clayey-sand with a slightly higher proportion of sand; many angular to subangular pebbles of pale grey marble up to 5 cm.
5.30-7.85:	Brownish-red clayey-sand with a high proportion of clay at places; angular to subangular pebbles of grey marble, quartz and schist up to 3 cm.
7.85-10.00:	Brownish-yellow clayey-sand with a high proportion of either sand or clay at places; angular to subrounded pebbles of pale grey, yellow and red marble, and schist up to 5 cm.
10.00-11.00:	Brownish-yellow clayey-sand with a high proportion of angular to subrounded pebbles of marble and schist up to 10 cm.
11.00-12.30:	Brownish-yellow clayey-sand with a high proportion of more rounded pebbles (compared to above) of pale and rose marble up to 3 cm.
12.30-12.60:	Brownish-yellow clayey-sand with a high proportion of clay and subangular to subrounded pebbles of marble up to 2 cm.
12.60-14.50:	Brownish-yellow clayey-sand with a high proportion of clay and fewer angular to subrounded pebbles of marble up to 2 cm.
14.50-15.30:	Brownish-yellow clayey-sand with a high proportion of angular to subrounded pebbles of grey and red marble up to 6 cm.
15.30-17.20:	Weathered grey-green schist with iron oxide patches. Its appearance is weathered C-horizon

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G13

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			Cd (ppm)	Pb (ppm)	Zn (ppm)	pH
BAθOΣ m	ліоологікн томн	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	.6 46.5	07.0	80.0	6
0.40	~ 7 ~	Καφέ έδαφος με Mrb, Qtz, Κεραμ.	1	57 T	4 03	8 6
1.00	000000	ΚΚο έδαφος με Mrb, σκουριές				1
1.00		ΚΚο έδαφος με Mrb, σκουριές				4
3.20 5.30	• • • • • • • • • • • • • • • • • • •	ΚΚο αμμώδες έδαφος με Mrb				
		KKo Αργ. έδαφος με Qtz, Mrb, Sch				
7.85		ΚΚι Αργ-Αμμ έδαφος, Mrb, Sch				
1.00	0 0 0	ΚΚι Αργ-Αμμ έδαφος, Mrb, Sch				
2.30		ΚΚι Αργ-Αμμι έδαφος με Μrb ΚΚι Αργ-Αμμι με Mrb				
4.50		KKo Αργ-Αμμ έδαφος με Mrb				
4.00	<u>°</u> 0 - °	ΚΚο Αργ-Αμμ έδαφος με Mrb				
15.30 .	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Αποσαθρωμένος σχιστόλιθος	2	2	2	
7.20	~~~~~					

ΣΧΗΜΑ 4.21, σελίδα 4.32

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G13

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			As (ppm)	Hg (ppm)	Sb (ppm)	pH
BAΘOΣ m	ЛІӨОЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	9.9 515.7	5	.5	.6
0.40	~ ~ ~	Καφέ έδαφος με Mrb, Qtz, Κεραμ.	7//////////////////////////////////////	01111111	×/////////////////////////////////////	a
0.40	000000	ΚΚο έδαφος με Mrb. σκουριές				E I
1.00		ΚΚο έδαφος με Mrb, σκουριές				4
3.20 - 5.30		ΚΚο αμμώδες έδαφος με Mrb				
7.85		KKo Αργ. έδαφος με Qtz, Mrb, Sch				
10.00	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	ΚΚι Αργ-Αμμ έδαφος, Mrb. Sch				
11.00	0 0 0	ΚΚι Αργ-Αμμ έδαφος, Mrb, Sch				
	0.0	ΚΚι Αργ-Αμμ έδαφος με Mrb				
12.30 12.60	0_0_0	ΚΚι Αργ-Αμμ με Mrb				
		ΚΚο Αργ-Αμμ έδαφος με Mrb				
14.50	0 0 -0					CHINA I
15.30	0_0_0	ΚΚΟ Αργ-Αμμ έδαφος με Mrb		73		(IIIA)
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Αποσαθρωμένος σχιστόλιθος				
17 00	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~					////////
#### 4.2.12. DRILL-HOLE G14 (Table 4.12, Figs. 4.23-.24)

The drill-hole was sited on fluvial deposits at Nichtochori (Map 2.14).

The pH is in the alkaline range (8.2-9.3); it has a sudden minor peak in the section with the black metallic sand (comminuted slag) at a depth of 1.45-1.80 m, probably due to the release of carbonates from the weathered slag; from section 3.50-4.50 m it decreases gradually to the bottom of the drill-hole. The geochemical patterns do not seem, however, to follow the pH variation, probably because of the alkaline range >8.2 conditions, which render immobile the studied elements. It is assumed, therefore, that the patterns reflect the chemical composition of each layer.

From the drill-hole log and the geochemical patterns, with higher element concentrations, it occurs in the section with metallurgical processing wastes, dumped in this area, and which have a thickness of approximately 2.50 m; the drill-hole section from 1.80-2.50 m is considered to be transitional with a mixture of fluvial sediments and metallurgical wastes, and has distinctly lower element levels. The fluvial material from 2.50 to 5.30 m depicts local background concentrations, *i.e.*, Cd <1 ppm, Pb 24 ppm, Zn 70 ppm, As 14 ppm, Hg <1 ppm and Sb 8 ppm.

This is another drill-hole that has intersected parent rocks, *i.e.*, marble (5.30-6.20 m) underlain by schist (>6.20 m). Element concentrations in the marble are: Cd <1 ppm, Pb 104 ppm, Zn 119 ppm, As 20 ppm, Hg <1 ppm, and Sb <5 ppm; in the schist with marble intercalations element levels are: Cd <1 ppm, Pb 24 ppm, Zn 70 ppm, As 14 ppm, Hg <1 ppm, and Sb <5 ppm.

Depth	Description
(m)	
0-0.60:	Greyish-yellow clayey-sand with organic material with angular to subangular pebbles marble, schist and slag up to 4 cm; there are patches with a higher proportion of clay.
0.60-1.00:	Brownish-red clayey-sand with angular to subangular pebbles of marble, schist and slag up to 4 cm.
1.00-1.45:	Brownish-red clayey-sand with a high proportion of clay and angular to subangular pebbles of oxidised marble, schist and slag up to 4 cm.
1.45-1.80:	Grey-black clayey-sand with a high proportion of black metallic sand. Rounded pebbles of grey and rose marble up to 9 cm; the pebbles are covered by black coating, which may have been derived from the metallic sand. There are also glassy slag pebbles from 2 to 9 cm.
1.80-2.50:	Greyish-red clayey-sand with a high proportion of clay and rounded pebbles of marble and slag up to 10 cm. It is noted that the clayey-sand in contact with slag has a black colour.
2.50-3.50:	Greyish clayey-sand with a high proportion of clay. Locally it is slightly greyish-red.
3.50-4.50:	Reddish clayey material.
4.50-5.30:	Brownish-red clayey-sand with a high proportion of clay and a multitude of angular to subangular pebbles of grey and red marble up to 4 cm. It appears to be a transitional layer.
5.30-6.20:	Rose porous marble.
6.20-7.00:	Weathered grey schist with marble intercalations.

Table 4.12. Log of drill-hole G14: fluvial deposits at Nichtochori.

Πίνακας 4.12. Περιγραφή γεώτρησης G14: ποτάμιες αποθέσεις στο Νυχτοχώρι.

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G14

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			Cd (ppm)	Pb (ppm)	Zn (ppm)	рн
BAΘOΣ m	ЛІӨСЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	0.5 71.8	24.0 39600.0	70.0 37200.0	8.8 9.3
	0 0 0	ΓΚι Αργ-Αμμ, Org, Slg, Mrb, Sch				
0.60 . 1.00 .	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	KKo Αργ-Αμμ, Slg, Mrb, Sch				
1.45	0,010	KKo Αργ-Αμμ, Slg, Mrb, Sch				
1.80 .	00000	ΓΜα, Cl , Mrb, Μαύρη μεταλλ. άμμος				
	0 0 0	ΓΚο Αργ-Αμμ, Slg, Mrb				
2.50 .	0_7_0					
		Γκριζωπό Αργ-Αμμ έδαφοs				
3.50 .						
		Κόκκινο αργιλικό έδαφος				
4.50						
	0 0 0	ΚΚο Αργ-Αμμ. Μεδ				
5.30 .	0 0 0					
		Ροδόχρουν πορώδες μάρμαρο				
6.20						
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Αποσαθρωμένος σχιστόλιθος+Mrb				
7.00	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~					

ΣΧΗΜΑ 4.23, σελίδα 4.35

EPFO: APOKATASTASH EDAQOYS STO DHMO AAYPIOY

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G14

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			As (ppm)	Hg (ppm)	so (ppm)	pn
BAΘOΣ m	ЛІӨОЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	14.2 3069.4	0.5 2.0	2.5 456.0	8.2
	0 0 0	ΓК: Аργ-Аμμ, Org, Slg, Mrb, Sch				
0.60 -	0 0 0	KKo Αργ-Αμμ. Slg. Mrb. Sch				
1.45	1000	KKo Αργ-Αμμ, Slg, Mrb, Sch				
1.80 _	00000000000000000000000000000000000000	ΓΜα, Cl , Mr b, Μαύρη μεταλλ. άμμος				
	0 0 0	ΓΚο Αργ-Αμμ, Slg, Mrb				
2.50 ₋ 3.50		Γκριζωπό Αργ-Αμμ έδαφοs	2			
4.50		Κόκκινο αργιλικό έδαφος				
5.30 _	10 10 10 10 10 10 10 10 10 10 10 10 10 1	ΚΚο Αργ-Αμμ, Mrb				
6.20 _		Ροδόχρουν πορώδες μάρμαρο				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Αποσαθρωμένος σχιστόλιθος+Mrb				

#### 4.2.13. DRILL-HOLE G15 (Table 4.13, Figs. 4.25-.26)

The drill-hole was sited on metallurgical processing wastes in the open space at the back of the old cast iron loading pier of the French company (Map 2.14).

The pH is in the alkaline range (8.3-8.8) and it does not, therefore, appear to affect the vertical distribution of elements. The drill-hole section with the greatest contamination is from 0.40 to 2.50 m, *i.e.*, Cd 11 ppm, Pb 55600 ppm, Zn 38000 ppm, As 3209 ppm and Sb 466 ppm. The surface layer (0-40 m) due to dilution with other materials has lower element concentrations. The lowest element concentrations occur in the bottom layer, *i.e.*, Cd <1 ppm, Pb 353 ppm, Zn 350 ppm, As 44 ppm and Sb <5 ppm.

The thickness of the metallurgical processing wastes is approximately 3.50 m at this site.

Table 4.13. Log of drill-hole G15: metallurgical processing wastes in the open space at the back of the French Pier at the beach of Agia Paraskevi.

Πίνακας 4.13. Περιγραφή γεώτρησης G15: μεταλλουργικά απορρίμματα πίσω από τη Γαλλική Σκάλα στην παραλία της Αγίας Παρασκευής.

Depth (m)	Description
0-0.40:	Brown clayey-sand with a high proportion of clay; it contains small pebbles of
0.40-2.50:	White marble and slag up to 2 cm. Brown clayey-sand with angular to subangular pebbles of slag.
2.50-4.30:	Greyish-yellow clayey-sand with a high proportion of clay; pebbles of slag up to 1 cm are restricted in the upper part of this section (2.50-3.50 m); angular to
	section.

APIOMOS EPFOY LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G15

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

ΒΑΘΟΣ	ΔΙΘΟΔΟΓΙΚΗ			0	0	
m	томн	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	0.5	353.0	350.0	8.3 8.8
).40	1012101 1012101	Καφέ Αργ-Αμμ, σκουριέs + Mrb				
<i></i>		Καφέ Αργ-Αμμ. σκουριές				
2.50 .		ΓΚι Αργ-Αμμ έδαφ. , σκουριέs+Mrb				

ΣΧΗΜΑ 4.25, σελίδα 4.38

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G15

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

ΒΑΘΟΣ	ΛΙΘΟΛΟΓΙΚΗ						
m	TOMH	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	44.4	3209.4	2.5	466.0	69 67 67 67 67 67 67 67 67 67 67 67 67 67
0.40	0 1 0 1 0 1 0 1 0 1 0 7	Καφέ Αργ-Αμμ, σκουριέs + Mrb					
		Καφέ Αργ-Αμμ. σκουριέs					
4.30		ΓΚι Αργ-Αμμ έδαφ., σκουριέs+Μrb					

ΣΧΗΜΑ 4.26, σελίδα 4.39

## 4.2.14. DRILL-HOLE G16 (Table 4.14, Figs. 4.27-.28)

The drill-hole was sited on pyritiferous sand in the open space outside the 2nd Primary School of Lavrion (Map 2.14).

The pH is in the alkaline range, and increases gradually from top (8.2) to bottom (8.7). Since, pH is in the alkaline range and does not appear to affect the vertical distribution of elements. All elements show a definite pattern of gradual decrease in their concentrations from top to bottom. Hence, the greatest contamination is down to a depth of 1.00 m: Cd 139 ppm, Pb 37600 ppm, Zn 33600 ppm, As 1789 ppm, Hg 5.1 ppm and Sb 646 ppm (0-0.70 m).

This is another drill-hole that has intersected bedrock, *i.e.*, schist, which has the lowest element concentrations: Cd <1 ppm, Pb 320 ppm, Zn 1020 ppm, As 43 ppm, Hg <1 ppm, and Sb 12 ppm.

Table 4.14. Log of drill-hole G16: pyritiferous sand in the open space outside the 2nd Primary School of Lavrion.

Πίνακας 4.14. Περιγραφή γεώτρησης G16: πυριτούχοι άμμοι στον ανοικτό χώρο έξω από το Β' Δημοτικό Σχολείο του Λαυρίου.

Depth	Description
( <i>m</i> )	
0-0.70:	Brownish-yellow fine-grained material with angular slag pebbles.
0.70-1.00:	Reddish clayey-sand with angular slag pebbles up to 4 cm.
1.00-4.00:	Reddish clayey-sand with a large proportion of angular slag pebbles up to 9
	cm.
4.00-5.00:	Greyish-yellow weathered schist.

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G16

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης



ΣΧΗΜΑ 4.27, σελίδα 4.41

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G16

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

BA002	ЛІФОЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	.6 88.5		6.0	
		ΚΚι Αργ έδαφος με σκουριές	42	0.0	11	
0.70	0,0,0,0 0,0,0,0	Κόκκινο Αργ-Αμμ έδαφ., σκουριές				
	0 1 0 1 0 1 0 1 0 1 0 1 0 1 0 1 0 1 0 1	Κόκκινο Αργ-Αμμ έδαφ., σκουριές				
¥.00 _		ΓΚι αποσαθρωμένος σχιστόλιθος				

ΣXHMA 4.28, σελίδα 4.42

## 4.2.15. DRILL-HOLE G17 (Table 4.15, Figs. 4.29-.30)

The drill-hole was sited on what seemed to be residual, and visually uncontaminated, soil in the open space directly opposite the Izola factory in southern part of Lavrion (Map 2.14).

The pH is in the alkaline range, and increases gradually from top (8.4) to bottom (9.5). Since, pH is in the alkaline range and does not appear to affect the vertical distribution of elements. The surface layer down to a depth of 0.37 m is contaminated, although it is not so extreme as in other parts of Lavrion, *i.e.*, Cd 20.1 ppm, Pb 3150 ppm, Zn 2190 ppm, As 488.9 ppm, Hg <1 ppm, Sb 29.9 ppm.

The remaining section down to a depth of 1.28 cm depicts local background conditions of "uncontaminated" soil, *i.e.*, Cd <1-1 ppm, Pb 121-186 ppm, Zn 125-137 ppm, As 16-26 ppm, Hg <1 ppm, and Sb <5 ppm.

This is another drill-hole that has intersected bedrock, *i.e.*, schist, which has the lowest element concentrations (4.60-5.30 m): Cd <1 ppm, Pb 9 ppm, Zn 101 ppm, As 7 ppm, Hg <1 ppm, and Sb <5 ppm.

It is apparent from the results of this drill-hole that even in the remotest parts of Lavrion the surface soil/overburden is contaminated by toxic elements.

Table 4.15.	Log of drill-hole G17:	residual '	"uncontaminated s	oil" in the open space	e opposite of
Izola factory	/ in the southern part of	Lavrion.			

Depth	Description
( <i>m</i> )	
0-0.37:	Brown clayey-sand with a high proportion of clay; angular pebbles of schist,
	rose marble, slag and red ceramics up to 3.5 cm.
0.37-0.58:	Brownish-red clayey-sand with a high proportion of clay; angular to
	subangular pebbles of rose and oxidised marble up to 4 cm.
0.58-1.28:	Greyish-yellow clayey-sand with a high proportion of clay; angular to
	subangular pebbles of grey marble and schist up to 4 cm.
1.28-4.60:	Weathered schist with grey marble intercalations, which is locally oxidised.
4.60-5.30:	Grey schist, which is less weathered and with local patches with iron oxides.

Πίνακας 4.15. Περιγραφή γεώτρησης G17: υπολειμματικό «μη ρυπασμένο έδαφος» στον ανοικτό χώρο απέναντι από το εργοστάσιο της Ιζόλα στο νότιο τμήμα του Λαυρίου.

ΕΡΓΟ: ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΥΣ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ ΑΡΙΘΜΟΣ ΕΡΓΟΥ LIFE: 93/GR/A14/GR/4576 Γεώτρηση: G17 Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη,

Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			Cd (ppm)	Pb (ppm)	Zn (ppm)	pH
ΒΑΘΟΣ	ЛІӨОЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	.5	.0	01.0	4
	0 0 0	Καφέ Αργ-Αμμ, Sch, Mrb, κεραμικά	2	6	2	80 0
0.37	0_0_0	ΚΚο Αργ-Αμμ έδαφος με Mrb				
0.56		ΓΚι Αργ-Αμμ έδαφος με Mrb. Sch	4		•	
1.28	- <u></u> - <u></u> - <u></u> - <u></u> - <u></u> - <u></u> - <u></u> - <u></u> - <u></u> - <u></u>					
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~					
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~					
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Αποσαθρωμένοs Sch με ενστρ. Mrb				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~					
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~					
4.60	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~					
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Γκρίζος σχιστόλιθος				
5.30	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~					

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G17

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			As (ppm)	Sb (ppm)	pH
ΒΑΘΟΣ	ΛΙΘΟΛΟΓΙΚΗ	TEDIFICALL SVINATISMON	G		
m	томн	HEFII PAYN ZANMAHZMUN	7.0	2.5	8.4
	11				
	0 0 0	Καφέ Αργ-Αμμ, Sch, Mrb, κεραμικά			
0.37	-			411111111111111	
0.58	0-4-0	ΚΚο Αργ-Αμμ εσαφος με Mrb	1		
	0_0_0				
	0.0.0				
	0_0_0	ΓΚι Αργ-Αμμ έδαφος με Mrb, Sch			
	0-0-0				
1.28			4		HAM
	~~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
	~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
	~~~~~~				
	~~~~~~				
	~~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Αποσαθρωμενος Sch με ενστρ. Mrb			
	~~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
	~~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
	~~~~~		E		
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
	~~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	4	E		
4.60	~~~~~		2		HIMMIN
	~~~~~				
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Fraites aviatoria intes			
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Tupiços oztorontoos			
	~~~~~				
5.30	~~~~			11	VIIIIIIIIIII

## 4.2.16. DRILL-HOLE G18 (Table 4.16, Figs. 4.31-.32)

This drill-hole site was selected to check incoming contamination from a stream draining an ancient mining and smelting area. It was sited on what seemed to be fluvial and "uncontaminated" soil at the southern edge of the beneficiation/flotation residues or tailings at Noria (Map 2.14). It is an interesting section, for its stratigraphy shows the fluvial layers deposited at different times. Since, the stream drains an area with ancient washing and smelting plants one of the conglomerate layers contains pebbles of ancient slag (Map 1.2).

The pH is in the alkaline range with an increasing trend from top (8.4) to bottom (8.8). Since, pH is in the alkaline range, it does not appear to have affected the vertical distribution of elements. The surface layer down to a depth of 0.40 m is contaminated, although it is not so extreme as in other parts of Lavrion, *i.e.*, Cd 18.7 ppm, Pb 4750 ppm, Zn 3410 ppm, As 414.2 ppm, Hg <1 ppm, Sb 55.1 ppm.

Element levels in the underlying sections depict local background conditions of "uncontaminated" fluviatile deposits (1.0-1.40 m), *i.e.*, Cd <1 ppm, Pb 211 ppm, Zn 500 ppm, As 40.2 ppm, Hg <1 ppm, and Sb <6.2 ppm.

This is another drill-hole that has intersected bedrock, in this case two layers of conglomerate (upper: 1.40-2.80 m; lower: 3.26-5.30 m), and an old fluvial sediment is sandwiched between them (2.80-3.26 m). Element concentrations in these three units are:

- Upper conglomerate (1.40-2.80 m): Cd 5 ppm, Pb 1140 ppm, Zn 1190 ppm, As 92 ppm, Hg <1 ppm, and Sb 13 ppm.
- Old fluvial sediment (2.80-3.26 m): Cd 6 ppm, Pb 289 ppm, Zn 910 ppm, As 59 ppm, Hg <1 ppm, and Sb 9 ppm.
- Lower conglomerate (3.26-5.30 m): Cd 4 ppm, Pb 358 ppm, Zn 820 ppm, As 42 ppm, Hg <1 ppm, and Sb 8 ppm.</li>

The levels of elements in the lower conglomerate, and the old fluvial sediment, are approximately similar suggesting, therefore, that the same erosion sources were active during their deposition. These element levels are lower than the ones occurring in the Lavrion urban area, which have been caused by the recent metallurgical wastes.

Table 4.16. Log of drill-hole G18: fluvial "uncontaminated" deposits at Noria.

Πίνακας 4.16. Πε	ριγραφή γεώτρησης G18: ποτάμιες «μη ρυπασμένες» αποθέσεις στην περιοχή Νόρια.
Depth	Description
( <i>m</i> )	
0-0.40:	Brownish-red clayey-sand with angular pebbles of marble and schist up to 4
0.40-1.00:	Brownish-yellow clayey-sand with angular to subangular pebbles of mainly sandstone, and to a lesser extent marble up to 9 cm.
1.00-1.40:	Brownish-yellow clayey-sand with a high proportion of clay; angular to subangular pebbles of mainly sandstone, and to a lesser extent marble up to 8 cm.
1.40-2.80:	Conglomerate consisting of angular pebbles of grey marble, quartz, and schist up to 8 cm, and ancient slag. The cementing material is calcareous clayey-sand.
2.80-3.26:	Loose brownish-yellow clayey-sand with a large quantity of angular pebbles of mainly marble, and to a lesser extent quartz, schist and sandstone; there are also remnants of organic matter.
3.26-5.30:	Conglomerate consisting of large angular pebbles of grey marble, quartz and schist: some of the pebbles are up to 13 cm

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G18

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			Cd (ppm)	Pb (ppm)	Zn (ppm)	pH
ΒΑΘΟΣ	ΛΙΘΟΛΟΓΊΚΗ	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	5	1.0	0.0	9 8
0.40		ΚΚο Αργ-Αμμ έδαφος, Mrb, Sch	1	45	34	<u>iii</u> iii
1.00		ΚΚι έδαφος, Sst. Mrb				
1.40 .	**************************************	ΚΚι Αργ-Αμμ έδαφος, Sst, Mrb	2			
		Κροκαλοπαγές με Slg, Mrb, Sch				
2.80 . 3.26 .	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	KKι Αργ-Αμμ, Qtz, Mrb, Sch, Sst				
		Κροκαλοπαγέs, Slg, Mrb, Qtz, Sch				
5.30	0_0_0					

ΣΧΗΜΑ 4.31, σελίδα 4.47

APIOMOS EPGOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G18

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			As (ppm)	Sb (ppm)	pH
ΒΑΘΟΣ	ЛІӨОЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	0.2	5.1	3.4 a B
0.40	0 - 0 - 0 - 0 - 0	ΚΚο Αργ-Αμμ έδαφος, Mrb, Sch			777772
		ΚΚι έδαφος, Sst. Mrb			
.00		ΚΚι Αργ-Αμμ έδαφος, Sst, Mrb			
	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0				
		Κροκαλοπαγές με Slg, Mrb, Sch			
8.80					
3.26	01010	KKι Αργ-Αμμ, Qtz, Mrb, Sch, Sst			
	0 0 0 0 0	Κροκαλοπαγέs, Slg, Mrb, Qtz, Sch			
		2			
5.30	01010	2			

ΣΧΗΜΑ 4.32, σελίδα 4.48

#### 4.2.17. DRILL-HOLE G19 (Table 4.17, Figs. 4.33-.34)

The drill-hole was sited in the open space in front of the Lavrion Medical Centre (Map 2.14). The reports from the local people were that metallurgical processing wastes were dumped in this area, and the objective was to define their depth. The log indicates that the thickness of the metallurgical processing wastes is 2.48 m, which is also verified by the geochemical patterns. Underlying the wastes are fluvial sediments with distinctly lower element concentrations.

The pH is in the alkaline range with an increasing trend from top (8.4) to bottom (9.2). Since, pH is in the alkaline range and does not appear to have affected the vertical distribution of elements. Element patterns indicate an overall gradual decrease of element concentrations from top to bottom. Apart from As, the highest concentration of all elements occur in the surface layer (0-0.40 m), *i.e.*, Cd 175.3 ppm, Pb 29400 ppm, Zn 24800 ppm, As 3951 ppm, Hg 3.2 ppm, Sb 496 ppm. Arsenic has its highest levels in section 1.00-1.60 m: 5613 ppm As.

Element levels in the underlying fluvial deposits depict "local background" conditions (2.48-6.00 m): Cd 1-3 ppm, Pb 241-394 ppm, Zn 580-560 ppm, As 19-47 ppm, Hg <1 ppm, and Sb <5-9 ppm.

Table 4.17. Log of drill-hole G19: metallurgical processing wastes in the open space in front of the Lavrion Medical Centre.

Depth	Description
( <i>m</i> )	
0-0.40:	Brownish-yellow clayey-sand with small angular pebbles of schist, marble and slag up to 4 cm.
0.40-1.00:	Brownish-yellow clayey-sand with angular pebbles of schist, marble and slag up to 4 cm.
1.00-1.30:	Brownish-yellow clayey-sand with angular pebbles of schist, marble, slag and a pebble from a red brick.
1.30-1.60:	Brown clayey-sand with a high proportion of clay, and angular pebbles of schist, marble and slag; there is a thin 10-cm thick red clay layer.
1.60-2.48:	Brownish-red clayey-sand with a high proportion of clay; small angular pebbles of marble, schist and slag up to 3 cm; also sand-blast material from Kavodokanos.
2.48-4.00:	Brownish-red clayey-sand with a high proportion of clay; small angular to subangular pebbles of schist, marble and quartz up to 2 cm; Fe-Mn coatings on the clayey-sand.
4.00-5.00:	Brownish-red clayey-sand with a high proportion of clay, and small angular to subangular pebbles of marble up to 2 cm.
5.00-6.00:	Brownish-yellow clayey-sand with a high proportion of clay, and small angular to subangular pebbles of marble up to 2 cm.

Πίνακας 4.17. Περιγραφή γεώτρησης G19: μεταλλουργικά απορρίμματα στον ανοικτό χώρο μπροστά από το Κέντρο Υγείας του Λαυρίου.

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G19

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			Cd (ppm)	Pb (ppm)	Zn (ppm)	PH
BAθOΣ m	ліоологікн томн	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΟΝ	1.3 175.3	241.0 29700.0	280.0 24800.0	8.4
0.40	0 0 0 0	KKι Αργ-Αμμ, Sch, Mrb, Slg				
1.00	0 0 0 0 0 0	KKι Αργ-Αμμ, Sch, Mrb, Slg				
1.30	0_0_0	KKι Αργ-Αμμ, Sch, Mrb, Slg				
1.60		Καφέ έδαφος, τούβλο, Mrb, Slg				
2.48		KKo Αργ-Αμμ, Mrb, Sch, Slg				
		KKo Αργ-Αμμ, Sch, Mrb, Qtz, Fe-Mn				
4.00		ΚΚο Αργ-Αμμ έδαφος, Mrb				
5.00						
	0 0 0	ΚΚι Αργ-Αμμ έδαφος, Mrb				
3.00	0_0_0					

ΣΧΗΜΑ 4.33, σελίδα 4.50

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G19

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			As (ppm)	Hg (ppm)	SD (ppm)	рн
BAΘOΣ m	ЛІΘОЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	19.1 5613.0	0.5	2.5 496.0	8.4
0.40	0 0 0	KKι Αργ-Αμμ, Sch, Mrb, Slg				
	000	KKι Αργ-Αμμι, Sch, Mrb, Slg				
	° 0 ° 0 ° 0	KKι Αργ-Αμμι, Sch, Mrb, Slg				
.60		Καφέ έδαφος,τούβλο, Mrb, Slg				
	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	ККо Аργ-Аμμ, Mrb, Sch, Slg				
2.48		KKo Αργ-Αμμ, Sch, Mrb, Qtz, Fe-Mn	2	2/////2		
±.00		ΚΚο Αργ-Αμμ έδαφος, Mrb				
5.00	0 0 0 0 0 0 0 0 0 0 0 0	ΚΚι Αργ-Αιμι έδαφος. Μτο				
6.00	0 0 0 0 0 0 0 0 0 0 0					

ΣΧΗΜΑ 4.34, σελίδα 4.51

#### 4.2.18. DRILL-HOLE G21 (Table 4.18, Figs. 4.35-.36)

The drill-hole was sited on the bank of the stream draining from Agios Constantinos (Map 2.14). The reason for selecting this site was to examine the geochemical composition of material derived from the drainage basin of Agios Constantinos-Lavrion, where there are only mining wastes (Map 1.2).

The pH is in the alkaline range, which increases, with minor variations, from top (8.4) to bottom (8.9). Since, pH is in the alkaline range and does not appear to have affected the vertical distribution of elements. Element patterns indicate that they are depended on erosion sources active at the time of deposition of the fluvial sediments. Overall the two sedimentary sequences have the following range of element concentrations:

- loose fluvial deposits: Cd 3-5 ppm, Pb 497-670 ppm, Zn 750-1220 ppm, As 94-181 ppm, Hg <1 ppm, Sb 10-29 ppm.</li>
- conglomeratic beds: Cd 2-4 ppm, Pb 384-717 ppm, Zn 440-1230 ppm, As 89-146 ppm, Hg <1 ppm, Sb 10-34 ppm.</li>

The variation in element concentrations shows that different erosion sources were active during the deposition of the three loose fluvial and conglomeratic beds.

It is indeed interesting that the highest element concentrations, excluding Cd and Zn, occur in the underlying bedrock, which is marble, *i.e.* (2.11-5.30 m): Cd 1.9 ppm, Pb 1210 ppm, Zn 260 ppm, As 1032.4 ppm, Hg <1 ppm, and Sb 41.9 ppm, suggesting potential primary mineralisation at depth.

The results of this drill-hole indicate that the levels of incoming mining waste contamination outside Lavrion are significantly lower than those occurring within the Lavrion urban area, which has its source in the metallurgical processing wastes.

Table 4.18. Log of drill-hole G21: fluvial deposits of the stream draining the catchment basin from Agios Constantinos to Lavrion.

Πίνακας 4.18. Πει	οιγραφή γεώτρησης G21:ποτάμιες αποθέσεις του ρέμματος που αποστραγγίζει την	
λεκάνη απορροής	Αγίου Κωνσταντίνου-Λαυρίου.	

Depth	Description
<i>(m)</i>	
0-0.30:	Pale brownish-yellow clayey-sand with angular pebbles of weathered- oxidised schist and marble up to 3 cm.
0.30-0.50:	Conglomerate consisting of subrounded to rounded pebbles of schist, reddish marble up to 4 cm; the cementing material is red clayey material with iron oxides.
0.50-0.84:	Loose pale brownish-red fluvial clayey-sand with pebbles derived from the underlying conglomerates containing fragments of marble and schist up to 3 cm and a clay-sand cement.
0.84-1.30:	Conglomerate consisting of subrounded to rounded pebbles of schist and red marble up to 8 cm; cementing material is red clay-sand with iron oxides.
1.30-1.78:	Loose red clayey material with rounded pebbles of schist and red marble up to 7 cm.
1.78-2.11:	Conglomerate consisting of rounded pebbles of marble and schist up to 2 cm; the cementing material from 1.78-1.88 m appears to be clayey-sand, which is more calcareous from 1.88-2.11 m.
2.11-5.30:	Pale grey marble, locally rosy.

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G21

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			Cd (ppm)	Pb (ppm)	Zn (ppm)	pH
BAθOΣ m	ЛІӨОЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	1.9	384.0 1210.0	260.0 1230.0	8.4
0.30	0 0 0	KKι έδαφος, Sch, Mrb				
0.50	0_0_0	Κροκαλοπαγές από Sch, Mrb, FeOx		7		
0 84	0 0 0	ΚΚο Αργ-Αμμ έδαφος με Mrb, Sch				
1.30	0100	Κροκαλοπαγές από Sch, Mrb, FeOx				
1 78		Κο αργιλικό έδαφος με Sch, Mrb				
2.11 .	0 0	Κροκαλοπαγές από Mrb, Sch				
		Γκρίζο μάρμαρο				
5.30		j.				

ΣΧΗΜΑ 4.35, σελίδα 4.53

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G21

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			As (ppm)	Sb (ppm)	pH
ΒΑΘΟΣ	ΛΙΘΟΛΟΓΙΚΗ	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΟΝ	4		
m	томн	IIII III ATII ZAIMATIZMIN	88.7	9.6	8.4
	000	W. Sama Sab Mak			
0.30	0 7 0	KKt 200405, Sell, Mrb			
150	0_0_0	Κροκαλοπαγές από Sch, Mrb, FeOx	[		VIIIIA
1.50				1	1 de la companya de l
	0 0 0	ΚΚο Αργ-Αμμ έδαφος με Mrb, Sch			
).84	=				H
		Kookalomayés and Sch Mrb FeOx			
30	0_0_0	iponationarios and ben, m b, reox			
	0-0-0		8		100000
	0 0 0 0	Κο αργιλικό έδαφος με Sch. Mrb			
~	0-0-0	· · · · · · · · · · · · · · · · · · ·			
	0-0-0			CHIIIIAN	
	0_0_0	Κροκαλοπαγές από Mrb, Sch			
3.11 .					Ammini
		Γκρίζο μάρμαρο			
30					

ΣΧΗΜΑ 4.36, σελίδα 4.54

#### 4.2.19. DRILL-HOLE G22 (Table 4.19, Figs. 4.37-.38)

The drill-hole was sited on the bank of the stream draining from Plaka (Map 2.14). The reason for selecting this site was to examine the geochemical composition of material derived from the drainage basin of Plaka and other mining areas, where there are extensive mining wastes only (Map 1.2).

The pH is variable within the alkaline range (8.3 to 9.1), and does not appear, therefore, to have affected the vertical distribution of elements. The surface layer down to 1.30 m is a mixture of wastes from the demolition of buildings and contaminated soil from sites within the Lavrion urban area and, consequently, shows the highest element levels. The material penetrated by this drill-hole from 1.30 m down to 14.60 has been deposited under low to high-energy fluvial conditions. Element patterns reflect, therefore, erosion sources active at the time of deposition of the fluvial sediments. This is indicated by the variable range of elements concentrations in the fluvial deposits: Cd <1-3 ppm, Pb 132-2280 ppm, 175-1230 Zn ppm, As 23-182 ppm, Hg <1 ppm, Sb <5-28 ppm. Local background conditions are depicted by the rose marble, *e.g.*, Cd 2 ppm, Pb 144 ppm, Zn 154 ppm, As 26 ppm, Hg <1 ppm, Sb <5 ppm.

It is apparent, therefore, that element concentrations in the eroded mining wastes, although geochemically anomalous, are not as high as those of the Lavrion urban area, which are due to contamination from metallurgical processing wastes.

Table 4.19. Log of drill-hole G22: fluvial deposits of the stream draining the catchment basin of the mining area of Plaka and its hinterland.

Πίνακας 4.19.	Περιγραφή γεώτρησης G22: ποτάμιες αποθέσεις του ρέμματος που αποστραγγίζει την
λεκάνη απορρ	οής της ευρύτερης μεταλλευτικής περιοχής Πλάκας.
Donth	Description

Depth	Description
( <i>m</i> )	
0-1.30:	Grey clayey-sandy material and at places reddish-brown and with a high
	proportion of clay, mixed with angular pebbles of building materials such as
	polished marble, mosaics, red tiles and bricks.
1.30-2.50:	Greyish-red clayey-sand with a high proportion of clay (floodplain sediments -
	intermediate-energy environment).
2.50-3.10:	Brownish-yellow clayey-sand with angular pebbles of marble up to 2 cm
	(fluvial sediments – high-energy environment).
3.10-9.00:	A fairly uniform section of greyish-black clayey sediments (floodplain
	sediments – low-energy environment); black coloured sediments suggest
	reducing conditions.
9.00-9.40:	Greyish-yellow clayey-sand with a high proportion of sand; angular pebbles of
	rose marble and subangular quartz up to 4 cm (fluvial sediments – high-
	energy environment).
9.40-11.20:	Greyish-black clayey floodplain sediments (low-energy environment).
11.20-11.50:	Greyish-yellow clayey-sand; coarse-grain sand at places; an angular pebble
	of rosy marble (fluvial sediments – intermediate-energy environment).
11.50-12.10:	Greyish to greyish-yellow clayey floodplain sediments; organic remains at
40.40.40.00	places (low-energy environment).
12.10-12.30:	Greyish-red clayey-sand floodplain sediments (low-energy environment).
12.30-12.90:	Greyish-red clayey floodplain sediments with organic remains at places (low-
40.00.40.00	energy environment).
12.90-13.20:	Brownish-red clayey-sand floodplain sediments with rounded pebbles of
40.00.44.00	marble and quartz (high-energy environment).
13.20-14.60:	Reddish clayey-sand floodplain sediments with a high proportion of angular to
44.00 44.00	subangular peoples of rose marble up to 10 cm (high-energy environment).
14.60-14.80:	Kose marple.

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G22

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			Cd (ppm)	Pb (ppm)	Zn (ppm)	pH
BAθOΣ m	ЛІӨОЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	0.5 25.8	132.0 3420.0	154.0 3200.0	8.3 9.1
1.30	Y Y Y Y Y Y Y Y	Γκρ Αργ-Αμμ έδαφος με μπάζα				
0.50	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	ΓΚο Αργ-Αμμ πλημμυρικές αποθέσ				
3.10	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	ΓΚι Αργ πλημμωρικέs αποθέσειs				
0.00	>       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >       >	ΓΜα Αργ πλημμυρικές αποθέσεις				
9.40		ΓΚι Αργ-Αμμ πλημμυρικές αποθέσ ΓΜα Αργ πλημμυρικές αποθέσεις	-	3		
11.20 11.50 12:10 12:30 12:90 13:20		ΓΚι Αργ-Αμμ πλημμυρικές αποθέσ Γκρ Αργ πλημμυρικές αποθέσεις ΓΚο Αργ-Αμμ πλημμυρικές αποθέσ ΓΚο Αργ πλημμυρικές αποθέσεις ΚΚο Αργ-Αμμ πλημμυρικές αποθέσ				
14.60 14.80		Κο Αργ-Αμμ πλημμυρικές αποθέσ. Ροδόχρουν Μάρμαρο	a			

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G22

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

		F	As (ppm)	Sb (ppm)	pH
BAθ0Σ m	ЛІФОЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	19.6	2.5 35.9	3.3
	Y Y Y Y	Γκρ Αργ-Αμμ έδαφος με μπάζα			3
1.30		ΓΚο Αργ-Αμμ πλημμυρικέs αποθέσ			
2.50 3.10	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	ΓΚι Αργ πλημμυρικές αποθέσεις			
	$\begin{array}{c} \vee - \vee - \vee \\ - \vee - \vee - \\ \vee - \vee - \vee \end{array}$				
	$\begin{array}{c} - \lor - \lor - \lor \\ \lor - \lor - \lor \\ - \lor - \lor - \lor \end{array}$				
	$\begin{array}{c} \vee - \vee - \vee \\ - \vee - \vee - \\ \vee - \vee - \vee \end{array}$	ΓΜα Αργ πλημμυρικές αποθέσεις			
	$\begin{array}{c} - \lor - \lor - \lor - \lor \\ \lor - \lor - \lor \\ - \lor - \lor -$				
	$\begin{vmatrix} \vee - \vee - \vee \\ - \vee - \vee - \\ \vee - \vee - \vee \end{vmatrix}$				
.00	- V - V -	ΓΚι Αργ-Αμμ πλημμυρικές αποθέσ			
		ΓΜα Αργ πλημμυρικές αποθέσεις			
1.20 1.50	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \begin{array}{c} \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \begin{array}{c} \end{array}{} \\ \\ \\ \end{array}{} \\ \end{array}{} \\ \\ \\ \end{array}{} \\ \\ \end{array}{} \\ \\ \\ \end{array}{} \\$ }	ΓΚι Αργ-Αμμ πλημμυρικές αποθέσ	a		
2:38		ΓΚο Αργ-Αμμ πλημμυρικές αποθέσεις ΓΚο Αργ πλημμυρικές αποθέσεις			
2.90 3.20		ΚΚο Αργ-Αμμ πλημμυρικές αποθέσ		A	
4.60		Κο Αργ-Αμμ πλημμυρικές αποθέσ.			
4:80		Ροδόχρουν Μάρμαρο			

#### 4.2.20. DRILL-HOLE G23 (Table 4.20, Figs. 4.39-.40)

The drill-hole was sited at the edge of the floodplain of the catchment basin draining the western part of Thorikon (Map 2.14). The reason for selecting this site was to examine the geochemical composition of material derived from the drainage basin of western Thorikon with ancient mining and beneficiation activities (Map 1.2). To the south of the site there is an ancient washing plant from the 5th to the 4th century BC (refer to Volume 1, Chapter 1, p.1). The small fragments of red ceramics, occurring from 0.40 to 3.00 m, are considered to belong to ancient activities of this period.

The pH, with minor variations, is in the alkaline range (8.3-8.7), and does not appear to have affected greatly the vertical distribution of elements. The high proportion of clay and iron oxides has apparently acted as sinks for contaminant elements. It is assumed, therefore, that distribution patterns below a depth of 1.00 m have changed very little with time. The horizon with a high proportion of clay and iron oxides acted as a geochemical barrier to recent extreme contamination, having in some cases higher element concentrations than the surface layer, *i.e.*,

• surface layer (0-0.32 m): Cd 69 ppm, Pb 30100 ppm, Zn 13000 ppm, As 915 ppm, Hg 3 ppm, and Sb 405 ppm;

• sink layer (0.32-0.40 m): Cd 82 ppm, Pb 23800 ppm, Zn 16500 ppm, As 1615 ppm, Hg 2 ppm, and Sb 424 ppm.

The underlying layer (0.40-1.00 m) also appears to have been affected by the downward leaching of contaminant elements. The layers from 1.00 to 3.00 are assumed to represent ancient patterns with distinctly lower levels: Cd 31-35 ppm, Pb 11200-11700 ppm, Zn 6150-7150 ppm, As 533-662 ppm, Hg 1 ppm, Sb 155-195 ppm. Finally, the sections from 3.00 to 8.00 m depict local natural background patterns: Cd 1-2 ppm, Pb 125-317 ppm, Zn 162-360 ppm, As 39-52 ppm, Hg <1 ppm and Sb <5-7 ppm.

Table 4.20. Log of drill-hole G23: fluvial deposits at the edge of the floodplain of the catchment basin draining the western part of Thorikon.

Πίνακας 4.20. Περιγραφή γεώτρησης G23: ποτάμιες αποθέσεις στην άκρη της πλημμυρικής πεδιάδας της λεκάνης απορροής που αποστραγγίζει το δυτικό τμήμα του Θορικού.

Depth	Description				
(m)					
0-0.32:	Brown clayey-sand with angular pebbles of schist, marble and slag up to 6 cm, fragments of red-coloured ceramics, and organic remains.				
0.32-0.40:	Dark brown clayey-sand with a high proportion of clay; angular pebbles of marble and slag up to 7 cm; iron oxides coatings on marble.				
0.40-1.00:	Brown clayey-sand with a high proportion of clay; angular pebbles of marble, and schist up to 6 cm and small fragments of red ceramics.				
1.00-2.00:	Brown clayey-sand with a high proportion of clay; angular to subangular pebbles of marble and schist up to 7 cm, and many small fragments of red ceramics.				
2.00-3.00:	Brownish-yellow clayey-sand with pockets having a high proportion of clay; angular pebbles of schist and marble up to 11 cm, and many small fragments of red ceramics.				
3.00-6.00:	Brownish-red clayey-sand with a very high proportion of clay, and between 5.00-6.00 m it is compacted; angular to subangular pebbles of marble and fewer of schist up to 6 cm.				
6.00-6.60:	Brownish-yellow clayey-sand with a very high proportion of angular to subangular pebbles of marble and schist up to 7 cm.				
6.60-7.00:	Conglomerate consisting of angular to subangular pebbles of mainly marble and less schist, which are cemented by brownish-yellow calcareous clayey sand.				
7.00-8.00:	Brownish-red clayey-sand with a very high proportion of angular to subangular pebbles of mainly marble and fewer schist up to 6 cm.				

ΕΡΓΟ: ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΥΣ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576 Γεώτρηση: G23 Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης | Cd (ppm) || Pb (ppm) || Zn (ppm) || pH ΒΑΘΟΣ ΛΙΘΟΛΟΓΙΚΗ 30000.0 17400.0 81.8 ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ 162.0 TOMH m 8.3 8.7 0_0_0 Kaφέ Apγ-Aμμ, Sch, Mrb, Slg, Kεραμ 8:38 Καφέ Αργ-Αμμ έδαφος, Mrb, Slg Καφέ Αργ-Αμμ έδαφος, Mrb, Sch 1.00



ΣΧΗΜΑ 4.39, σελίδα 4.59

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: G23

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			As (ppm)	Hg (ppm)	Sb (ppm)	pH
BAθOΣ m	ЛІΘОЛОГІКН ТОМН	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	40.5 1615.0	0.5 2.9	2.5 424.0	8°.
8:38		Καφέ Αργ-Αμμ, Sch, Mrb, Slg, Κεραμ Καφέ Αργ-Αμμ έδαφος, Mrb, Slg Καφέ Αργ-Αμμ έδαφος, Mrb, Sch				
1.00		Καφέ Αργ-Αμμ, Mrb, Sch, Κεραμικά				
3.00 .		ΚΚι Αργ-Αμμ, Mrb, Sch, Κεραμικά				
		ΚΚο Αργ-Αμμ έδαφος, Mrb, Sch				
6.00		ΚΚι Αργ-Αμμ έδαφος, Mrb, Sch				
7.00 _	0_0_0	Κροκαλοπαγές από Mrb, Sch				
		KKo Αργ-Αμμ έδαφος, Mrb, Sch				
8.00 _	0-0-0					8
## 4.2.21. VERTICAL PROFILE PS1 (Table 4.21, Figs. 4.41-.42)

This vertical profile is sited in the open space next to the 3rd Primary School of Lavrion, between Komobil and Santorineika, where the drill-hole G13 was subsequently carried out (Map 2.14). It can be said that this profile is a detailed section of the contaminated overburden of the first two metres of drill-hole G13. The reasons for selecting this particular site for drill-hole G13 and vertical profile PS1 were: (a) to examine the depth of metallurgical processing wastes, and (b) the contamination of fluvial sediments for at one time there was a stream flowing nearby (refer to Map 2.1).

The pH, although it was not determined is assumed, nevertheless, to be in the alkaline range, since drill-hole G13 is very close. There are three distinct patterns, *i.e.*, (a) the levels of Cd and Zn gradually increase from the surface to a depth of 51-76 cm, and then they gradually decrease until the bottom of the profile, (b) the levels of Pb, As and Sb they have an increasing trend from the surface to a depth of 124-154 cm, and then they drop to a lower concentration at the bottom part, and (c) Hg has approximately a similar pattern with Cd and Zn, but with a peak at 27-51 cm.

The drill-hole log, the geochemical patterns and the correlation with drill-hole G13 (p.4.31-.33) indicate that the whole vertical profile reflects the contamination of the metallurgical activities in Lavrion, *i.e.*, Cd 123-199 ppm, Pb 41600-60400 ppm, Zn 23200-33200 ppm, As 4943-11276, Hg 3.5-8.0 ppm and Sb 593-743 ppm.

Table 4.21. Log of vertical profile PS1: metallurgical wastes and fluvial deposits close to the 3rd Primary School in Lavrion (see also G13, Table 4.11, Figs. 4.21-.22).

Depth	Description
(centimetres)	
0-10:	Brownish-yellow sandy-clay with a variable amount of angular to subangular
	pebbles of schist and marble up to 6 cm.
10-27:	Brownish-yellow sandy-clay with a variable amount of angular to subangular
	pebbles of schist and marble up to 6 cm.
27-51:	Brownish-red clay with some charcoal, and fragments of slag.
51-76:	Brownish-yellow sandy-clay with charcoal.
76-93:	Brownish-red clay with charcoal.
93-124:	Brownish-red conglomerate consisting from angular to subangular pebbles of
	marble and schist up to 20 cm, and the odd slag fragment; the cement is
	calcareous sandy-clay.
124-154:	Brownish-yellow sandy layer with pebbles of marble and schist up to 2 cm.
154-195:	Brownish-red sandy-clay layer with a lens of sand (the water level is at 195
	cm).

Blank back page Λευκή οπίσθια σελίδα ΕΡΓΟ: ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΥΣ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: PS1

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

	and the second second		Cd (ppm)	Pb (ppm)	Zn (ppm)
BAθOΣ m	ліфологікн томн	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	122.5	41600.0	23200.0
10.00		ΚΚι Αμμ-Αργ υλικό, Sch, Mrb			
27 00		ΚΚι Αμμ-Αργ υλικό, Sch, Mrb			
51.00		ΚΚο αργιλ. υλικό, Slg, Κάρβουνο			
76.00		ΚΚι Αμμ-Αργ υλικό, Κάρβουνο			
93.00		ΚΚο αργιλικό υλικό, Κάρβουνο			
		ΚΚο κροκαλοπαγές με σκουριές			
124.00		ΚΚι αμμώδες υλικό, Sch, Mrb			
104.00		ΚΚο Αμμ-Αργυλικό, Sch, Mrb			
195 00	0,0000000		E		

ΣΧΗΜΑ 4.41, σελίδα 4.62

ΕΡΓΟ: ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΥΣ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: PS1

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			As (ppm)	Hg (ppm)	SB (ppm)
BAΘOΣ m	ліөслогікн томн	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	4942.9	3.5 8.0	593.0
0.00		ΚΚι Αμμ-Αργ υλικό, Sch, Mrb			
7.00		ΚΚι Αμμ-Αργ υλικό, Sch, Mrb			
j1.00 .		ΚΚο αργιλ. υλικό, Slg, Κάρβουνο			
76.00		ΚΚι Αμμ-Αργ υλικό, Κάρβουνο			
		ΚΚο αργιλικό υλικό, Κάρβουνο			
24.00		ΚΚο κροκαλοπαγές με σκουριές			
		ΚΚι αμμμώδες υλικό, Sch, Mrb			
54.00 .		ΚΚο Αμμ-Αργυλικό, Sch, Mrb			
.95.00					

ΣΧΗΜΑ 4.42, σελίδα 4.63

## 4.2.22. VERTICAL PROFILE PS2 (Table 4.22, Figs. 4.43-.43)

This vertical profile is sited in the grounds of the Lavrion old people's occupation and enjoyment centre (Map 2.14). The first 110-cm consists of a fairly uniform material, *i.e.*, brownish-yellow clayey-sand with pebbles of schist and marble, but also fragments of slag. The geochemical patterns of all elements are approximately similar. The first 10 cm have comparatively higher element concentrations than the underlying sections. Generally, there is an increasing trend in the contents of all elements towards the bottom of this clayey-sandy layer.

All elements reach their maximum concentrations between 110-122 cm, which is again a clayey-sand layer, but the proportion of clay is higher than that of the overlying layer. The underlying layer has still a higher proportion of clay, with evidence of reducing conditions (black colour), but distinctly lower element contents, and the bottom horizon is again rich in clay, and has the lowest element levels.

This is an interesting section for it indicates that there is a slow downward leaching of elements, and precipitation in the first layer (110-122 cm) with a comparatively higher proportion in clay, and above the reducing layer (122-135 cm) with still a higher clay content. Hence, it is quite apparent that reducing conditions have rendered almost completely immobile the studied elements.

The bottom layer, although it has the lowest element concentrations, they are still high, *i.e.*, Cd 13.4 ppm, Pb 4440 ppm, Zn 2300 ppm, As 160.4 ppm, Hg <1 ppm and Sb 59.7 ppm. Consequently, the whole profile down to a depth of 175 cm is seriously contaminated by toxic elements.

Table 4.22.	Log of vertical	profile PS2:	overburden in	the premises	of the old people's
occupation a	and enjoyment	centre in La	vrion.		

Πίνακας 4.22. Περιγραφή της κάθετης τομής PS2: εδαφικό κάλυμμα στο χώρο του κτιρίου του ΚΑΠΗ Λαυρίου.

Depth	Description
(centimetres)	
0-10:	From 0 to 110 cm is a fairly uniform laver, which has been subdivided into
10-20:	seven intervals in order to study in detail element distribution
20-40:	
40-60:	Brownish-vellow clavey-sand with a large proportion of angular, subangular to
60-80:	subrounded pebbles of schist and marble to 25 cm: there are also scattered
80-100:	fragments of slag.
100-110:	
110-122:	Brownish-yellow clayey-sandy layer with subangular to subrounded pebbles of schist and marble up to 5 cm. The proportion of clay is higher in this layer than that of the overlying section.
122-135:	Brownish-black clayey layer with angular to subangular pebbles of schist and marble up to 5 cm. The black colour suggests reducing conditions.
135-175:	Brownish-red clayey horizon with dispersed subangular to subrounded pebbles of schist and marble up to 4 cm.

Blank back page Λευκή οπίσθια σελίδα ΕΡΓΟ: ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΥΣ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ

APIOMOS EPFOT LIFE: 93/GR/A14/GR/4576

Γεώτρηση: PS2

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

			Cd (ppm)	Pb (ppm)	Zn (ppm)
ΒΑΘΟΣ Λ m	100логікн томн	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	13.4 83.3	4440.0	2300.0 18500.0
10.00	0 0 0	ΚΚι Αργ-Αμμιυλικό, Sch, Mrb			
20.00	0 0 0	KKι Αργ-Αμμιυλικό. Sch. Mrb			
40.00	0 0 0	ΚΚι Αργ-Αμμ υλικό, Sch, Mrb			
60.00		ΚΚι Αργ-Αμμ υλικό, Sch, Mrb			
80.00	010 010	ΚΚι Αργ-Αμμ υλικό, Sch, Mrb			
	- 10 - 10 - 10 - 10 - 10 - 10 - 10 - 10	ΚΚι Αργ-Αμμιυλικό, Sch, Mrb			
110.00	0 0	ΚΚι Αργ-Αμμ υλικό, Sch, Mrb			
122.00		ΚΚι Αμμ-Αργ υλικό, Sch, Mrb			
135.00	2_0_0	ΚΜα αργιλικό υλικό, Sch, Mrb			
0,010,01	0 -0 -0	ΚΚο αργιλικό υλικό, Sch, Mrb			
175.00					

ΣΧΗΜΑ 4.43, σελίδα 4.65

ΕΡΓΟ: ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΥΣ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ

APIOMOS EPFOY LIFE: 93/GR/A14/GR/4576

Γεώτρηση: PS2

Μελέτη: Αλ. Δημητριάδης, Ν. Παπασιώπη, Αικ. Βέργου-Βήχου & Π. Σταυράκη

Επεξεργασία και παρουσίαση: Ε. Βασιλειάδης

		As (ppm)	Hg (ppm)	Sb (ppm)
ΒΑΘΟΣ ΛΙΘΟΛΟΓΙΚΗ m τοmh	ΠΕΡΙΓΡΑΦΗ ΣΧΗΜΑΤΙΣΜΩΝ	160.4 9861.9	0.5	59.7 563.0
	ΚΚι Αργ-Αμμ υλικό, Sch, Mrb			
20.00	ΚΚι Αργ-Αμμ υλικό, Sch, Mrb			
40.00	ΚΚι Αργ-Αμμιυλικό, Sch, Mrb			
	ΚΚι Αργ-Αμμιυλικό, Sch, Mrb			
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ΣΧΗΜΑ 4.44, σελίδα 4.66

## 4.3. DISCUSSION AND CONCLUSIONS

The drilling and vertical profile results have given valuable site data with respect to

- the approximate thickness of metallurgical processing wastes,
- the approximate thickness of contaminated overburden,
- transported contamination from drainage basins having their outlets in the Lavrion study area,
- possible element levels of historical contamination,
- mobility of contaminants and potential future problems to ground water supplies,
- geochemical background of residual soil,
- geochemical background of fluvial sediments, and
- lithogeochemical data, which have given the natural variation in rocks, but also possible mineralisation at depth.

As it has been stressed drill-holes and vertical profiles in such an area as Lavrion with extremely variable contamination, provide information about the site only. Consequently, such information cannot be extrapolated.

These results have shown that the thickness of metallurgical processing wastes is not as important as that of contaminated overburden, which in some cases reaches bedrock. Depending, therefore, on drill-hole site, the thickness of contaminated overburden varies from as little as 0.37 m (G17), a residual soil background area, to 14.60 m (G10), which is situated at Noria in an area with beneficiation/flotation residues. Information from site G17 is very significant, for it was carefully selected, as a location with undisturbed residual soil, and away from all smelting activities and dump sites. Nevertheless, fragments of slag were found in the contaminated surface layer. It is noted that slag is found in almost the remotest parts of Lavrion.

Three drill-hole sites were selected to examine transported contamination from mining areas outside Lavrion, *i.e.*,

- G18, in the south-west at Noria, to check the drainage basin from Elafos and Vilanoria, an area with mainly ancient mining and beneficiation activities,
- G21, in the western-central border part of the study area, to check the drainage basin from the mining area of Agios Constantinos, and
- G22, in the north at Thorikon, to check the drainage basin from the mining area of Plaka and its hinterland.

The results have shown that the levels of toxic elements in transported fluvial overburden, derived from the erosion of mining wastes, are significantly lower than those occurring in the Lavrion urban area overburden, which is derived from the metallurgical processing activities.

Drill-hole G23 was very interesting because it was sited next to an ancient washing plant at Thorikon, which according to archaeological evidence dates back to the 5th-4th century BC. The section from a depth of 1.00 to 3.00 m is ascribed to possible ancient contamination, which is distinctly lower, than the levels of recent mining and smelting activities.

Mobility of contaminants is considerable in the areas with pyritiferous wastes, and especially the pyrite tailings on the beach between Komobil and Kiprianos, because of

the generation of acid drainage (*e.g.*, drill-holes G2, G5). In these cases, the pH of aqueous solutions is a major factor in controlling the leaching and subsequent precipitation of cations. Also, the pH of hydrolysis or hydroxide precipitation has been shown to explain very well the distribution patterns of drill-hole G2 and G12. Further, there appears to be some downward leaching of contaminants even in areas with an alkaline pH and high carbonate contents. This minor, but significant movement of contaminants, is perhaps due to over-saturated aqueous solutions of toxic elements. The evidence for this downward movement of contaminants is shown by the ground water itself, *e.g.*, above normal toxic elements contents (refer to Chapter 10 in Volumes 1 & 2, and Appendix Report 5B in Volume 1B).

Drill-hole G17 has given data about *"normal local background"* concentrations in residual soil at a depth of 0.37-1.28 m, *e.g.*, Cd <1-1 ppm, Pb 121-186 ppm, Zn 125-137 ppm, As 16-26 ppm, Hg <1 ppm, and Sb <5 ppm. Nevertheless, even these values may have been slightly affected by the extreme surficial contamination, which is a ubiquitous feature of Lavrion.

Fluvial sediments were intersected by nine drill-holes (G4, G11, G12, G13, G14, G18, G19, G21, G22 and G23), and the results are indeed very interesting, for they possibly depict natural background conditions, peculiar to a richly metalliferous area as is Lavrion and its hinterland, before mining and smelting activities began. As an example, the results of fluvial sediments from drill-hole G14 (depth 2.50-5.30 m) are mentioned: Cd<1, Pb 24 ppm, Zn 70 ppm, As 14 ppm, Hg <1 ppm and Sb 8 ppm.

Nine drill-holes have intersected bedrock, *e.g.*, marble (G6, G7, G10, G21, G22), schist (G13, G16, G17), and marble and schist (G14). Also, four drill-holes have intersected conglomerate (G4, G18, G21, G23). Basal conglomerates were most likely intersected by drill-holes: G4 (thickness >2.80 m), G18 (the lower horizon >2.04 m thick), and G21, which is underlain by marble. The conglomerate of drill-hole G23 is underlain by brownish-red clayey-sand, and its stratigraphical position appears to be similar to the intermediate conglomerate of drill-hole G18, which is underlain by brownish-yellow clayey-sand.

Finally, it is interesting to note that six drill-holes have intersected geochemically anomalous bedrock, *e.g.*,

- marble: G6 (As, Pb, Zn),
- marble: G7 (As, Sb),
- marble: G10 (As, Cd, Pb, Sb, Zn),
- schist: G13 (As, Pb, Zn),
- schist: G16 (As, Pb, Sb, Zn), and
- marble: G21 (As, Pb, Sb, Zn).

Drill-holes G6 and G7 are in the Kavodokanos area, G10 has located a known mineralised zone (refer to Maps 3.1 & 4.30 in Volume 2), G13 has outcrops of ankeritised and silicified marble, G16 occurs in a lithogeochemical zone with above normal Pb and Zn contents, and G21 is closed to a known mineralised zone (ancient and recent adit within the premises of the smelter at Kiprianos).

It is concluded that the drill-holes and vertical profiles have given valuable information about the subsurface geochemistry in the Lavrion urban area, and the potential contamination problems of ground water resources.

# **Appendix Report 5**

# **GEOCHEMISTRY OF GROUND WATER, LAVRION**

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# **EXPLANATORY COMMENTS**

The geochemistry of ground water has already been described and discussed in Chapter 10 of Volume 1 (p.304-310) and distribution maps of different variables presented in Volume 2 (Maps 10.1 to 10.2). In this Appendix Report, all the parameters measured with the acceptable admissible limits, and certain indices and ionic ratios, are tabulated in Figures 5.1 to 5.15. Below explanations are given to aid the interpretation of results by the reader. The software producing this pictorial presentation of hydrogeological results was developed by E. Vassiliades for the IGME Hydrogeology Sector (Vassiliades and Zangouroglou, 1998).

## SODIUM ABSORPTION RATIO (SAR)

The Sodium Absorption Ratio (SAR) or Coefficient of Sodium Absorption is a fundamental criterion for the suitability of ground water for irrigation purposes (Kallergis, 1986). SAR is estimated by the following equation, where the concentrations of Na, Ca and Mg are in units of milliequivalent/litre (meq/l):

Sodium Absorption Ratio (SAR) = 
$$\frac{\text{Na}}{\sqrt{(\text{Ca+Mg})/2}}$$

If the value of SAR exceeds unity, then ground water does not have the power to dissolve Ca, and is precipitated on soil as carbonates of calcium creating, therefore, problems in agricultural productivity.

## **REVELLE INDEX**

The Revelle Index indicates sea water intrusion (values expressed in meq/I), and is estimated as follows (Revelle, 1941):

Revelle index = 
$$\frac{CI}{(CO_3+HCO_3)}$$

This index should be used, however, with caution if the hydrogeological regime of the area is not known. Table 5.1 gives the degree of ground water pollution according to the Revelle Index.

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Table 5.1. Characterisation of the degree of ground water pollution from sea water intrusion according to Revelle (1941) with modifications by Kallergis (1986, Table 7.22, p.7-83). Πίνακας 5.1. Χαρακτηρισμός βαθμού ρύπανσης υπόγειου νερού από τη διείσδυση της θάλασσας, κατά Revelle (1941) με τροποποιήσεις από Καλλέργη (1986, Πίν. 7.22, σελ. 7-83).

Revelle index		Ground water characterisation
Revelle (1941) limits	Kallergis (1986) proposed limits	
<0.5	<1	Good ground water without contamination from sea water
1.3	1-2	Weakly polluted ground water
2.8	2-6	Moderately polluted ground water
6.6	6-10	Severely polluted ground water
15.5	10-150	Dangerously polluted ground water
200+	>150	Sea water

## ALKALINITY

Alkalinity is the ability of water to neutralise acid. It is defined as the quantity of ions, such as  $CO_3^{2-}$ ,  $HCO_3^{-}$ ,  $OH^-$ ,  $HSiO_3^{-}$ ,  $H_2BO_3^{-}$ ,  $HPO_4^{2-}$  and  $H_2PO_4^{-}$ , in water that will neutralise hydrogen ions (Salminen and Tarvainen *et al.*, 1998). Since, alkalinity is practically due to the exclusive presence of carbonates and bicarbonates, it is often expressed as milligrams per litre of CaCO₃ (Kallergis, 1986). This means that the determined total amount of all ions neutralising acid is converted to an equivalent concentration of CaCO₃ by calculation, *i.e.*, the sum of  $CO_3^{2-}$  and  $HCO_3^{-}$  expressed in equivalents of CaCO₃ (mg/l). Alkalinity provides, therefore, an index to the nature of the rocks that ground water passes through.

## Mg²⁺/Ca²⁺ ratio

Ground water type	Mg ²⁺ /Ca ²⁺ (meq/l)	Rock unit of aquifer
Calcareous ground water:	0.5-0.7	Limestone
Dolomitic ground water:	0.7-0.9	Dolomitic
Siliceous ground water:	>0.9	Silicate rocks

## Na⁺/Cl⁻ ratio

Characterisation of ground water	Na⁺/Cl⁻
	(meq/l)
Ordinary ground water:	0.876±10%
Ground water from alkaline igneous or metamorphic rocks:	>1.0
Ground water pollution from sea water intrusion:	<0.788

## Na⁺/K⁺ ratio

Ground water type and location	Na⁺/K⁺
	(meq/l)
Sea water:	~47
Rain water:	<10
Area of ground water enrichment:	15-25
Down slope part of aquifer due to absorption of Na:	50-70

## (Ca²⁺+Mg²⁺)/(K⁺+Na⁺) ratio

Location of aquifer	(Ca ²⁺ +Mg ²⁺ )/(K ⁺ +Na ⁺ )
	(meq/l)
In the area of ground water enrichment:	>1.0
Down slope part of aquifer:	<1.0

## HCO₃-/Cl⁻ and SO₄²⁻/Cl⁻ ratios

Near to areas of ground water recharge, bicarbonate ( $HCO_3^{-}$ ) is the dominant ion. Its concentration increases up to a certain level, which is determined by the solubility product of CaCO₃ (Kallergis, 1986). The concentrations of SO₄²⁻ and Cl⁻ tend to increase down slope. However, the levels of Cl⁻ increase at a faster rate, until chlorides become the dominant ions, despite the fact that the concentration of SO₄²⁻ increases continuously, since it never reaches the solubility product of CaSO₄.

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#### ΙΝΣΤΙΤΟΥΤΟ ΓΕΩΛΟΓΙΚΩΝ ΚΑΙ ΜΕΤΑΛΛΕΥΤΙΚΩΝ ΕΡΕΥΝΩΝ ΔΙΕΥΘΥΝΣΗ ΓΕΩΧΗΜΕΙΑΣ τιτλος εργοτ: αποκαταστάση εδαφούς στο δημο λατριού

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ΣΧΗΜΑ 5.1, σελίδα 5.1

### ΙΝΣΤΙΤΟΥΤΟ ΓΕΩΛΟΓΙΚΩΝ ΚΑΙ ΜΕΤΑΛΛΕΥΤΙΚΩΝ ΕΡΕΥΝΩΝ ΔΙΕΥΘΥΝΣΗ ΓΕΩΧΗΜΕΙΑΣ τιτλός εργού: αποκατάσταση εδαφούς στο δημό λατριού

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Χημική ανάλυση νερού



ΣΧΗΜΑ 5.2, σελίδα 5.3

## ΙΝΣΤΙΤΟΥΤΟ ΓΕΩΛΟΓΙΚΩΝ ΚΑΙ ΜΕΤΑΛΛΕΥΤΙΚΩΝ ΕΡΕΥΝΩΝ ΔΙΕΥΘΥΝΣΗ ΓΕΩΧΗΜΕΙΑΣ τιτλος εργοτ: αποκατάσταση εδάφοτς στο δημο λατριού

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ΣΧΗΜΑ 5.6α, σελίδα 5.8

#### ΙΝΣΤΙΤΟΥΤΟ ΓΕΩΛΟΓΙΚΩΝ ΚΑΙ ΜΕΤΑΛΛΕΥΤΙΚΩΝ ΕΡΕΥΝΩΝ ΔΙΕΥΘΥΝΣΗ ΓΕΩΧΗΜΕΙΑΣ ΤΙΤΛΟΣ ΕΡΓΟΤ: ΑΠΟΚΑΤΑΣΤΑΣΗ ΕΔΑΦΟΥΣ ΣΤΟ ΔΗΜΟ ΛΑΥΡΙΟΥ

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#### ΙΝΣΤΙΤΟΥΤΟ ΓΕΩΛΟΓΙΚΩΝ ΚΑΙ ΜΕΤΑΛΛΕΥΤΙΚΩΝ ΕΡΕΥΝΩΝ ΔΙΕΥΘΥΝΣΗ ΓΕΩΧΗΜΕΙΑΣ τιτλος έργοτ: αποκατάσταση εδάφοτς στο δημο λάτριος

#### KOAIKOS APIOMOS EPFOT: LIFE 93/GR/A14/GR/4576



#### ΙΝΣΤΙΤΟΥΤΟ ΓΕΩΛΟΓΙΚΩΝ ΚΑΙ ΜΕΤΑΛΛΕΥΤΙΚΩΝ ΕΡΕΥΝΩΝ ΔΙΕΥΘΥΝΣΗ ΓΕΩΧΗΜΕΙΑΣ τιτλός εργοτ: αποκατάσταση εδαφούς στο δημο λατριού

#### KOAIKOS APIOMOS EPFOT: LIFE 93/GR/A14/GR/4576



#### ΙΝΣΤΙΤΟΥΤΌ ΓΕΩΛΟΓΙΚΩΝ ΚΑΙ ΜΕΤΑΛΛΕΥΤΙΚΩΝ ΕΡΕΥΝΩΝ ΔΙΕΥΘΥΝΣΗ ΓΕΩΧΗΜΕΙΑΣ τίτας εργοτ: αποκατάσταση εδαφούς στο δημο λατριού

ΚΩΔΙΚΟΣ ΑΡΙΘΜΟΣ ΕΡΓΟΥ: LIFE 34/GR/A14/GR/4576



#### ΙΝΣΤΙΤΟΥΤΟ ΓΕΩΛΟΓΙΚΩΝ ΚΑΙ ΜΕΤΑΛΛΕΥΤΙΚΩΝ ΕΡΕΥΝΩΝ ΔΙΕΥΘΥΝΣΗ ΓΕΩΧΗΜΕΙΑΣ τιτλός έργος: αποκατάσταση εδάφους στο δήμο λατριού

KOAIKOS APIOMOS EPFOT: LIFE 93/GR/A14/GR/4576

