

# Bauxite ore as an energy source for bacteria driving iron-leaching and bio-mineralization\*

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**ABSTRACT:** The Greek bauxite deposits belong to the Mediterranean karst bauxite belt, and have been formed mainly during four different geological periods. The large (defined reserves approximately 300 million tons) Parnassos-Ghiona bauxite deposits and bauxite occurrences of Crece are of karst-type, hosted within carbonate rocks of Middle Cretaceous to Eocene age. Three bauxite horizons, B1, B2 and B3, can be distinguished (from the bottom to the top), which are intercalated with shallow-water limestone. Approximately 30 vol. % of these bauxite ores along and near to their contact with faults show a brittle deformation and change in colour from red to black-grey, are aluminum-enriched (>70 wt%  $Al_2O_3$ ) and iron depleted. The most salient feature of the bauxite ores of black-grey colour is the abundance of biogenic pyrite, of varying size and form, which is closely associated with fossilized and present day micro-organisms. The replacement of goethite by pyrite under the form of framboidal and pyrite and veins crosscutting sulphide-rich zones, and the subsequently oxidation of pyrite to Fe-Al-sulphates and goethite reflect a multistage transformation of the bauxite ore.

The development of micro-organisms, on the surface of grey bauxite, exposed to room temperature and moderate air humidity (atmospheric water) may indicate that they play a major role in controlling the redox reactions and facilitate the development of secondary hydrous iron sulphates. The compilation of the texture features, supporting the interaction between micro-organisms and minerals, with available (literature) experimental and calculated thermodynamic data for hydrated sulphides, may suggest that micro-organisms capture some of the releasing energy during the oxidation of iron (exothermic reaction) to drive their metabolism. It has been suggested that they produce enzymes, a powerful catalyst, catalyzing the oxidation reactions, and facilitate the production of ferrous- and ferric sulphates and other sulphates. In addition, the physico/chemical conditions (pH, Eh) seems to be a controlling factor of the role of micro-organisms in the mineralogical and chemical composition of laterite ores, in leaching and beneficiation of low grade ores and the stability of various mineral phases.

**Key-words:** bauxite, bio-mineralization, micro-organism, fossilized bacteria, Parnassos-Ghiona, Greece.

**ΠΕΡΙΛΗΨΗ:** Τα ελληνικά κοιτάσματα βωξίτη ανήκουν στην μεσογειακή καρστική ζώνη βωξιτών, η οποία έχει δημιουργηθεί κυρίως κατά τη διάρκεια τεσσάρων διαφορετικών γεωλογικών περιόδων. Οι μεγαλύτερες βωξιτικές αποθέσεις (υπολογίζονται περίπου 300.000 τόνοι) είναι της ζώνης Παρνασσού – Γκιόνας. Τρεις βωξιτικοί ορίζοντες (B1, B2 και B3) μπορούν να διακριθούν (από τη βάση προς την κορυφή), με βάση την ηλικία των ασβεστολίθων που παρεμβάλλονται μεταξύ τους. Σχεδόν το 30% αυτών των βωξιτικών κοιτασμάτων, βρίσκονται κατά μήκος και κοντά στα σημεία επαφής με ρήγματα, και εμφανίζουν θραυστική παραμόρφωση και αλλαγές στο χρώμα από κόκκινο σε γκρι και μεγάλο εμπλουτισμό σε αργίλιο (>70 wt%  $Al_2O_3$ ) ενώ ο σίδηρος έχει αποπλυθεί. Το πιο σημαντικό χαρακτηριστικό των γκρι βωξιτικών κοιτασμάτων είναι η αφθονία βιογενούς σιδηροπυρίτη, σε ποικίλη μορφή και μέγεθος, ο οποίος σχετίζεται άμεσα με τους απολιθωμένους και τους σύγχρονους μικροοργανισμούς. Η αντικατάσταση του γκαϊτίτη από βιογενή σιδηροπυρίτη και ακολούθως η οξείδωση του σιδηροπυρίτη σε θειικά ορυκτά σιδήρου-αργιλίου και γκαϊτίτη αντανακλά μια αναμόρφωση του βωξιτικού μεταλλεύματος σε πολλά στάδια.

Η ανάπτυξη των μικροοργανισμών, στην επιφάνεια του γκρι βωξίτη, που εκτίθεται σε θερμοκρασία δωματίου και μέση υγρασία αέρα (ατμοσφαιρικό νερό), μπορεί να υποδηλώνει ότι αυτοί οι παράγοντες δυνατόν να διαδραματίζουν σημαντικό ρόλο στον έλεγχο των οξειδοαναγωγικών αντιδράσεων και να διευκολύνουν την ανάπτυξη δευτερογενών ένυδρων θειικών ορυκτών του σιδήρου. Ο συνδυασμός των χαρακτηριστικών δομών, που δείχνουν την αλληλεπίδραση μεταξύ μικροοργανισμών και ορυκτών, με τα διαθέσιμα βιβλιογραφικά εργαστηριακά και θερμοδυναμικά δεδομένα για ένυδρα θειοξείδη ορυκτά, υποδηλώνει ότι οι μικροοργανισμοί δεσμεύουν κάποια από την ενέργεια που απελευθερώνεται κατά την οξείδωση του σιδήρου (εξώθερμη αντίδραση) για τον μεταβολισμό τους. Τα παραγόμενα ένζυμα θεωρούνται ένας πολύ δυνατός καταλύτης για τις οξειδωτικές αντιδράσεις, και διευκολύνουν την παραγωγή θειικών ορυκτών δισθενούς και τρισθενούς σιδήρου και άλλων θειικών ορυκτών. Επίσης, οι φυσικοχημικές συνθήκες (pH, Eh) φαίνεται ότι είναι ο ένας παράγων που ελέγχει το ρόλο των μικροοργανισμών στην ορυκτολογική και τη χημική σύσταση των λατεριτών, στην απόπλυση και τον εμπλουτισμό των κοιτασμάτων με μικρή περιεκτικότητα μετάλλων και τη σταθερότητα ποικίλων ορυκτών φάσεων.

**Λέξεις-κλειδιά:** βωξίτες, βιο-ορυκτογένεση, μικροοργανισμοί, απολιθωμένα βακτήρια, Παρνασσός – Γκιόνα, Ελλάδα.

## INTRODUCTION

Recently, several studies have focused on the role of bacteria in metal cycling, driving rock weathering and/or mineral formation processes. Oxidation-reduction reactions involving minerals directly or indirectly supply energy that permits

and sustains subsurface life. Many metals can be enzymatically concentrated and dispersed by micro-organism in their environment. Changes in the valence state of elements are accompanied by significant changes in their mobility, bioavailability and toxicity (BASKAR *et al.*, 2003; SOUTHAM & SAUNDERS, 2005; RUSSELL *et al.*, 2005).

\* Μετάλλευμα βωξίτη ως μία πηγή ενέργειας για βακτήρια τα οποία ελέγχουν την βιο-αποσιδήρωση και την βιο-ορυκτογένεση

Some of these activities are commercially exploited or have a potential significance (EHRlich, 1997). It has been suggested that such microbial interactions of certain species of microbes with metals are able to leach nickel selectively from low-grade Ni-laterites of Greece (ALIBHAI *et al.*, 1991). Recently, the research interest has focused on the presence of micro-organisms in bauxites, which is the major source of aluminium raw material. Although the typical colour of the Parnassos-Ghiona bauxite ores is red, the presence of micro-organisms in multi-coloured bauxites, along faults within the Parnassos-Ghiona deposits was considered to play a major role in controlling the redox conditions, since they can drive the formation of pyrite or Fe-oxides (LASKOU & ECONOMOU-ELIOPOULOS, 2005, 2007).

In the present study, using SEM/EDS and XRD data, some examples of dissolution of primary rock-forming minerals and formation of secondary minerals by oxidation-reduction reactions in bauxite ores from Greece, hosting fossilized and present day grown bacteria, are given, supporting the link between the mineral involvements to the energy requirements of micro-organisms.

## METHODS OF INVESTIGATION

The bauxite ore samples were investigated as follows. X-ray power diffraction patterns (XRD) were obtained with a Siemens D5005 X-ray diffractometer at the University of Athens. Major- and trace elements, including rare earth elements (REE), were determined at X-ray Assay Laboratories (XRAL), Ontario, Canada. Platinum, palladium and gold were determined at the University of Athens, using the AAS (flameless system) method, after preconcentration by lead Fire Assay, technique on large (30 g) samples.

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.

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, livetime 50secs, and a beam diameter of 1-2  $\mu m$ .

## CHARACTERISTIC FEATURES OF THE BAUXITE DEPOSITS AND OCCURRENCES OF GREECE

The major Greek bauxite deposits are located and formed within the Parnassos-Ghiona Mountain, they belong to the Mediterranean karst type bauxite deposits and are hosted within carbonate rocks of the Mesozoic age. The defined reserves are approximately 300 million tons (11<sup>th</sup> largest baux-

ite deposit worldwide). 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 (Fig. 1). The economically most important deposits occur in the B3 bauxite horizon, which is developed over long distance as a continuous layer of 1–10 m in thickness (PAPASTAVROU, 1986; VALETON *et al.*, 1987). The Parnassos-Ghiona bauxite deposit has been classified among the largest deposits described in the United States, South America (Brazil, Venezuela, Guiana), Europe (France, Austria, Germany, Hungary, Romania, Russia), Asia (China, India, Indonesia, Malaysia, Philippines, Turkey), Africa (Guinea, Mozambique, Rhodesia, Sierra Leone) and Australia (BARDOSSY, 1982; KLEIN & HURLBUT, 1993; ÖZTÜRK *et al.*, 2002; BOGATYREV *et al.*, 2009).

Also, large bauxite deposits of Eocene age (B4 horizon) have been described in Yugoslavia, Italy Guyana, Surinam, French Guiana, Australia (Queensland, Northern Territory, Tasmania), USA (Arkansas, Alabama, Georgia), and India (Deccan peninsula) gibbsitic, and in (Kashmir-Jammu) diasporic (VALETON 1972). Bauxite occurrences hosted by the Upper Eocene limestone have been described in the areas of Nafpaktos, Smerna and Pylos of Greece. In spite of the small thickness of the Western Greece bauxites, the lateral extent of these deposits is wide, (PAPASTAVROU, 1986; LASKOU, 2003) while the mineralogical and chemical (bulk and mineral chemistry) characteristics have been given in previous studies (LASKOU & ECONOMOU, 1989, 1991; LASKOU, 1991, 2003).

The geological characteristic of bauxites, their formation conditions, and distribution are described in many publications. The principal aluminum hydroxide minerals found in varying proportions within the Parnassos-Ghiona bauxite deposits are the polymorphs boehmite and diasporite ( $Al_2O_3 \cdot H_2O$ ) and in smaller amounts gibbsite ( $Al_2O_3 \cdot 3H_2O$ ), kaolinite, haematite, goethite, anatase, illite, clinocllore, chamosite and zircon (VALETON *et al.*, 1987; LASKOU, 2001; LASKOU & ANDREOU, 2003). Minor manganese hydroxide minerals, including lithiophorite and brindleyite, REE-bearing minerals and small chromite fragments are also present (VALETON *et al.*, 1987; LASKOU, 2001; LASKOU & ANDREOU, 2003). The REE minerals rhabdophane and florencite (minerals of LREE), churchite and xenotime (minerals of HREE) have been described by LASKOU & ANDREOU (2003).

Although more than 70 volume % of the Parnassos-Ghiona bauxite deposits belong to the red-coloured type there is a significant proportion of yellow and grey to whitish bauxites. These bauxite types differ in their mineralogical and chemical composition as well. Commonly grey to whitish bauxites are aluminum-enriched ( $>70$  wt%  $Al_2O_3$ ) and iron depleted (PAPASTAVROU, 1986). The multicoloured bauxite ores are probably related to the pyrite oxidation, covers a major proportion of the deposit occurs as irregular bodies along to- and near their contact with faults with a strong deformation. There is a gradual change in their colour from red

to black-grey, extending in a distance of tens of meters.

The dominant aluminium mineral in the Nafpaktos and Smerna deposits is diaspore (diasporic type) whilst boehmite is occasionally present. The dominant aluminium mineral in the Pylos deposits is boehmite (boehmitic type). Black-gray-red colored bauxite ores from the Parnassos-Ghiona deposits and Eocene bauxite occurrences of Nafpaktos, Smerna and Pylos occurrences are characterized by the presence of abundant pyrite, which is associated with organic matter in a goethite–diaspore matrix (LASKOU & ECONOMOU-ELIOPOULOS, 2005, 2007).

**GEOCHEMICAL CHARACTERISTICS AND MINERAL CHEMISTRY**

Whole rock analyses (major, trace, rare earth elements and platinum-group elements) of representative samples of each type are presented in the Table 1. A characteristic feature of the Parnassos-Ghiona bauxite deposits and of Skopelos bauxite occurrences of Greece is the significant content in chromium, reaching concentrations of up to 1180 ppm and 3090 ppm (VALETON *et al.*, 1987; MACKSIMOVIC & PANTO, 1991; LASKOU, 2001, 2003, 2005; Table 1). The combined investigation, using XRD and SEM/EDS revealed the presence of very small fragments of chromite. Although they are commonly Fe-rich chromites, due to epigenetic processes,

the average values of the Cr/(Cr+Al) and Mg/(Mg+Fe<sup>2+</sup>) ratios in primary cores range between 0.53 and 0.58, and 0.52 and 0.55, respectively. Spinel saven in deeply weathered environments, transferred and enclosed into bauxitic ores indicate the contribution of basic to ultrabasic rocks, and reflect the trivalent oxidation state of chromium in those bauxite deposits (LASKOU, 2001). The rare earth element (REE) content show a wide variation in the total (ΣREE) content. The low value (76 ppm) recorded in grey bauxite ore (Table 1; 5 and 6 samples) is much lower compared to the average value (260 ppm) in red bauxite samples (Table 1; 7 and 8 samples) (LASKOU & ECONOMOU-ELIOPOULOS, 2005, 2007). Total organic carbon (TOC) content ranges in red-coloured bauxite ores is low (average = 0.06), whilst in grey pyrite-rich samples reaches the values of 2.78 wt% (Table 1).

At least two stages of transformation of the bauxite ores can be distinguished: (a) reduction of ferric to ferrous iron, resulted in the formation of pyrite in a variety of forms and size (Fig. 2). In addition to pyrite, which is a major iron monosulphide, pyrrhotite and pentlandite are occasionally dispersed throughout the matrix of the red-grey bauxite ore. Sulphide veins crosscutting sulphide-rich zones are occasionally present.

(b) Subsequently, the oxidation of pyrite, resulted in the replacement of relatively large pyrite crystals by goethite (Fig. 3).

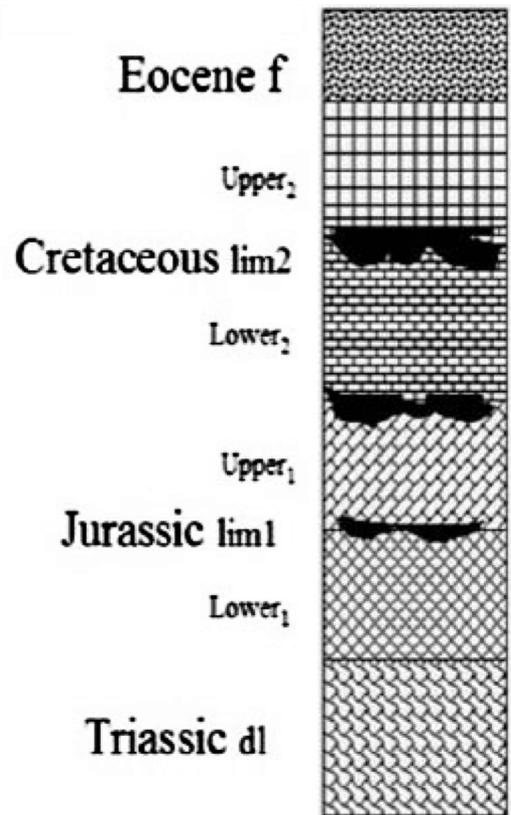


Fig. 1. Location map and stratigraphic column of the Parnassos-Ghiona bauxite deposits. Symbols: dl.=dolomitic limestone; lim1=gray (Lower) and dark colored (Upper) Jurassic limestone; lim2=limestone; f=flysch, overlying the Quaternary conglomerates; B1=first bauxite horizon, B2=second bauxite horizon, B3=third bauxite horizon.

TABLE 1  
Chemical Composition of bauxites Ores (B1, B2, B3 and B4 horizons) from Greece.

wt %	1 (B1)	2(B1)	3(B2)	4(B2)	5 (B3)	6 (B3)	7 (B3)	8 (B3)	9(B4)	10(B4)	11(B4)
SiO <sub>2</sub>	1.50	11.56	6.20	11.00	1.23	4.03	0.71	2.12	10.76	7.64	11.91
Al <sub>2</sub> O <sub>3</sub>	59.40	65.14	58.75	59.32	52.83	54.72	58.1	61.77	49.28	49.27	51.11
Fe <sub>2</sub> O <sub>3</sub> T	24.34	4.22	18.16	11.80	21.43	17.4	26.9	19.2	24.56	30.00	21.11
MnO	0.04	0.17	0.07	0.06	0.02	n.d.	0.26	0.01	0.09	0.03	0.05
MgO	0.12	0.10	0.32	0.58	0.04	0.06	0.26	0.04	0.00	0.07	0.33
CaO	0.98	0.00	0.13	0.21	0.03	0.06	0.00	0.08	0.09	0.10	0.18
Na <sub>2</sub> O	0.44	1.08	0.00	0.13	n.d.	n.d.	n.d.	n.d.	0.33	0.17	0.18
K <sub>2</sub> O	0.10	1.11	0.79	1.58	0.02	0.23	n.d.	0.05	0.30	0.17	0.35
TiO <sub>2</sub>	2.42	4.03	2.39	2.57	2.35	2.11	2.87	2.93	1.40	1.61	1.76
P <sub>2</sub> O <sub>5</sub>	0.05	0.00	0.07	0.11	0.02	0.01	0.06	0.06	0.12	0.12	0.08
TOC	n.d.	n.d.	n.d.	n.d.	2.72	1.65	0.07	0.06	n.d.	n.d.	n.d.
LOI	11.55	12.64	12.96	12.65	21.21	20.66	11.1	12.83	13.70	11.04	12.84
Total	100.94	100.05	99.84	100.1	99.11	99.25	100.07	99.00	100.63	100.22	99.90
<b>ppm</b>											
As	n.d.	n.d.	n.d.	n.d.	300	230	54	43	189	172	398
Ag	n.d.	n.d.	n.d.	n.d.	0.9	0.5	0.7	0.6	n.d.	n.d.	n.d.
Ba	110	69	n.d.	n.d.	100	390	180	26	122	132	83
Be	n.d.	n.d.	n.d.	n.d.	1	5	4	3	n.d.	n.d.	n.d.
Bi	n.d.	n.d.	n.d.	n.d.	4	3	6	6	n.d.	n.d.	n.d.
Cd	n.d.	n.d.	n.d.	n.d.	1.3	0.6	2	1.1	n.d.	n.d.	n.d.
Co	n.d.	n.d.	n.d.	n.d.	50	10	29	31	20	21	40
Cr	460	480	410	310	950	630	1180	1150	2015	2327	2002
Cu	90	4	80	110	2	14	8	n.d.	61	43	53
Hf	n.d.	n.d.	n.d.	n.d.	13	15	12	11	16	15	14
Mo	n.d.	n.d.	n.d.	n.d.	59	15	16	n.d.	78	99	703
Nb	100	120	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	38	31	34
Ni	410	200	290	350	490	490	610	690	153	313	315
Pb	n.d.	n.d.	n.d.	n.d.	34	38	37	30	n.d.	n.d.	n.d.
S	n.d.	n.d.	n.d.	n.d.	12	9	n.d.	n.d.	n.d.	n.d.	n.d.
Sb	n.d.	n.d.	n.d.	n.d.	32	33	12	4	25	16	120
Sc	75	62	50	50	29	32	30	64	26	23	18
Sr	150	32	100	150	22	24	12	26	262	146	191
Ta	n.d.	n.d.	n.d.	n.d.	3	3	4	4	n.d.	n.d.	n.d.
Th	n.d.	n.d.	n.d.	n.d.	41	29	55	49	49	46	42
U	n.d.	n.d.	n.d.	n.d.	9	16	9	7	23	25	29
V	190	100	420	230	750	520	270	320	402	609	878
W	n.d.	n.d.	n.d.	n.d.	38	12	65	70	46	86	14
Zn	n.d.	350	350	330	18	38	64	110	176	148	170
Zr	660	1160	n.d.	n.d.	420	360	680	540	485	398	404
Y	46	14	n.d.	n.d.	24	26	51	33	59	46	35
La	90	n.d.	n.d.	n.d.	9	8	16	15	135	68	50
Ce	222	240	n.d.	n.d.	55	64	220	210	191	129	89
Pr	18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	15	10	7
Nd	69	98	n.d.	n.d.	n.d.	n.d.	28	10	64	45	30
Sm	13	n.d.	n.d.	n.d.	2	3	4	4	10	8	6
Eu	2,8	n.d.	n.d.	n.d.	0.5	0.8	1.4	1	4,0	1.7	1,0
Gd	11.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9.9	6.3	4.5
Tb	1.8	n.d.	n.d.	n.d.	n.d.	n.d.	2	n.d.	1.6	0.9	1,0
Dy	10.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	12.1	6.9	5.3
Ho	2.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.8	1.6	1.2
Er	6.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9.3	5.3	3.9
Tm	0.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.4	0.7	0.6
Yb	5.8	n.d.	n.d.	n.d.	4.3	4.6	6	5	9.4	5.9	4.8
Lu	0.9	n.d.	n.d.	n.d.	0.7	0.8	0.8	0.8	1.6	1.0	1.0
<b>ppb</b>											
Au	1	7	n.d.	n.d.	2	3	6	8	<0.5	5	7
Rh	<0.5	<0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1	<0.5	<0.5
Pt	1	1	n.d.	n.d.	n.d.	n.d.	3	2	<0.5	<0.5	<0.5
Pd	14	6	n.d.	n.d.	2	2	13	4	1	6	1

Symbols: 1. Atalandi; 2. Glypha; 3, 4, 5, 6, 7, 8 Parnassos-Ghiona; 9. Nafpactos; 10. Smerna; 11. Pylos.

Present data and from LASKOU & ECONOMOU-ELIOPOULOS (1991); (2007).

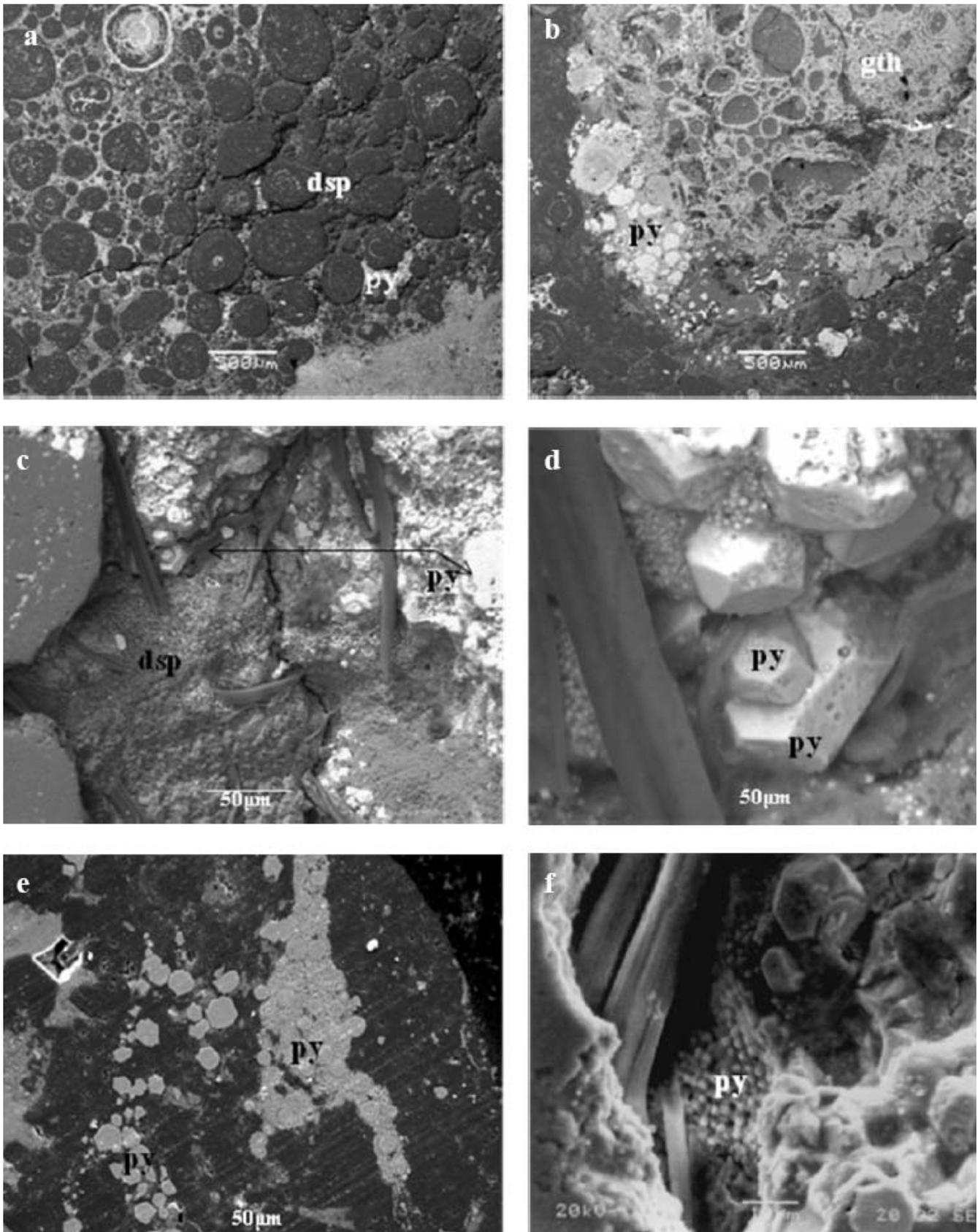


Fig. 2. Selected backscattered images from bauxites showing an association of pyrite with goethite, in both pisoliths and matrix dominated by diaspore (gray). The close association of sulfides and microorganisms may suggest that facilitate the nucleation and growth of the sulfides. Abbreviations: py=pyrite; gth=goethite; dsp=diaspore.

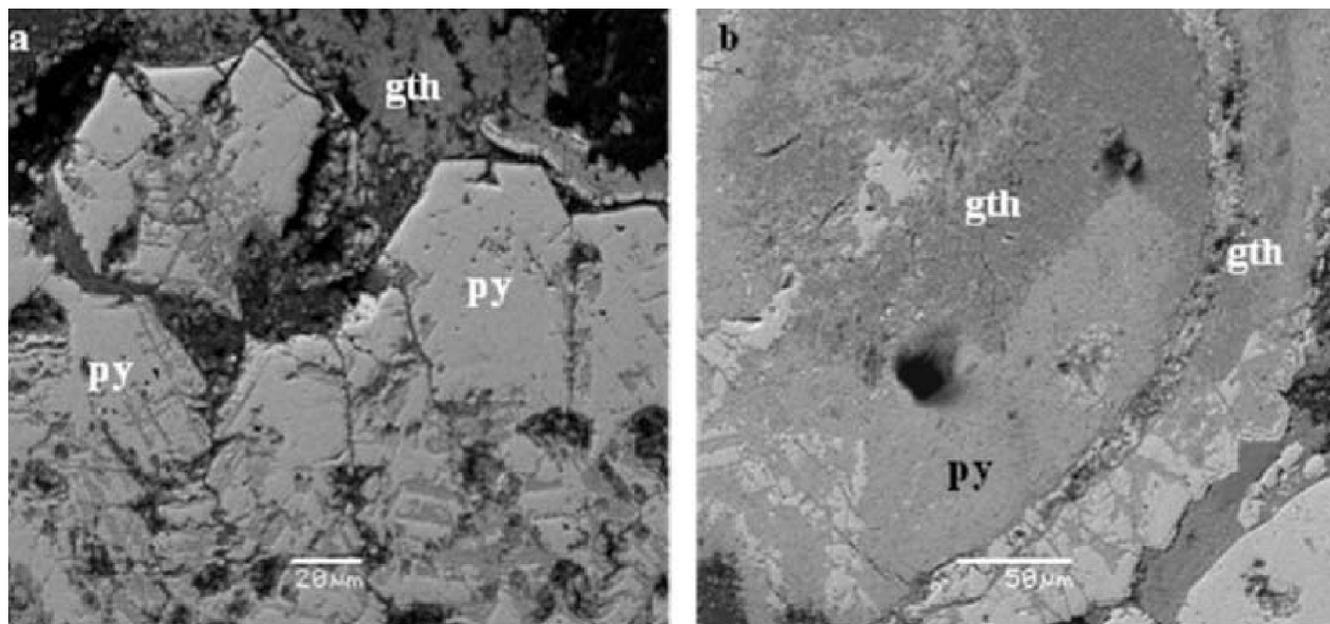


Fig. 3. Selected backscattered images from bauxites, showing the oxidation of pyrite crystals, of an earlier stage, into goethite from gray-red bauxite samples. The replacement of pyrite by goethite and the co-existence of euhedral crystals of pyrite may reflect a multistage pyrite formation and wide range in Eh-pH conditions during diagenetic and epigenetic stages. Abbreviations: py=pyrite; gth=goethite.

### Fossilized bacteria

The most salient feature of the black-grey bauxite samples is close association of sulphides and Fe-oxides with a consortium of bacteria, with various morphological forms such as filament-like and spherical to lenticular of an average size of 2  $\mu\text{m}$  (Fig. 4). It is known that various minerals, like Fe-oxides, Al-oxides and chlorite, grow on bacteria, also causing the occurrence of bacteria with a bigger size (Fig. 4) (RENAUT *et al.*, 2002). On the other hand the enlargement of their frame, shown in the majority of them emphasizes the inter-connection of bacteria with minerals.

### Present day grown bacteria and bio-mineralization

A whitish material has been observed to grow, after two weeks, on the surface of polished sections of grey bauxite, exposed to air oxidation, in the room conditions (20-25°C) and moderate air humidity (atmospheric water). The combined investigation using SEM/EDS and XRD revealed the growth of micro-organisms, which in turn facilitated the development of secondary hydrous iron sulphates.

Pyrite in grey-whitish bauxite ore shows evidence of extensive oxidation and replacement by a mixture of filament-like bacteria and aggregates of secondary minerals, occurring as characteristic crusts on surfaces (Figs 5 & 6). The secondary minerals identified, with a varying degree of hydration, are mostly halotrichite ( $\text{Fe}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22(\text{H}_2\text{O})$ ), of a needle-like morphology, and in lesser amounts alunogen ( $\text{Al}_2(\text{SO}_4)_3 \cdot 17(\text{H}_2\text{O})$ ), szomolnokite ( $\text{Fe}^{2+}\text{SO}_4 \cdot (\text{H}_2\text{O})$ ), coquimbite ( $\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 9(\text{H}_2\text{O})$ ) and voltaite ( $\text{K}_2\text{Fe}^{2+}_5\text{Fe}^{3+}_3\text{Al}(\text{SO}_4)_{12} \cdot 18(\text{H}_2\text{O})$ ). Also, a change in crystal size from very small crys-

tals to large ones is evident (Figs 5 & 6).

### DISCUSSION

The Fe- and Al-hydrous oxides are commonly insoluble components of bauxite. However, the replacement of goethite by abundant pyrite is widespread in the grey-whitish colour ores, which in turn are characterized by a close association with micro-organisms (LASKOU & ECONOMOU-ELIOPOULOS, 2005, 2007). Pyrite has been described elsewhere in bauxite deposits like in Hungary, Croatia and the Taurides, Turkey (KOMLOSSY, 1968; BARDOSSY, 1982; SINKOVEC *et al.*, 1994; D' ARGENIO & MINDZENTY, 1995; RAISWELL, *et al.*, 1988; BERNER, 1984; ÖZTÜRK *et al.*, 2002). Sulphur isotope analyses of such sulphide-bearing samples from the Parnassos-Ghiona bauxite deposits of Greece and the Dogçankuzu and Mortas bauxite Deposits, Turkey showed that pyrite has low  $\delta^{34}\text{S}$  values, supporting the biogenic origin of the pyrite (ÖZTÜRK *et al.*, 2002; ELIOPOULOS & ECONOMOU-ELIOPOULOS, 2010).

### The role of micro-organisms in the mineral-forming processes

The oxidation paths of pyrite and the interaction between minerals and bacteria is still a subject of debate (NORDSTROM & SOUTHAM, 1997; CRUNDWELL, 2003; SOUTHAM & SAUNDERS, 2005; RUSSELL *et al.*, 2005; KOCK & SCHIPPERS, 2006 and references therein). The presented data provide an example of (a) bacteria (micro-organism) attachment to the thermodynamically unstable pyrite, facilitating its conversion to a lower-energy state mineral, and (b) the production of ferrous- and ferric sulphates and other sulphates on living

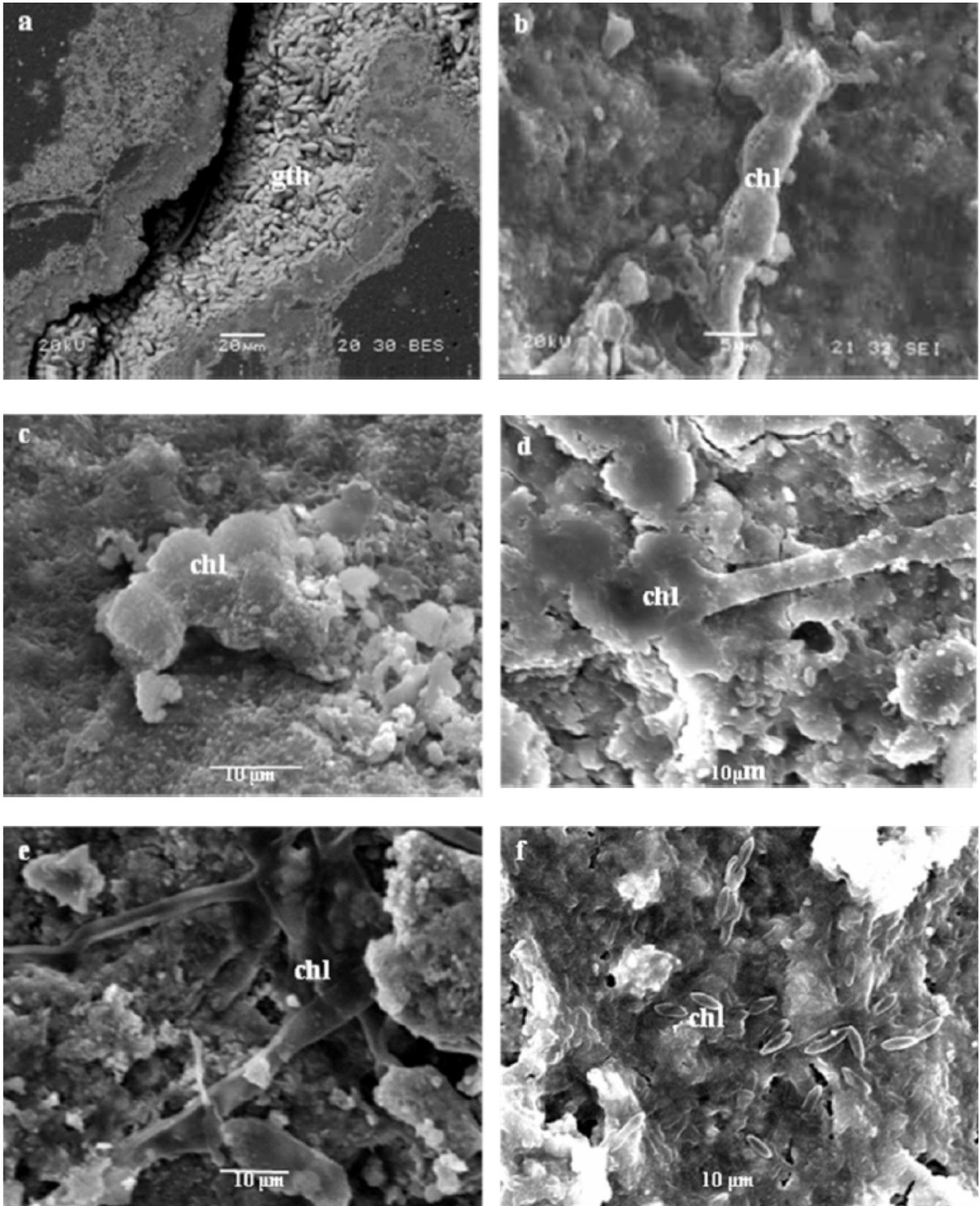


Fig. 4. Selected backscattered images showing fossilized microorganisms with various morphological forms, enclosed in bauxite samples from the first Jurassic bauxite horizon, Parnassos-Ghiona (a and b), and Atalandi (c, d) and from the fourth Eocene bauxite horizon, Pylos (e, f). The fossilized bacteria exhibit a variation in their chemical composition (goethite or chlorite). Abbreviations : gth=goethite (Al-rich); chl=chlorite.

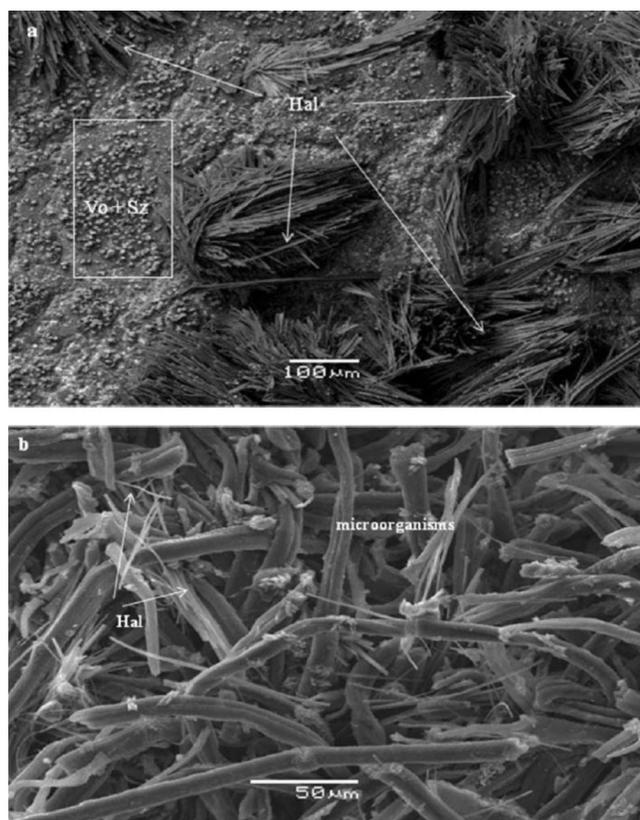


Fig. 5. Selected backscattered images from bauxites, showing aggregates of hydrous sulfate minerals: halotrichite (hal); szomolnokite (sz); voltaite (vo) and microorganisms.

bacteria (Figs 2-6; Tables 2 & 3). That is consistent with the increase of the solubility of Al in the resulted acidic environment and in the presence of completing ligands, such as  $\text{SO}_4^{2-}$  suggesting that bacterial activity is playing a critical role in the mineralization. More specifically, the reaction of pyrite, oxygen and water (atmospheric water) produce ferric hydroxide [ $\text{Fe}(\text{OH})_3$ ], sulphate ( $\text{SO}_4^{2-}$ ), hydrogen ions ( $\text{H}^+$ ) and heat energy (exothermic process). On the basis of enthalpies given by ROBBIE *et al.* (1978) and NAUMOV *et al.* (1974), the heat energy produced in this reaction for complete conversion of one mole of pyrite to ferric hydroxide amounts to about 1490 kJoules at 25°C (ROSE & CRAVOTTA, 2005). Furthermore, it has been suggested that the involved bacteria, which use the part of the released energy for their metabolism, produce enzymes, a powerful catalyst, catalyzing the oxidation reactions, and transforming inorganic carbon into cellular matter, e.g. the bacteria capture some of the releasing energy to drive their metabolism (SILVERMAN, 1967; HISKEY & SCHLITT, 1982; NOWACZYK *et al.*, 1999; SOUTHAM & SAUNDERS, 2005; RUSSELL *et al.*, 2005; KOCK & SCHIPPERS, 2006 and references therein).

#### Application of thermodynamic data for hydrated sulphates

Due to remediation of problems that arise from release of the components from soluble Fe-Al-sulphates to acid-mine

TABLE 2  
Mineralogical composition of secondary phases on bauxites surface identified by XRD.

Sample	Alunogen	Halotrichite	Szomolnokite	Coquinbite	Voltaite
V-1	MD	MJ	MD	-	NIN
V-1-b	MJ	TR	MD	-	MIN
V-1-c	TR	MJ	-	-	MIN
V-2	MJ	MIN	MD	TR	TR
V-2-b	MJ	MIN	MIN	TR	TR
V-2-c	MJ	TR	MD	TR	TR
V-2-d	MJ	MIN	MD	TR	-

MJ=major constituent, MD=medium, MIN=minor and TR=trace constituent

drainage, investigators have focused on the geochemical modeling of the rock-water interactions that require an extensive thermodynamic data base (DEKOCK, (1982); HEMINGWAY & SPOSITO (1996); HEMINGWAY *et al.* (2002) reviewed the experimental data for soluble iron- and other sulphate phases and estimated thermodynamic data at 298.15 K and 1 bar for phases for which no experimental data exist. The thermodynamic data available for hydrated ferrous sulphates consist of values for the enthalpy and entropy of formation of szomolnokite among others, while the Gibbs energy of formation for szomolnokite was easily calculated, since the Gibbs energy of formation is related to the enthalpy of formation through the following thermodynamic equality:  $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$ , where  $\Delta_r S^\circ$  is the entropy of formation at temperature T in kelvins. They concluded that the enthalpy and Gibbs energy of formation of each  $\text{H}_2\text{O}$  molecule of crystallization, except of the first, in the ferrous sulphates -  $\text{H}_2\text{O}$  system is -295.15 and -238.0  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively, while entropy has positive values.

The occurrence and stability of Fe-Al-sulphides in association with pyrite (Figs 2-6; Tables 2 & 3) and the change in their crystal size (Figs 5 & 6) probably due to the larger specific surface area of small crystals (thermodynamically less stable) can be explained by the application of both kinetic and thermodynamic approaches. The thermodynamic properties of Fe-sulphate minerals allow the estimation of the stability and compute the solubility of these phases in natural systems. A few thermodynamic studies have been carried out on Fe(III) sulphate minerals (BARON & PALMER, 2002; MAJZLAN *et al.*, 2006; ACKERMANN *et al.*, 2009). The formation of secondary Fe-sulphate minerals may affect the Fe and sulphate concentration, but also the concentration of pollutants incorporated into the structure of the Fe-sulphates or adsorbed onto their surfaces (BALISTRERI *et al.*, 2007). ACKERMANN *et al.* (2009) have focussed their research on the calculation of phase diagrams for the ferric sulphates and predict their dissolution-crystallization behaviour in nature, which would be applicable to regions affected by acid mine drainage.

#### CONCLUSIONS

Available mineralogical, geochemical and mineral chemistry data from the Parnassos-Ghiona deposit and bauxite occurrence, covering all bauxite horizons of Greece lead to the following:

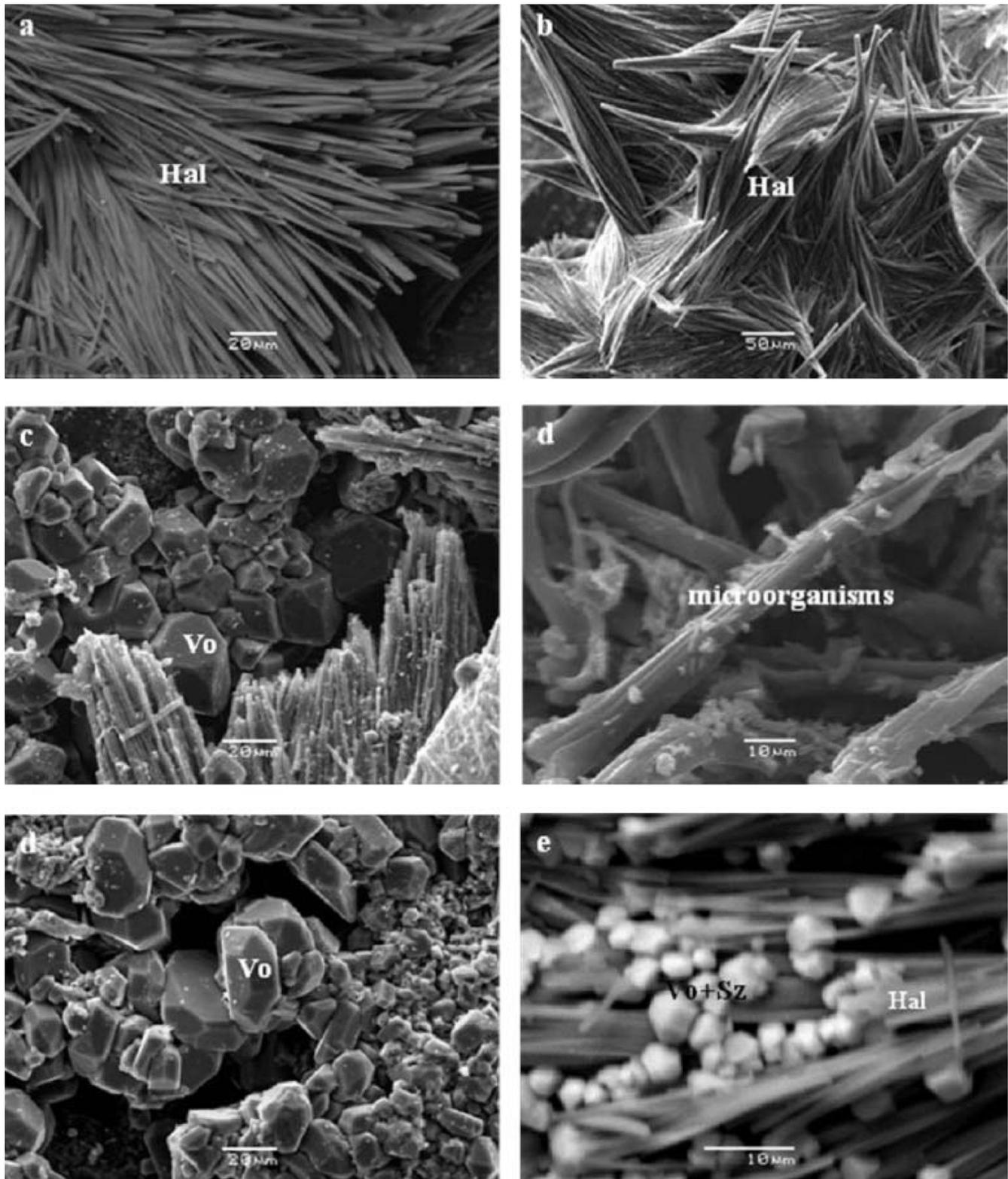


Fig. 6. Selected backscattered images from bauxites, showing aggregates of needle-like halotrichite (hal); voltaite (vo); szomolnokite (sz); and microorganisms.

1. Grey-whitish to multicoloured bauxite ores are Al-enriched (>70 wt%  $\text{Al}_2\text{O}_3$ ) and independent of their age, covering the period from Middle Cretaceous to Eocene.

2. Grey-whitish bauxite ores are characterized by the presence of abundant pyrite of biogenic origin, fossilized and present day grown micro-organisms.

TABLE 3

Representative microanalyses (wt%) of halotrichite, szomolnokite and voltaite from (B3) Parnassos-Ghiona bauxite samples.

Sample	VB-1	VB-1	VB-1	VB-1	V-2b	V2-e	V-1	V-2	V2-2i	V2	V2
Mineral	Hal	Hal	Hal	Hal	Hal	Hal	Sz	Sz	Sz	Vo	Vo
Al <sub>2</sub> O <sub>3</sub>	11.47	11.24	11.44	11.29	10.85	11.17	0.15	0.20	0.28	2.69	2.08
SO <sub>3</sub>	36.02	35.89	36.11	35.93	35.76	35.88	46.98	47.23	46.74	47.12	46.85
K <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.33	4.57
Fe <sub>2</sub> O <sub>3</sub>	8.67	8.43	8.22	8.27	9.07	8.53	42.11	43.21	42.51	29.76	31.46
<b>Total</b>	<b>56.16</b>	<b>55.56</b>	<b>55.77</b>	<b>55.49</b>	<b>55.68</b>	<b>55.58</b>	<b>89.24</b>	<b>90.64</b>	<b>89.53</b>	<b>83.90</b>	<b>84.96</b>

3. The development of micro-organisms, on the surface of grey bauxite, exposed to room temperature and moderate air humidity (atmospheric water) play a major role in controlling the redox conditions and facilitated the development of secondary hydrous iron sulphates.

4. Micro-organisms attach to the thermodynamically unstable pyrite, capturing some of the releasing energy to drive their metabolism, and facilitated the production of ferrous and ferric sulphates and other sulphates.

5. Since approximately 30 volume % of the Parnassos-Ghiona bauxite ores, are grey-whitish coloured ores with an Al-enrichment >70 wt% Al<sub>2</sub>O<sub>3</sub>, the presence of micro-organisms plays a major role in the removal of iron and of other elements, and may be a beneficiary and effective technique.

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