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ARSENIC DISTRIBUTION IN LATERITE DEPOSITS OF THE BALKAN PENINSULA

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Abstract: The laterite deposits (Fe–Ni-laterite and bauxites) in the Balkan Peninsula are mainly located in the Mirdita–Sub-Pelagonian and Pelagonian geotectonic zones and are of great economic significance. These deposits have been affected by intense tectonism, which has created overthrusting, foliation, folding, and faulting. The investigation of arsenic in laterites is thought to be important for the ferronickel smelting process and the serious affect of the health. Minerals such as iron oxides and pyrite are of particular significance in controlling arsenic mobility, and hence aquifer contamination. Laterite samples from Ni-laterite deposits of Greece (Lokris, Vermio, Edessa, Olympos, Kastoria), Albania (Bitinca and Gouri- Perjuegjiun), Serbia (Rzanovo and Topola), bauxitic laterites and the Parnassos-Ghiona bauxite deposit were analyzed for major and trace elements, including arsenic (As). Arsenic concentrations for all laterite samples from the Balkan Peninsula range from < 2ppm to a few decades ppm. However, arsenic concentrations for the individual laterite occurrences and deposits from Aghios Ioannis vary significantly from <2 ppm to 2600 ppm. Arsenic in the Parnassos-Ghiona deposit ranges from <10 ppm in typical red colored ore to 900 ppm in yellow-grey colored ore. The latter type occurs along and near faults and constitutes a significant (approximately 30 vol. %) portion of the bauxite ores. They are characterized by the presence of abundant pyrite and micro-organisms. Elevated arsenic contents are mostly associated with Fe-oxides/hydroxides in Ni-laterites, showing enrichment in REE, Co, Ni, Th and U contents, and with Al-oxides in bauxites. The sulphur isotope compositions of Fe sulphides from the bauxite deposit show a range from +10.2 to –30.2 per mil. Most negative values were obtained from grey-coloured ore samples. The organic matter may be related to the source of arsenic and play a major role in controlling the redox conditions, since they can drive the formation of pyrite or Fe-oxides.

Keywords: Balkan Peninsula, Greece, arsenic, Ni-laterites, bauxites, organic matter

1. Introduction

Nickel, is a transition element of strategic significance, that is widespread as both siderophile (associated with iron) and chalcophile (associated with sulphur), and it is mined throughout the world from two types of ore deposits (a) laterites where the principal ore minerals are Ni- bearing iron oxides and hydrous nickel silicates and (b) magmatic sulphide deposits where the principal ore mineral is pentlandite [$(Ni,Fe)_9S_8$].The main world production comes from Russia, Canada, Australia and New Caledonia. The potential of Ferro-Nickel ore reserves in Greece is currently estimated to be in the range of 100 million tonnes, grading 1-1, 4 % Ni. The Fe–Ni-laterite deposits in the Balkan Peninsula are mainly found in the Mirdita–Sub-Pelagonian and Pelagonian geotectonic zones (Fig. 1) and are related to ophiolites of Upper Jurassic to Lower Cretaceous age. These deposits have been affected by intense tectonism, which has created overthrusting, foliation, folding, and faulting. This has resulted in the transportation of the laterite bodies, disrupting their continuity and in some cases mixing them with underlying rocks. The multistage deposition of the Fe–Ni ores, the redistribution of ore metals, the intense tectonism and the metamorphism, which have affected all the Ni-laterite deposits of Greece, have almost totally changed the initial mineralogical and chemical composition of the ores (Albandakis, 1980; Valeton et al., 1987; Eliopoulos and Economou-Eliopoulos, 2000).

Larko is the Hellenic Mining and Metallurgical Company for the extraction and processing of Ni. The mining operations are based at Psachna (north central Euboea Island), Aghios Ioannis (Lokris area) and Kastoria whereas the metallurgical plant is located at Larymna. Larko's production level corresponds to some 2-3% of the world total nickel output and is exported to various destinations in Western Europe. Based on bibliographic data, high As content (As>0.15%) in Ni-laterites is unacceptable in stainless steel production since it affects the ore quality. More specifically the higher portion of As in the feed, results to the higher As % content in the alloy (Zevgoles, 2004).

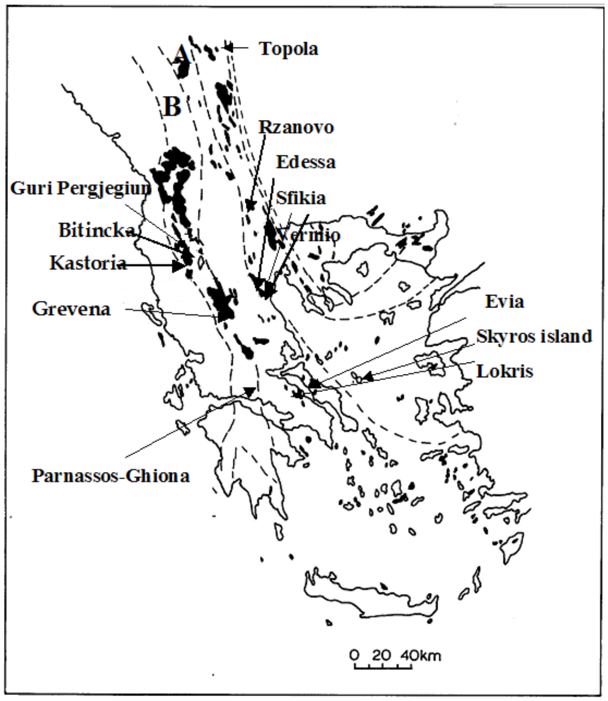

Fig. 1. Sketch map showing the Pelagonian (A) and Sub-Pelagonian (B) geotectonic zones of Greece, the distribution of ophiolites, and the location of the studied Fe-Ni-laterite and bauxite deposits.

The objective of this study is to define the As-distribution in Ni-laterites and bauxitic laterites in Greece and the Balkan Peninsula and bauxite deposits in Greece, using geochemical methods and mineral chemistry techniques in an attempt to explain its genetic significance and environmental impact.

2. Methods of investigation

Major elements were determined by atomic absorption at the University of Athens, and minor and trace elements by neutron activation analysis, at XRA Laboratories, Canada. The organic matter was determined at the University of Athens, following a wet oxidation method (Walkley- Black), using 1 N $K_2Cr_2O_7$ solution. The heat generated when two volumes of H_2SO_4 are mixed with one volume of the dichromate, assists the reaction. The remaining dichromate was titrated with ferrous sulphate. Mineralogical composition of the studied laterites was investigated by optical microscopy, and X-ray diffraction (XRD) using a Siemens D5005 power diffractometer.

The Electron microprobe analyses were carried out at the University of Athens using a Cambridge Microscan-5 instrument and a JEOL JSM-5600 scanning electron microscope, both equipped with automated energy dispersive analysis system, Link 2000 and ISIS 300 OXFORD, respectively, with the following operating conditions: accelerating voltage 20kV, beam current 0.5 nA, live time 50 secs, and a beam diameter of 1-2μm.

Sulphur isotopes were determined at Geochron Laboratories on representative bauxite samples (whole-rock) from the Parnassos-Ghiona deposit, in which the only detectable form of sulphur was Fe sulphide. Data were normalized to CDT with $^{34}S/^{32}S$ of 0.0450045.

3. Characteristic features of laterites

The majority of the Fe–Ni deposits in the Balkan peninsula are allochthonous, are developed on the Upper Jurassic–Lower Cretaceous serpentinized ultramafic ophiolites and are overlain by Tertiary molasses, such as the Kastoria and Bitincka deposits or Cretaceous limestones, such as the Tsouka (Lokris) deposit (Plastiras, 1979; Mountrakis, 1983; Valeton et al., 1987; Skarpelis et al., 1993). In the vicinity of the Aghios Ioannis laterite deposits the oldest volcanic rocks are a sequence of Triassic volcanic rocks consisting of several hundred meters of both mafic and acid pyroclastics and lavas at the Melidoni area, Lokris (Pe-Piper et al., 1981).

Commonly a goethite zone, is followed by the pelitic zone, characterized by fine-grained groundmass, composed of a pelitic matrix (goethite, hematite, clastic grains of quartz and chromite, as well as silicates), Mn-oxides (pyrolusite, lithiophorite). Pisolitic ore, overlies the pelitomorphic ore, and covers the whole section.

The Aghios Ioannis (Lokris) deposits lie on a karstified Jurassic limestone and are conformably overlain by Lower Cretaceous limestone. The Fe–Ni-laterite ore is mainly composed of goethite, hematite, Ni-bearing chlorite, illite, quartz, calcite, and chromite. The bauxitic-laterite contains mainly boehmite, gibbsite, kaolinite, goethite, and hematite. Chromite is usually found as very small fragments. Rutile, and sulphides (pyrite) and Ni-pyrite are also present, whereas smectite and takovite are more abundant towards the lowest part of the deposit (Alevizos, 1997; Veleton et al., 1987; Eliopoulos and Economou-Eliopoulos, 2000). Studied samples of re-worked Ni-laterite deposits from Lokris are composed by angular to rounded fragments of Fe-Ni laterite ore, saprolite, carbonate, silcrete, cemented by calcite, laterite material dominated by spheroidals, and re-deposition of the laterite components towards and within the carbonate basement (Fig. 2).

Small Fe–Ni occurrences in the form of lenses (1x15 m) are found in the east Vermion, Edessa, Olympos, Sfikia and Skyros Island in Greece, Topola and Rzanovo, central part of the Kozuf Mountain, former Yugoslavia (Fig. 1). They are located at the contact of serpentinized harzburgites with Upper Cretaceous limestones–conglomerates or within the serpentinites themselves. Due to intense tectonism, the Fe–Ni-laterite occurrences are often entirely enclosed within serpentinized harzburgites, near to their contact with transgressive limestones (Mihajilovic et al., 1972; Macksimovic and Panto, 1982; Economou-Eliopoulos, 2003).

Bitincka and Guri-Perjuegjiun Ni-laterite deposits in Albania (Fig. 1) are located in the central and southern parts of the Mirdita zone. They have the characteristics of allochthonous deposits, lie on highly serpentizized peridotites and are unconformably overlain by Tertiary molasses the former and Cretaceous limestones the later (Xhomo et al., 1995; Eliopoulos and Economou-Eliopoulos, 2000).

The Parnassos-Ghiona geotectonic zone, including the major bauxite deposits of Greece, is part of the Mediterranean karst bauxite belt. These deposits are hosted within carbonate rocks and have been formed during different geological ages. Three bauxite horizons, B1, B2 and B3, can be distinguished (from the bottom to the top), which are intercalated with shallow-water limestone, within an Upper Jurassic to Middle Cretaceous sequence of the Parnassos-Ghiona zone. Typical bauxite ore of predominant coarse-grained layers with pisoliths and/or oolites and fine-grained layers is of dark red to red-brown color. However, there is a significant proportion (approximately 30 volume %) of yellow and grey to whitish bauxites, associated with faults and zones of high deformation (Papastavrou, 1986; Valeton et al., 1987; Laskou and Economou-Eliopoulos, 2007). There is a gradual change in their colour from red to black-grey extending in a distance of tens of meters (Fig. 3a). The most abundant mineral phases are boehmite or diaspore, hematite/goethite or pyrite. Sulphide veins crosscutting sulphide-rich zones (Fig. 3b) and thin-sulphide layers underlying a layer of organic matter between bauxite bodies and limestone cover is a characteristic feature as well. Thin-layered marine limestone on top of the bauxite horizons showing a dark colour and enrichment in organic material

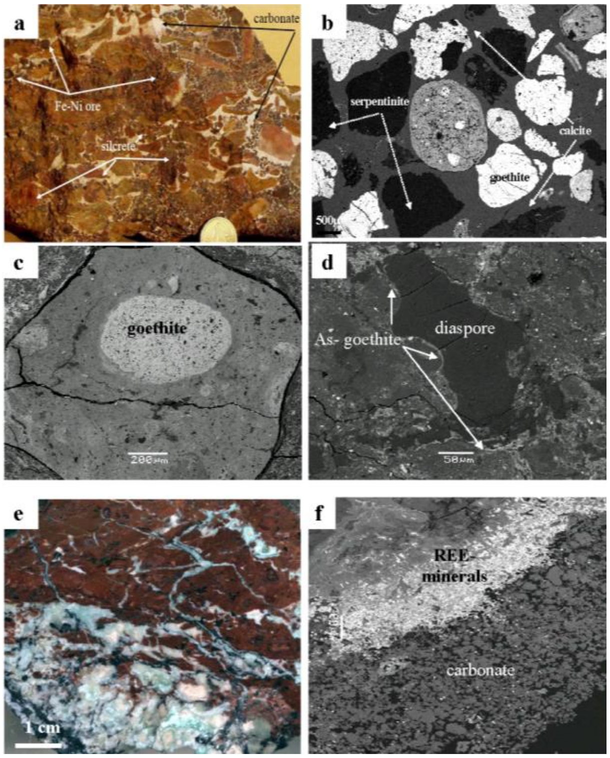

Fig. 2. Photos of re-worked Ni-laterite deposits from Lokris, showing a conglomerate composed of angular to rounded fragments of Fe-Ni laterite ore, saprolite, carbonate, silcrete, cemented by calcite and laterite material dominated by spheroidals (2a), and the re- mobilization and re-deposition of the laterite components towards and within the carbonate basement (2b). Back scattered electron SEM images from re-worked Fe-Ni laterite derposit of Lokris, showing a general view of Fe-Ni ore (2c), containing chromite fragments of varying size and composition (light and dark gray) in a matrix of goethite (2d), As-bearing goethite of subsequent stage (2e) and abundant rare earth minerals (REE-minerals) towards the contact of the laterite with the limestone basement (2f).

Table 1. Electron microprobe analyses of Fe- and Al-oxides from Ni-laterites and bauxites.

	Ni-laterites					Bauxites		
wt%	Fe-oxides					Al-oxides		
SiO_2	2,58	1,87	2,38	2,47	2,81	0,81	0,87	0,34
Fe_2O_3	69,52	70,62	76,23	75,61	78,33	0,88	1,57	2,43
Al_2O_3	1,57	1,29	0,88	1,12	1,26	84,12	79,15	75,77
Cr_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,42	0,22
TiO_2	0,26	4,85	0,71	0,24	n.d.	0,42	1,78	1,09
NiO	0,96	1,04	0,82	1,03	1,21	n.d.	n.d.	n.d.
As_2O_3	0,77	0,75	1,2	n.d.	n.d.	n.d.	1,39	n.d.
SO_3	0,74	0,89	0,73	0,51	n.d.	n.d.	n.d.	n.d.
Total	76,4	81,31	82,95	80,98	83,61	86,23	85,18	79,85

have been attributed stagnating and reducing conditions in coastal plains during tectonic down warping (Valeton et al., 1987). A layer of coal overlying the Parnassos-Ghiona B3 horizon has been studied recently (Kalaitzidis et al., 2009). Also, fossils of organic matter occur in Ni-laterite deposits of Edessa (Greece) and Katjeli (Albania), as Mn-bearing siderite having the form of plant fossils (Economou-Eliopoulos, 2003; Economou-Eliopoulos et al., 2003), resembling those in a laterite deposit on the south plateau of New Caledonia, characterized by the formation of a 4cm thick, Mn-rich siderite layer, which has the form of plant fossils (Golightly, personal communication). The remobilization/re-distribution of major and trace elements in Ni-laterite and bauxite deposits has been facilitated by the influence of bacteria (Fig. 3g, h). They may play a major role in controlling the redox conditions, since they can drive the formation of pyrite or Fe- oxides (Economou-Eliopoulos et al., 2003; Laskou and Economou-Eliopoulos, 2007).

4. Mineral chemistry

Although oolites seem to be a major component of the Ni-laterites, the microscopic examination and investigation using SEM/EDS analysis indicate that a concentric layering is lacking (Fig. 2). Rounded fragments of a pelitic matrix consist mostly of goethite containing clastic grains of quartz, chromite and chlorite (Fig. 2c, d) is suggesting a multistage re-deposition of Fe-Ni ore. Chromite exhibits a wide variation of the Cr/(Cr+Al) ratio ranging from 0.7 to 0.4. Rounded fragments of goethite containing clastic grains of various minerals, show a core with low aluminium and titanium contents, whilst outwards it is followed by a zone enriched in Al and Ti (Fig. 2c). Arsenic in such goethite ranges between 0.5 to 1.2 wt% As_2O_3 (Tab. 1, Fig. 2e). Arsenic in yellow-coloured bauxite is mostly hosted in Al-oxides, ranging between 0.6 to 1.4 wt% As_2O_3 (Tab. 1).

Bauxitic laterite from Aghios Ioannis (Nissi), Lokris shows the highest As and REE contents (Tab. 2) and it is characterized by the presence of abun-

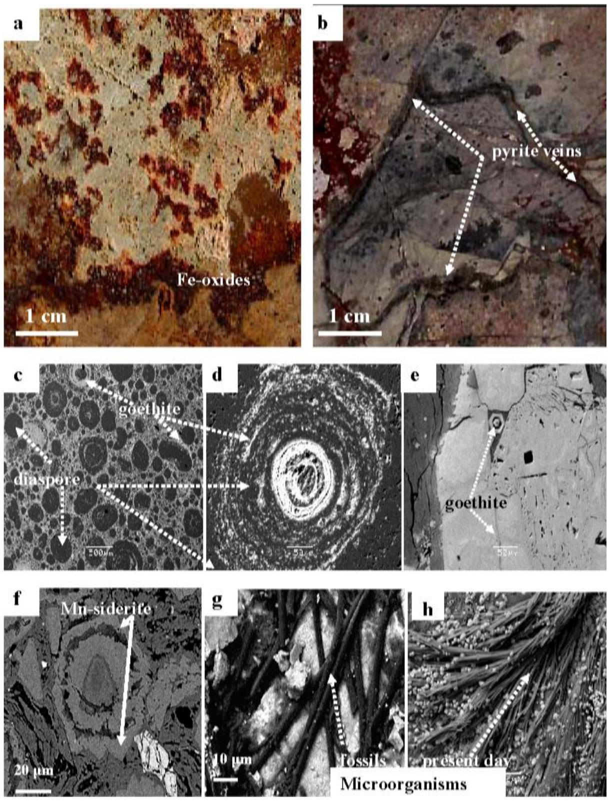

Fig. 3. Photograph of bauxite showing the transition zone between red and grey ore, and the occurrence of sulphide veins, from the Parnassos-Ghiona bauxite deposit (3a & 3b). Back scattered electron SEM images from the above zone (3c-h), showing the association of goethite and diaspore in pisoliths and matrix and their close association with filament-like microorganisms, either fossilized (3g) or present day microorganisms (3h). Fig. 3f shows a cross-section of Mn-siderite surrounding partially decomposed sticks of plant fossils, from a laterite deposit.

dant rare earth minerals (Fig. 2f). These minerals have been already described and reviewed along with the description of two new REE- minerals by Panto and Maksimovic (2001).

5. Whole rock chemistry

The whole rock analysis data have been published in previous papers (Eliopoulos and Economou-Eliopoulos, 2000; Economou-Eliopoulos et al., 2003). This study focuses on the distribution of arsenic in laterite samples from Ni-laterite deposits of Greece (Lokris, Vermio, Edessa, Olympos, Kastoria), Albania (Bitinca and Gouri Pergjegium), Serbia (Rzanovo and Topola), bauxitic laterites of Greece and bauxite deposit of Parnassos-Ghiona. Arsenic distribution shows a wide content range from lower than 2 to a few decades ppm (Tab. 2). However, arsenic concentrations for individual laterite occurrences and deposits of the Aghios Ioannis – Lokris area, Central Greece vary significantly and attain values up to 2600 ppm. The highest values were determined at the lowest part of the deposits lying on the karstified Jurassic limestone, and are accompanied by enrichment in rare earth elements (REE), Co, Ni, Th and U (Tab. 2; Economou-Eliopoulos et al., 1997). In addition these deposits are characterized by the presence of pellets rather than oolites or pisolites, due to the lack of a concentric development (Golightly 1981; Augustidis 1982), resulted from a multistage transportation and re-deposition of allochthonous Fe-Ni laterite material (Fig. 2). High As values were also determined in the Parnassos-Ghiona deposit ranging from <10 ppm in the typical red colored ore to 900 ppm in yellow-grey colored ore type (Fig. 3, Tab. 2). The common characteristic of all bauxite samples having elevated As content is their location near the top of bauxite horizons, associated with dark colour limestone which enriched in organic material and/or thin layers of coal (Kalaitzidis et al., 2009).

Total organic carbon (TOC) content in Ni-laterite samples from Lokris show relatively high As content ranging from 0.14 to 0.56 wt. %. TOC, while in grey-yellow coloured bauxite samples it reaches 2.8 wt. %, suggesting biological activity. Sulphur content ranges from 0.01 to 0.12 wt. % in Ni- laterite samples from Lokris, and from 0.06 to 18.2 wt. % in yellow-grey bauxites (Tab.3). The sulphur isotope compositions of Fe sulphides from the transitional zone between typical red-coloured and grey-whitish bauxite ore (sample 3B), grey- coloured (samples 3A and 4A) and a thin sulphide-layer from the top of the deposit, underlying the Cretaceous limestone (sample Sf.top1) show a wide range from +10.2 to –30.2 per mil (Tab. 3). The most negative values, obtained from grey-coloured samples, typical of sulphides formed by the action of bacteria (Laskou and Economou-Eliopoulos, 2007).

6. Discussion

Present data on the Fe-Ni ores feeding the metallurgical facilities indicate an As-enrichment up to a few thousands ppm As in the Aghios Ioannis laterite mines, although As in general in laterite deposits is lower than 10 ppm (Tab. 2). Such a variation seems to be consistent with the As variation from 0.1 to 0.5 wt% As in the metallurgical product (ferro-nickel alloy) of the Hellenic Mining and Metallurgical Company at Larymna (Zevgolis, 2004). The presence of elevated As contents in strongly re-worked Ni-laterites ores of Lokris (Fig.3; Tab. 1) and in the yellow-grey coloured bauxite ores occurring in a spatial association with organic matter, either micro-organisms (Fig. 3g, h) or layers of coal overlying bauxite ores (Kalaitzidis et al., 2009) suggest that the As-enrichment has taken place during a subsequent stage postdated that of the laterite re-deposition and that organic matter has played a significant role.

6.1. The role of organic matter-micro-organisms in the As-enrichment

The multistage development of the allochthonous laterite ores, by re-working and re-deposition in shallow sea environment is widespread in the Balkan Peninsula (Valeton et al., 1987; Alevizos, 1997; Eliopoulos and Economou-Eliopoulos, 2000). The development and characteristics of Fe-Ni laterite deposits are influenced by a number of geological and environmental factors including parent lithology, structure and alteration, and the conditions during deposition, diagenesis and meta-diagenesis stages. The role of the organic matter developed in stagnating and reducing conditions in coastal plains, (Valeton et al., 1987), which is a characteristic feature of certain Ni-laterites of Greece and Albania (Fig. 3f, g; Eliopoulos et al., 2003) and bauxites (Fig. 3g, h; Laskou and Economou-Eliopoulos, 2007; Öztürk et al., 2002) and in fluvial sediments in the Pilbara district of Western Australia (Freyssinet et al., 2005) seem to be of particular genetic significance. The stability of various iron oxides depends on

Table 2. Major and trace element content in representative Ni-laterite and bauxite samples from the Balkan Peninsula.

		wt%						ppm							
Location	Samples	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	MnO	As	Ni	Cr	Co	Zn	ΣREE	Th	U
Ni-LATERITES															
GREECE	A.I.1	21,1	24,98	35,9	1,3	2,6	0,22	2600	5500	5100	1400	330	1367	10	7
Aghios Ioannis	A.I.2	15,9	16,1	42,1	0,35	1,25	0,55	1800	40000	4500	1400	340	6325	6	46
	A.I.3	23,1	18,8	35,1	1,24	3,4	0,1	200	27800	15100	430	300	480	5	66
	A.I.4	24,1	20,3	35,6	1,1	3,65	0,3	140	27500	12000	2200	350	438	12	13
	A.I.7	1,9	44	41,6	2,7	0,25	0,17	230	1500	5500	60	320	480	25	7
	A.I.11	34	8,6	42,5	0,4	3,4	0,3	120	7500	20000	510	270	80	2,2	<0.5
	A.I.14	23,5	6,85	54,5	0,25	2,85	0,21	14	7690	24300	570	270	42	1,1	<0.5
	A.I.16	31,2	7,1	44	0,35	4,37	0,3	52	9000	25100	520	250	54	1	<0.5
	A.I.Ts	8,5	5,15	69,8	0,05	2,3	0,2	4	13000	20500	450	320	2	<0.5	<0.5
Euboea Triada	E.Tr.1	25,6	5,6	45,1	0,13	0,3	0,12	2	100	20000	590	360	63	1,7	<0.5
	E.Tr.2	14,6	7,1	55,2	0,15	0,1	0,4	3	14000	17000	590	100	8,2	0,5	<0.5
	E.Tr.3	15,9	7,2	57,3	0,12	0,1	0,4	2	12000	22000	830	520	47	1,2	<0.5
Kastoria	Ka-5	3,8	3	77,6	0,03	0,55	1,7	3	8000	20000	330	370	0,5	<0.5	<0.5
	Ka-6	3,8	3	77,6	0,03	0,55	1,7	15	9100	15000	820	280	5,3	<0.5	<0.5
	Ka-7	4.5	1,8	68.1	0.03	0.80	0.79	17	7100	23000	420	390	3,6	<0.5	1.3
	Ka-8	4.05	3,4	78.20	0.10	0.60	0.30	14	4400	17000	330	320	4,2	<0.5	<0.5
Edessa	Ed.P.10	17,5	8,7	59,5	0,3	3,3	0,6	4	9500	9600	800	60	194	4	2,1
Olympos	OL.1	4,2	3,4	71,5	0,07	3,4	1,05	7	8600	91000	300	340	3	0,6	0,5
	OL.3	3,9	2,9	76,8	0,09	2,85	0,77	2	9300	82000	320	430	2,5	<0.5	2,3
	OL.5x	7	5,8	74	0,06	4,35	0,27	19	16000	20000	1200	850	32	1	0,6
Sfikia	Sf.G.1	7,5	5,1	80,9	0,15	2,05	0,26	3	9200	14000	1200	440	15	<0.5	<0.5
	Sf.G.5	25,3	1,6	52,9	0,1	8,4	0,33	6	12000	21000	920	530	8	<0.5	<0.5
E. Vermio															
Mavrolivado	A.K.	17,5	8,2	53,8	0,5	4,1	0,56	14	11000	14000	600	590	62	1,7	1,2
	A.K.1	17,5	29	36	1,28	3,6	0,37	57	5200	5500	400	700	294	19	4,2
Alonakia	AL.4	7,1	6,7	78,5	1,03	0,6	0,04	22	1400	16000	120	90	261	37	12,5
	AL.5	15,6	14,8	60,4	1,25	1,05	0,11	10	800	12000	100	80	113	22	5,1
Stournari	St.1	11,1	6,1	68,9	0,1	3,9	0,69	28	5300	21000	370	560	42	<0.5	<0.5
	St.2	15,1	7,5	54,8	0,15	11,5	0,49	22	6900	16000	1400	580	64	<0.5	2,8
Grevena	G.P.X.1	12,3	4,8	67,4	0,18	4,2	0,42	11	9700	13000	800	370	56	6,3	<0.5
Skyros island	Sk.3	11	7,4	69,7	0,21	2,4	0,36	24	9800	22000	360	60	2	3,6	1
	Sk.4	11,1	9,4	66,7	0,27	2,05	0,16	140	10000	23000	320	110	22	2,8	1
SERBIA															
Topola	Yu3	19,5	5,4	58,5	0,1	5,7	0,05	12	5500	21000	250	330	16	0,7	<0.5
	Yu4	20,8	5,2	61,65	0,3	3,8	0,1	2	9200	17000	250	90	10	0,6	0,8
Rzanovo	RZ1	29,6	5,4	41,3	0,4	8,8	0,2	3	5100	25000	260	150	18	1	<0.5
	RZ2	12,8	4,4	64,7	0,15	10,2	0,45	2	8200	15000	990	430	7	1	<0.5
ALBANIA															
Bitincka	B.43	17,1	2,3	56,6	0,03	5,68	0,2	11	16000	26000	960	650	33	1	4,1
	B.44	5,1	6,1	71,4	0,08	1,2	0,17	10	7200	17000	650	310	31	0,9	5
	B.45	7,9	6,8	66,5	0,05	1,4	0,8	5	13000	19000	2100	680	2	1,9	0,05
	B.46	6,1	6,5	69,8	0,05	1,34	0,3	3	9800	21000	410	410	2	<0.5	<0.5
Guri - Perjuegjiun	G.39	3,5	2,8	79,9	0,15	1,1	0,36	32	13000	22000	570	510	61	1,6	1,6
	G.40	4,1	3,9	77,3	0,1	0,7	0,26	31	35000	35000	550	400	8,6	<0.5	4,7
	G.41	3,9	2,9	81,4	0,13	0,75	0,29	25	6600	26000	390	180	2,2	<0.5	<0.5
BAUXITES															
Parnassos - Ghiona	P.-G.B.	1,4	60,1	23,1	2,9	0,2	0,1	50	650	1170	30	90	260	52	8
	P.-G.B2	1,2	52,8	21,8	2,4	0,1	0,02	300	490	950	50	18	72	41	9
	P.-G.B3	4,1	54,7	17,4	2,11	0,2	0,01	230	480	630	10	38	81	29	16
	P.-G.6	2,7	64,1	14,2	2,23	0,1	0,01	890	450	1100	12	25	125	60	7

physico-chemical conditions, such as pH, oxygen and sulphur availability, and the mechanism of biological activity. The abundant pyrite, in the case of grey or yellow-grey bauxite ore, appearing as a late diagenetic mineral compared to other iron minerals (goethite, hematite) within the bauxite deposit, suggest a variation in the redox conditions (Hartog et al., 2004; Laskou and Economou-Eliopoulos, 2007). The presence of fine-grained minerals developed on the filament type bacteria of a bauxite sample (Fig. 3h) is consistent with experimental and *in situ* studies revealed that bacterial communities may dissolve primary rock-forming minerals to obtain essential nutrients and act as nucleation sites for the precipitation of secondary minerals (Baskar et al. 2003). The minerals may appear external to the microbial cell responsible for its genesis, on or in the cell envelope, or within the cell. Some microbial mineral formation is active and may involve direct enzymatic intervention or metabolic production of specific chemical reactants that cause precipitates (Baskar et al. 2003).

Table 3. Sulfur isotope composition of pyrite from the Parnassos-Ghiona bauxite deposit.

Sample	Description	S (wt%)	δ^{34}S CDT
3B	Transitional zone, red colar	4,1	(+) 10.2
3A	Transitional zone, gray colar	10,6	(-) 26.0
4A	Transitional zone, gray colar	8,4	(-) 29.7
Sf.top1	Thin layer of pyrite from the top	18,2	(-) 30.2

The restriction of arsenic in Fe, Al-oxides hosted in certain parts of Fe-Ni-laterite and bauxite deposits only (Tabs. 1& 3) may point to the existence of an As-source, such as organic matter developed during stagnating stage of the laterite evolution, and the existence of the physico/chemical conditions that facilitated their reaction.

6.2. Association of arsenic with Fe, Al-oxides

The elevated As-contents in certain Ni-laterite and bauxite laterites (Tab. 1) coupled with the existence of As-bearing goethite and Al-oxides (Tab. 3) suggest that the reaction between arsenic and both Fe- and Al-oxides is favorable in nature under certain circumstances. These analytical data are in a good agreement with the experimental literature data showing a significant sorption capacity of Fe- and Al-oxides for both As (III) and As (V) species (Gupta 1998; Smedley and Kinniburgh 2001; Pinon-Miramontes et al. 2003; USEPA 2004). The investigation of As (III) and As (V) sorption onto Al-rich and Fe-rich lateritic soil concretions (LC) has demonstrated that As (V) sorption onto iron oxides has a great dependence on pH. The equilibrium sorption capacity for As (III) is larger than that for As (V) over temperatures ranging from 25° to 60°C and that both As (III) and As (V) form inner-sphere complexes on Fe-rich LC. Arsenic (III) forms outer- sphere sorption mechanisms on Al-rich LC because there is no shift in pH (point of zero charge) even with an increase in As (III) concentration (Partey 2008). Furthermore, thermodynamic data such as free energy, entropy and enthalpy seems to contribute to the better understanding of the stability of As-bearing Fe, Al-oxides in nature. The negative “Gibbs free energy ($\Delta G°$)” values for arsenite and arsenate sorption on Fe-rich LC are consistent with spontaneous reaction between the species and the medium. Also, positive “entropy ($\Delta S°$)” values suggest the affinity of LC for the arsenic species in solution and positive enthalpy ($\Delta H°$) values confirm that the sorption process is an endothermic process (Majzlan et al. 2000; Partey 2008). Therefore, the Fe and Al-oxides in laterites are considered of particular significance in controlling arsenic mobility, and hence aquifer contamination rather than they may be a source of environmental risk, due to the elevated As contents.

7. Conclusions

Although present study is in progress and much more research is required to define the controlling factors of the arsenic mobility during meta-deposition and diagenesis of laterites, and its oxidation state (arsenate or arsenite), the available data leads to the following conclusions:

1. As in laterites is low (< 10 ppm) in general. Elevated arsenic contents were determined in the karst-type bauxitic- and Ni-laterite and are associated with epigenetic processes after their re-deposition and diagenesis.

2. Arsenic is mostly associated with Fe-oxides/hydroxides in the Ni-laterites, showing enrichment in REE, Co, Ni, Th and U as well, and Al-oxides in bauxites.

3. The negative values obtained for the sulphur isotope compositions of Fe sulphides in grey bauxite ores (up to –30.2 per mil) confirm the sulphide formation by the action of micro- organisms.

4. The presence of organic matter, either plants or microorganisms plays a very crucial role to the stability or solubility of minerals and As-mobi-

lity, since they facilitate redox reactions, causing changes in the physicochemical conditions (pH, Eh).

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